The Radical Cation of Stannane: an Electron Spin Resonance Study

Akinori Hasegawa,[a] Shoji Kaminaka,[a] Toshio Wakabayashi,[a] Michiro Hayashi,[a] and Martyn C. R. Symons[b]

[a] *Department of Chemistry, Faculty of Science, Hiroshima University, Higashisenda-machi, Naka-ku, Hiroshima 730, Japan*

[b] *Department of Chemistry, The University, Leicester LE1 7RH, U.K.*

The cations SnH_4^+, prepared by exposing dilute solutions of SnH_4 in Freon to ^{60}Co γ-rays, are formed in two conformations having C_{2v} and C_{3v} symmetries, the latter being the more stable form.

E.s.r. studies have recently revealed the occurrence of large Jahn–Teller distortions in radical cations formed by positive-hole capture. For example, $C_2H_6^+$ has C_{2h} symmetry,[1] cyclopropane radical cations have C_{2v} symmetry,[2] benzene radical cations have D_{2h} symmetry,[3] $SiMe_4^+$ and $GeMe_4^+$ cations have C_{2v} symmetry,[4] and CMe_4^+[1] and $SnMe_4^+$[5] cations have C_{3v} symmetry. In all examples so far studied, only one structure was detected in a given experiment. However, in the present study, two different distorted structures for SnH_4^+ radical cations at 77 K have been detected, in almost equal abundance (Figure 1).

Exposure of a solid solution of $CFCl_3$ containing *ca.* 4 mol% SnH_4 to γ-rays at 77 K gave cations whose e.s.r. spectra are shown in Figure 1(a), recorded immediately after irradiation.

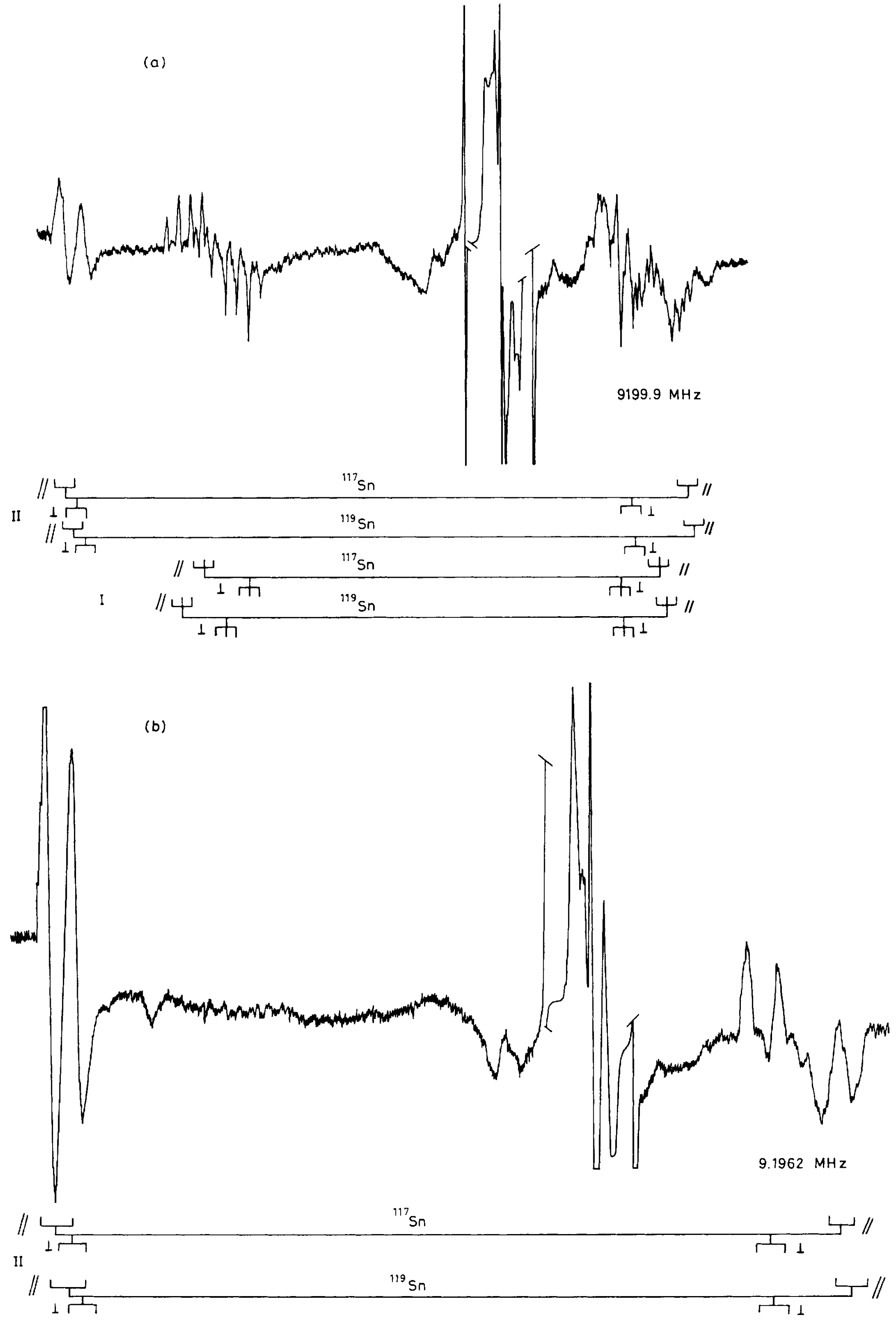

Figure 1. First derivative X-band e.s.r. spectrum for a solid solution of 4 mol% SnH_4 in $CFCl_3$ recorded (a) immediately after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to C_{2v} and C_{3v} structures of SnH_4^+ radical cations, and (b) after the storage of the irradiated sample for one week at 77 K.

The spectrum consists of intense signals appearing in the region of $g = 2$ and two pairs of tin satellites in the wing regions. All are assigned to SnH_4^+ cations, which are expected to be the major products in these experiments.[1–5] In addition to the hyperfine structure of hydrogen nuclei, isotope splittings due to ^{117}Sn ($I = \frac{1}{2}$, 7.7%) and ^{119}Sn ($I = \frac{1}{2}$, 8.7%) are resolved in the satellite features. However, the inner set of satellites were lost when the sample was stored for one week at 77 K [Figure 1(b)]. Similar experiments were also carried out with SnD_4 in $CFCl_3$, which confirmed our assignments. These results lead us to the conclusion that two different forms of SnH_4^+ are formed from SnH_4 in $CFCl_3$, one having a triplet structure due to two equivalent hydrogen nuclei (I), the other (II), a doublet structure due to a single strongly-coupled proton. The latter is the thermodynamically stable form.

We assign (I) with two equivalent hydrogens and (II) with one unique hydrogen to radical cations with C_{2v} and C_{3v} symmetries, respectively (Figure 2). As shown by the correspondence between the spectrum and the line diagrams in Figure 1, a satisfactory fit was obtained using the e.s.r. parameters listed in Table 1. The spin-density distributions calculated from the e.s.r. parameters are also given herein. For radical (I), the two equivalent hydrogen nuclei with coupling constants of 85 G[†] are expected to occupy the equatorial positions, which interact strongly with a semi-occupied hybrid orbital on the central Sn atom, as shown in Figure 2(a). This distortion is similar to those proposed for $SiMe_4^+$ and $GeMe_4^+$.[4] On the other hand, radical (II) has a C_{3v} structure similar to the structures proposed for CMe_4^+[1] and $SnMe_4^+$,[5] having a unique hydrogen with a coupling constant of 175 G, the unpaired electron being in the σ orbital composed primarily of an sp hybrid atomic orbital on tin and the s orbital of a unique hydrogen atom, as shown in Figure 2(b). It is interesting to note that the spin-density of the unique hydrogen of radical (II) is *ca.* twice as large as those of the equatorial hydrogens of radical (I).

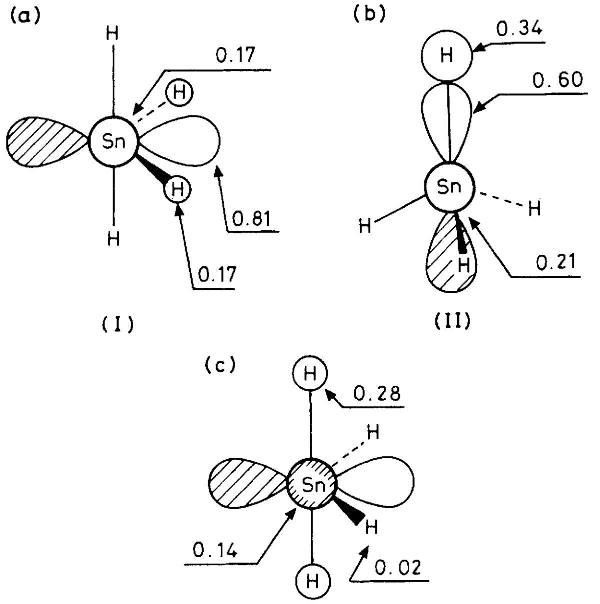

Figure 2. Structures with (a) C_{2v} and (b) C_{3v} symmetries and spin-density distributions of SnH_4^+ radical cations and (c) the structure and spin-density distribution reported for the SnH_4^- radical anion.

Table 1. E.s.r. parameters and spin-density distributions of SnH_4^+ radical cations and the SnH_4^- radical anion reported (ref. 7).

				Coupling constants[b]		Spin densities[c]	
Radical	$g_\perp$[a]	$g_{//}$[a]	Nucleus	$A_\perp$/G	$A_{//}$/G	ρ_s	ρ_p
			^{119}Sn	−2400	−3040	0.17	0.81
SnH_4^+ (I)	2.020	1.991	^{117}Sn	−2290	−2900	0.17	0.81
			H(2)	85	85	0.17	—
			^{119}Sn	−3180	−3650	0.21	0.60
SnH_4^+ (II)	2.016	1.984	^{117}Sn	−3040	−3490	0.21	0.60
			H(1)	175	175	0.34	—
			^{119}Sn	A_{iso} = −2227		0.14	—
SnH_4^- [d]	g_{iso} = 2.0037		^{117}Sn	A_{iso} = −2129		0.14	—
			H(2)	A_{iso} = 143.5		0.28	—
			H(2)	A_{iso} = 8.0		0.02	—

[a] Evaluated from intense central signals. [b] Evaluated from Sn satellites. [c] Calculated using atomic parameters listed by Morton and Preston (ref. 6) and the procedure given by Symons ('Chemical and Biochemical Aspects of Electron Spin Resonance Spectroscopy,' Van Nostrand Reinhold, Wokingham, 1978). [d] Ref. 7.

Despite the formal similarity in the structures for SnH_4^+ (II) and $SnMe_4^+$,[5] both having one electron in a single stretched σ-bond, there is a remarkable difference in that the tin orbital contribution to the SOMO for SnH_4^+ is strongly s–p hybridised, whereas that for $SnMe_4^+$ is almost pure p in character. One reason for this change is the increased methyl-radical character in the latter, and the high stability of the planar Me_3Sn^+ cation relative to the SnH_3^+ cation. Again, there is a formal similarity between the results for the C_{2v} cation (I) and our recent results for the 'isoelectronic' radical BH_4.[8] However, in that case, as with $SnMe_4^+$, the orbital on boron was pure p rather than being hybridised. In this case we suggest that this is because the SOMO has switched from $1b_2$ for BH_4 to $2a_1$ for SnH_4^+ (I).

It is interesting to compare these results with those for SnH_4^- anions, which are formed by electron capture in solid matrices of neopentane[7] and tetramethylsilane.[9] These anions have a C_{2v} structure. However, two hydrogen nuclei with coupling constants of 143.5 G are assigned to the axial positions, the SOMO being made up of their 1s atomic orbitals and an sp hybrid orbital on tin, as shown in Figure 2(c).

Similar studies of radical cations have been carried out with the series of methylstannanes, $SnMe_xH_{4-x}$ where $x = 1, 2, 3$ in $CFCl_3$. $SnMeH_3^+$ and $SnMe_2H_2^+$ have C_{2v} structures with the substituent methyl groups in the axial positions. On the other hand, $SnMe_3H^+$ probably has a single methyl group in the unique position of a quasi-C_{3v} structure similar to the structure reported for $SnMe_4^+$.[5] In the case of $SnMe_2H_2^+$, yet another type of cation has been detected. A full report of these results will be given elsewhere.

Received, 8th June 1983; Com. 746

References

1 M. Iwasaki, K. Toriyama, and K. Nunome, *J. Am. Chem. Soc.*, 1981, **103**, 3591; K. Toriyama, K. Nunome, and M. Iwasaki, *J. Chem. Phys.*, 1982, **77**, 5891.
2 M. Iwasaki, K. Toriyama, and K. Nunome, *J. Chem. Soc., Chem. Commun.*, 1983, 202.
3 M. Iwasaki, K. Toriyama, and K. Nunome, *J. Chem. Soc., Chem. Commun.*, 1983, 320.
4 B. W. Walther and F. Williams, *J. Chem. Soc., Chem. Commun.*, 1982, 270.
5 M. C. R. Symons, *J. Chem. Soc., Chem. Commun.*, 1982, 869.
6 J. R. Morton and K. F. Preston, *J. Magn. Reson.*, 1979, **30**, 577.
7 J. R. Morton and K. F. Preston, *Mol. Phys.*, 1975, **30**, 1213.
8 M. C. R. Symons, T. Chen, and C. Glidewell, *J. Chem. Soc., Chem. Commun.*, 1983, 326.
9 A. Hasegawa, T. Yamaguchi, and M. Hayashi, *Chem. Lett.*, 1980, 611.

[†] 1 G = 10^{-4} T.