Electron Spin Resonance Study of Some Silicon-, Germanium-, and Tin-Centered Radicals[1]

R. V. Lloyd and Max T. Rogers*

Contribution from the Department of Chemistry, Michigan State University, East Lansing, Michigan 48823. *Received October 24, 1972*

Abstract: The radicals $\cdot Sn(CH_3)_nCl_{3-n}$ (n = 0, 1, 2, 3), $\cdot GeCl_3$, and $\cdot SiCl_3$ have been prepared in either an adamantane matrix or the self-matrix and studied by esr spectroscopy. Anisotropic spectra were obtained for the two mixed chloromethylstannyl radicals but only isotropic spectra for the others; the observable esr parameters were evaluated in each case. The structures of the radicals have been discussed on the basis of the esr data, and these results, along with appropriate values from the literature, have permitted a comparative study of the chloro and methyl radicals of the group IVa elements. The series $\cdot M(CH_3)_3$ and $\cdot MH_3$ (M = Si, Ge, Sn) both appear to be strongly bent with not greatly different geometries. The carbon-centered analogs, on the other hand, vary from planar [$\cdot CH_3$] to a distortion of about 8–10° from planar [$\cdot CCl_3$] with the $\cdot C(CH_3)_3$ intermediate between these. It is found that the g values increase from carbon to tin in the $\cdot M(CH_3)_3$ series but decrease in the $\cdot MCl_3$ series. This surprising result indicates that ligand spin–orbit coupling from (d–p)π bonding involving chlorine is important in the latter series.

Radicals containing the higher homologs of carbon are of considerable interest to spectroscopists for comparison with the more familiar carbon radicals and for study of trends in the structures in going from carbon to tin. In particular, interest in radicals containing tin has been growing recently, and a few organotin radicals have been characterized by esr (Table I).[2–13] However, most of the tin radicals so far reported have the tin atom as a substituent β or γ to a trivalent carbon radical site. The only tin-centered radicals that have been studied so far are the trimethylstannyl[5,8,9] and triisobutylstannyl[4] radicals, in addition to stannyl radical ($\cdot SnH_3$) itself,[2,3] and reliable values of the tin hyperfine splittings (from ^{117}Sn and ^{119}Sn) have not been measured for any of these. It was also reported that $\cdot SnCl_3$ was formed upon the γ-irradiation of frozen $SnCl_4$, although esr parameters were not given.[14]

Therefore, we have obtained the epr parameters of the various chloromethylstannyl radicals, in order to determine their structures and to study the effects of two very different ligands ($-CH_3$ *vs.* $-Cl$) on the structures. In order to facilitate comparisons with analogous group IV radicals (*i.e.*, $\cdot M(CH_3)_3$ and $\cdot MCl_3$, where M = C, Si, Ge, Sn), we have obtained missing parameters for several silicon and germanium radicals. The adamantane matrix technique[15] was used in most cases so that well-resolved isotropic spectra could be obtained.

Experimental Section

The radical precursors were tetramethyltin (Metal and Thermit Co., Rahway, N. J.), methyltrichlorotin, dimethyldichlorotin, trimethylchlorotin, tetramethylgermanium (Alfa Inorganics, Inc., Beverley, Mass.), ethyltrichlorosilane (Columbia Inorganic Chemicals, Inc., Columbia, S. C.), and stannic chloride (Fisher Scientific Co., Pittsburgh, Pa.). The tetramethyltin was redistilled before use and the others were used as received. Adamantane (Aldrich Chemical Corp., Milwaukee, Wis.) was purified before use by treatment with activated carbon in n-heptane and recrystallization. For sample preparation, adamantane was dissolved in the appropriate liquid precursor, precipitated, and filtered as previously described.[15] If the precursor was a solid, it was cosublimed with adamantane. In either case the resulting solid was pressed into a pellet, which was γ-irradiated (^{60}Co) for 3 hr at 77°K at a dose rate of approximately 1 Mrad/hr. The dimethyl- and trimethyltin chlorides were also γ-irradiated neat at 77°K.

Spectra were taken with Varian V-4502 X-band and V-4503 Q-band esr spectrometers, equipped with Varian variable-temperature accessories. The g values were measured at X-band with a proton nmr magnetic marker and a microwave spectrum analyzer. The tin hyperfine splitting was measured at Q-band.

Results

In the case of the tin radicals in adamantane, complex anisotropic esr spectra were initially observed. However, the unwanted lines were sufficiently saturated at high microwave power to allow the lines from the desired radicals to be clearly seen. This is in accord with the expectation that radicals with spin density on heavy elements should saturate with greater difficulty than carbon-centered radicals, which are probably the other species produced on irradiation.

The irradiated tetramethyltin in adamantane gave an isotropic ten-line spectrum with binomial intensity ratios. The X-band spectrum at 213°K is shown in Figure 1, the two high-field lines being obscured by impurities. We assign the spectrum to the $\cdot Sn(CH_3)_3$ radical formed by loss of a methyl group from the starting compound; the esr parameters agree with those measured by Watts and Ingold[9] in solution at 208°K (Table I). The proton hyperfine splitting was independent of temperature over the observable range 193–233°K and the radical disappeared above that.

Irradiated tetramethylgermanium in adamantane

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[1] This work was supported through a contract with the Atomic Energy Commission and this is AEC Document No. COO-1385-46.

[2] R. L. Morehouse, J. J. Christiansen, and W. Gordy, *J. Chem. Phys.*, **45**, 1751 (1966).

[3] G. A. Jackel and W. Gordy, *Phys. Rev.*, **176**, 443 (1968).

[4] U. Schmidt, K. Kabitzke, K. Markau, and W. P. Neumann, *Chem. Ber.*, **98**, 3827 (1965).

[5] K. Höppner and G. Lassman, *Z. Naturforsch. A*, **23**, 1758 (1968).

[6] J. H. Mackey and D. E. Wood, *Mol. Phys.*, **18**, 783 (1970).

[7] A. Hudson and H. A. Hussain, *J. Chem. Soc. B*, 793 (1969).

[8] P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **91**, 6161 (1969); $a(CH_3)$ = 0.17 G.

[9] G. B. Watts and X. U. Ingold, *ibid.*, **94**, 491 (1972).

[10] J. E. Bennett and J. A. Howard, *Chem. Phys. Lett.*, **15**, 322 (1972).

[11] A. R. Lyons and M. C. R. Symons, *Chem. Commun.*, 1067 (1971).

[12] T. Kawamura and J. K. Kochi, *J. Amer. Chem. Soc.*, **94**, 648 (1972); the values for a(Sn) are corrected to second order.

[13] P. J. Krusic and J. K. Kochi, *ibid.*, **93**, 846 (1971).

[14] M. Magat, N. Leray, and J. Roncin, *Zh. Vses. Khim. Obshchest.*, **11**, 223 (1966).

[15] D. E. Wood and R. V. Lloyd, *J. Chem. Phys.*, **53**, 3932 (1970).

Table I. Esr Parameters of Neutral Organotin Radicals

Radical	$g_{\parallel}$	$g_{\perp}$	g_{iso}	$a(H_\alpha)$[a]	$a(H_\beta)$	$a(^{117}Sn)$	$a(^{119}Sn)$	Ref
$\cdot SnH_3$	2.003	2.025	2.017	26		380		2, 3
$(i\text{-}C_4H_9)_3Sn\cdot$	2.034	2.002	2.013					4
$(CH_3)_3Sn\dot{C}H_2$			2.067	21		132		5
$(CH_3)_3Sn\dot{C}H_2$	2.0029	1.9997	2.0008	21.4		130		6
$(CH_3)_3Sn\dot{C}H_2$				21.25		132.5	137.0	7
$(CH_3)_3Sn\dot{C}H_2$				20.84				8
$(CH_3)_3Sn\cdot$			2.023					5
$(CH_3)_3Sn\cdot$			2.017		2.75			8
$(CH_3)_3Sn\cdot$			2.0154		2.76	1899	1983	*b*
$(CH_3)_3Sn\cdot$	2.0296, 2.0243, 1.9950		2.0163			1530	1611	9
$(CH_3)_2Sn(Cl)\dot{C}H_2$			2.009	20		160		5
$(n\text{-}C_4H_9)_3SnCH_2\dot{C}H_2$				19.64	15.67			13
$(n\text{-}C_4H_9)_3SnCH_2\dot{C}HC_2H_5$						420		12
$(CH_3)_3SnCH_2\dot{C}H_2$			2.00205	19.69	15.84	467.7	488.9	12
$(CH_3)_3SnCH_2\dot{C}H_2$				19.74	15.75			13
$(C_6H_5)Sn(CH_3)_2\dot{C}H_2$				21.2		136.5	142.0	7
$(CH_3CH_2)_3Sn\dot{C}HCH_3$				20.41	25.89			8
$(CH_3CH_2)_3SnCH_2\dot{C}H_2$				19.77	16.12			8
				22[c]				5
$(n\text{-}C_4H_9)_3SnO\dot{C}H_2$				16.30				8

[a] The hyperfine splittings are given in gauss. [b] This work. The values for $a(Sn)$ are corrected to second order. [c] The value of $a(H)$ is for four equivalent protons.

Table II. Comparison of Esr Parameters and Structures of $\cdot M(CH_3)_3$ Radicals (M = C, Si, Ge, Sn)

M	$a(M)$ in $\cdot M(CH_3)_3$, G	g_{iso}	$g_{\perp}$(calcd)	$\rho(ns)$	$\Delta E \times 10^3$, cm^{-1}	ϕ,[a] deg	$a(M)$ in $\cdot MH_3$, G
^{13}C	46.2[b]	2.0029	2.0032	0.04	30	9	37.7[c]
^{29}Si	183[d]	2.0031	2.0035	0.12	109	13	180[e]
^{73}Ge	84.7[f]	2.0101	2.014	0.10	72	13	75
^{119}Sn	1983	2.0154	2.022	0.13	93	14	380[e]

[a] ϕ is the angle between the M–C bond and the plane through atom M perpendicular to the C_{3v} axis. [b] Reference 29. [c] M. T. Rogers and L. D. Kispert, *J. Chem. Phys.*, **46**, 221 (1967). [d] Reference 28. [e] Reference 3. [f] In an adamantane matrix $a(H_\beta)$ = 5.28 G at 173°K.

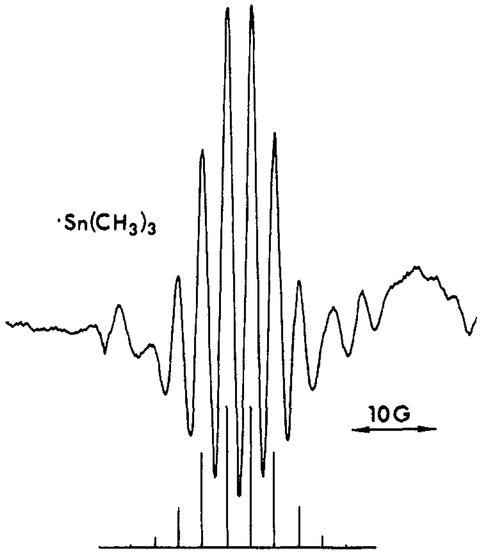

Figure 1. Second-derivative esr spectrum of irradiated tetramethyltin in an adamantane matrix.

gave results similar to the tin compound. The measured parameters (Table II) are in reasonable agreement with previously published values for the trimethylgermyl radical.[2,3,16] The proton hyperfine splitting was again temperature independent and the radical was stable up to 253°K. In the spectrum taken at 233°K the ten lines from ^{73}Ge (I = 9/2) in natural abundance were all observed, although several were obscured by interfering lines so that their positions could not be accurately measured. The hyperfine splitting constant was determined from the spacing between the I = 9/2 and I = −9/2 lines (Table II). The experimental line positions are compared in Table III with the line positions calculated from the Breit–Rabi equation following the formulation of Roncin and Debuyst.[17]

Table III. Field Positions for the ^{73}Ge Lines in $\cdot Ge(CH_3)_3$

I_z	Position, G	
	Exptl	Calcd
−9/2	2826	2825.5
−7/2	2902	2901.3
−5/2	2980	2979.2
−3/2	3059	3059.4
−1/2		3141.9
0	3212	
1/2		3226.6
3/2	3313	3313.5
5/2		3402.7
7/2		3494.2
9/2	3588	3587.8

The $\cdot MCl_3$ radicals with three equivalent chlorine atoms would be expected to have ten groups of lines with relative group intensities 1:3:6:10:12:12:10:6:3:1, although the presence of the two chlorine isotopes makes the actual pattern considerably more complicated.

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(16) S. W. Bunnett, C. Eaborn, A. Hudson, H. A. Hussain, and R. A. Jackson, *J. Organometal. Chem.*, **16**, P36 (1969).

(17) J. Roncin and R. Debuyst, *J. Chem. Phys.*, **51**, 577 (1969).

The outermost group (of unit intensity) should, for example, actually consist of four evenly spaced lines with relative intensities 27 : 27 : 9 : 1, from the isotopic species $\cdot M^{35}Cl_3$, $\cdot M^{35}Cl_2{}^{37}Cl$, $\cdot M^{35}Cl^{37}Cl_2$, and $\cdot M^{37}Cl_3$. Three of the four members of this outer group (with relative intensities 27 : 27 : 9) can actually be seen in the spectrum from irradiated ethyltrichlorosilane in adamantane (Figure 2A) while the fourth component is too weak to be observed. The radical is clearly the trichlorosilyl radical, $\cdot SiCl_3$, and the chlorine hyperfine splitting agrees with that reported by Roncin.[18]

Similarly, the irradiation of both stannic chloride and methyltrichlorotin in adamantane gave, in addition to different interfering radicals in each case, the same type of ten-line spectrum that was obtained with the silicon radical. The spectrum from irradiated CH_3SnCl_3 is shown in Figure 2B. Although it is partially obscured by another radical of higher g value, three lines of the outermost unit-intensity group can be seen on the high-field side. The esr parameters for the known $\cdot MCl_3$ radicals[17-19] are reported in Table IV.

Table IV. Esr Parameters of $\cdot MCl_3$ Radicals (M = C, Si, Ge, Sn)

M	g	$a(^{35}Cl)$, G	a(M), G	ϕ^a	Ref
^{13}C	2.0091	6.25	114	8–10°	*b*, 32
^{29}Si	2.0041	13.0	408 ± 10	19°	*c*
		13.1	416		18
^{73}Ge	2.0070	12.5	220	19°	17
^{119}Sn	1.9974	10.5			*d*
	1.9976	10.85			*e*

[a] ϕ is the angle between the M–C bond and the plane through atom M perpendicular to the C_{3v} axis. [b] L. D. Kispert and M. T. Rogers, *J. Chem. Phys.*, in press. [c] This work. The radical precursor was ethyltrichlorosilane in adamantane. [d] This work. The radical precursor was methyltrichlorostannane in adamantane. [e] This work. The radical precursor was stannic chloride in adamantane.

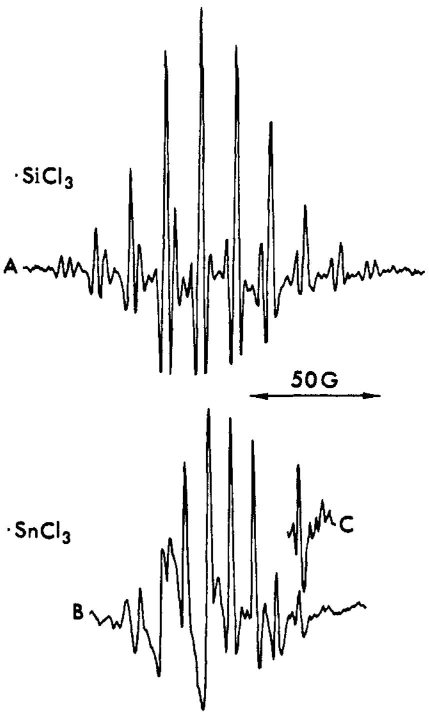

Figure 2. (A) Second-derivative esr spectrum of irradiated ethyltrichlorosilane in an adamantane matrix. (B) Second-derivative esr spectrum of irradiated methyltrichlorotin in an adamantane matrix. (C) Spectrum B at higher gain.

Table V. Comparison of the Esr Parameters of Chloromethylstannyl Radicals

Radical	Precursor	$g_\parallel$	$g_\perp$	g_{iso}	$a_\parallel$(Cl)	$a_\perp$(Cl)	a_{iso}(Cl)	$a(^{119}Sn)$
$\cdot Sn(CH_3)_3$	$Sn(CH_3)_4$ in adamantane	2.0023 (Assumed)	2.0154 (Calcd)	2.0154 (Obsd)				1983
$\cdot Sn(CH_3)_2Cl^a$	$Sn(CH_3)_3Cl$ in adamantane	2.0054	2.0142	2.0113	29.1	~0	9.7	
$\cdot Sn(CH_3)Cl_2{}^b$	$Sn(CH_3)_2Cl_2$	2.0164	1.9932	2.0009 (Calcd)	27.9	~0	9.3 (Calcd)	
$\cdot SnCl_3$	CH_3SnCl_3 in adamantane			1.9974 (Obsd)			10.5	

[a] $T = 213°K$; all hyperfine splittings in gauss. [b] $T = 143°K$.

For the $\cdot Sn(CH_3)_3$ radical the lines from the two isotopes ^{117}Sn and ^{119}Sn could be individually resolved. The lines had approximately the overall widths (25 G) to be expected on the basis of the proton splittings, but because of the high modulation amplitudes required, the individual proton lines were not resolved. The measured hyperfine splittings were corrected to second order with the Breit–Rabi equation. The ratio of the measured values for ^{117}Sn and ^{119}Sn is $a(^{119}Sn)/a(^{117}Sn) = 1.044$ compared with the ratio of the magnetic moments $\mu(^{119}Sn)/\mu(^{117}Sn) = 1.046$; the close agreement shows that the lines were correctly identified.

Dimethyldichlorotin and trimethylchlorotin when irradiated in adamantane did not give interpretable, isotropic spectra. However, the latter compound did give an anisotropic spectrum resulting from a radical containing one chlorine atom, which is probably the dimethylchlorostannyl radical, formed by loss of a methyl group from the trimethylchlorotin. We analyze the spectrum (Figure 3) in terms of axial g and hyperfine tensors, with $a_\perp(Cl) \sim 0$. The lines attributed to ^{35}Cl and ^{37}Cl have the correct relative intensities and spacings for the two isotopes. The parameters are listed in Table V. When trimethylchlorotin was irradiated neat, a different spectrum was obtained, similar to that found by Höppner and Lassman,[5] and ascribed by them to the substituted methyl radical $(CH_3)_2Sn(Cl)\dot{C}H_2$.

Dimethyldichlorotin, when irradiated neat at 77°K and examined at 133°K, gave the anisotropic spectrum shown in Figure 4. There are obviously several radicals present; the large doublet, in particular, was still

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(18) (a) J. Roncin, *Mol. Crystallogr.*, **3**, 117 (1967); (b) N. Leray and J. Roncin, *J. Chem. Phys.*, 42, 800 (1965).

(19) A. Hudson and H. A. Hussain, *Mol. Phys.*, **16**, 199 (1969).

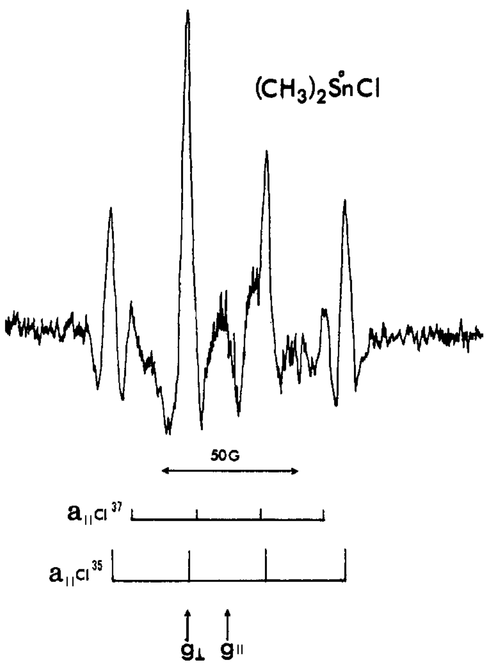

Figure 3. Second-derivative esr spectrum of irradiated trimethylchlorotin in an adamantane matrix.

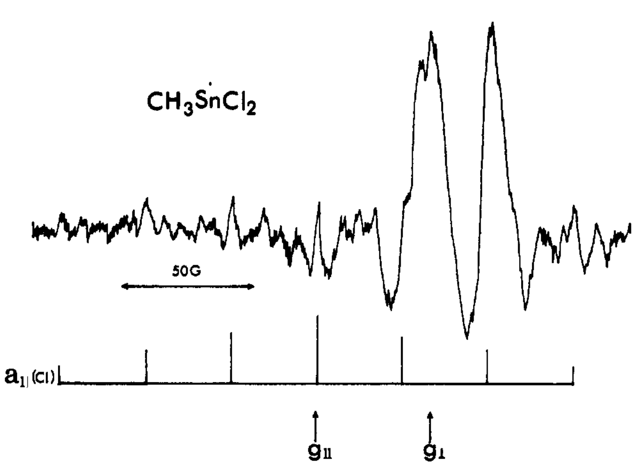

Figure 4. Second-derivative esr spectrum of irradiated neat dimethyldichlorotin.

present at room temperature when all other lines had disappeared. The lines identified in Figure 4 as $g_{\parallel}$, $g_{\perp}$, and $a_{\parallel}$(Cl) had a common temperature dependence and therefore were assigned to the same radical. The parallel lines have a constant spacing and the correct relative intensities for two equivalent chlorine atoms (1:2:3:4:3:2:1) and the perpendicular line are, as expected, more intense than the parallel lines; we therefore assume that the radical responsible is the methyldichlorotin radical, $CH_3\dot{S}nCl_2$. Again, as in the case of the dimethylchlorostannyl radical, $a_{\perp}$(Cl) is taken to be zero within the experimental resolution.

Discussion

Radiation Chemistry and Radical Stability. In the irradiation, both neat and in the adamantane matrix, of tin compounds of the type $(CH_3)_nSnCl_{4-n}$ the dominant mode of decomposition appears to be the breaking of a C–Sn bond, rather than a Cl–Sn bond. For example, CH_3SnCl_3 in adamantane did not yield any of the methyldichlorostannyl radical. Also, we did not obtain any of the substituted methyl radicals, $\cdot CH_2Sn(CH_3)_nCl_{3-n}$, in sufficiently high yield to be identified. These results would be expected on a simple thermodynamic basis since the M–Cl bond energies are larger than the M–C bond energies (M = Si, Ge, Sn) and they are in agreement with previous work. Janzen and Blackburn[20] irradiated tetraorganotin compounds and organotin chlorides in solution and obtained evidence for the formation of radicals by the removal of an organic group from the tin compound, although they were not able to get a radical from methyltrichlorotin itself. Dimethyldichlorotin has been shown to produce the methyldichlorostannyl radical by vapor phase thermal decomposition.[21] Our results with $CH_3CH_2SiCl_3$ and CH_3GeCl_3 (which we irradiated to check the parameters of the $\cdot GeCl_3$ radical) in adamantane were similar to those with CH_3SnCl_3 discussed above in that the trichloro radical was always formed in good yield. However, Hesse, Leray, and Roncin[22] irradiated the various methylchlorosilanes and found that the more abundant radical was the substituted methyl radical in each case, and radicals resulting from rupture of the Si–Cl or Si–C bonds were secondary products.

Radical formation and stability are related to the matrix. Trimethylchlorotin irradiated in adamantane gave the dimethylchlorostannyl radical, which did not disappear entirely until ~253°K; irradiated neat it did not give this radical at all. Apparently the radical in the pure solid reacts with its neighbors quite easily whereas it does not react with neighboring adamantane molecules. In this case, since the adamantane–trimethylchlorotin system was prepared by cosublimation, rather than by precipitation from solution, the substrate was not necessarily incorporated into the adamantane crystal lattice, and the molecules could well have gone into interstitial voids too small to allow free rotation, thus explaining the observed anisotropic spectra. However, the adamantane matrix would still act as a diluent to prevent the tin radicals from reacting with one another or with neutral trimethylchlorotin molecules. We do not understand why the dimethyldichlorotin in adamantane did not give an interpretable spectrum. However, the methyldichlorostannyl radical from neat dimethyldichlorotin was extremely unstable and disappeared above 153°K.

In general the stability of the radicals in adamantane decreases in going from carbon- to tin-centered species. For example, the *tert*-butyl radical is stable at room temperature, trimethylgermyl disappears at ~253°K, and trimethylstannyl disappears at ~233°K. Similarly, the trichlorosilyl radical has a half-life at room temperature of ~10 min, the trichlorostannyl radical disappears below 243°K, and the trichlorogermyl radical is intermediate in stability.

Hyperfine Splittings and Radical Geometries. As can be seen from comparison of the tin-centered radicals with those radicals in which a tin atom is α or β to

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(20) E. G. Janzen and B. J. Blackburn, *J. Amer. Chem. Soc.*, **91**, 4481 (1969).

(21) S. J. W. Price and A. F. Trotman-Dickenson, *Trans. Faraday Soc.*, **54**, 1630 (1958).

(22) C. Hesse, N. Leray, and J. Roncin, *J. Chem. Phys.*, **57**, 749 (1972).

the carbon carrying the unpaired electron (Table I), the tin hyperfine splittings fall into three distinct groups. For radicals of the type $\cdot SnR_3$, $a(Sn) \geq 1900$ G, which is mostly direct contact interaction, for $R_3Sn\dot{C}R_2$, $a(Sn) \sim 130$–160 G and is attributed to spin polarization through the Sn–C bond, for $R_3SnCH_2\dot{C}H_2$, $a(Sn) \sim 420$–470 G and is probably largely from hyperconjugation, although direct overlap of the odd-electron orbital with tin orbitals also becomes possible. The only apparent exception to these generalizations is the $\cdot SnH_3$ radical, which we discuss below.

The geometry of the $\cdot MR_3$ radicals can in principle be determined from an analysis of the central atom hyperfine splitting. Jackel and Gordy[3] concluded from the respective hyperfine splittings that the $\cdot SnH_3$, $\cdot GeH_3$, and $\cdot SnH_3$ radicals were nonplanar, in contrast to $\cdot CH_3$. In the case of all but the $\cdot SnH_3$ radical this conclusion is supported by matrix-isolation infrared studies,[23–25] but the $\cdot SnH_3$ radical has not been detected spectroscopically except by esr. Jackel and Gordy[3] suggested that the $^{117,119}Sn$ hyperfine interaction in $\cdot SnH_3$ was 380 G and, using their estimated value for a_0 (the splitting for a 5s electron on a tin atom) of 3260 G, they concluded that $\cdot SnH_3$ was pyramidal with the angle out-of-plane (the angle below the plane through the central atom and perpendicular to the C_{3v} axis) equal to 10°. However, in view of our experimental values for a(Sn) and the recent calculation of Mackey and Wood[6,26] giving $a_0 = 15{,}400$ G, the assignment of the tin satellites and the calculations of Jackel and Gordy are almost certainly incorrect,[10] although we agree that SnH_3 is probably nonplanar (*vide infra*).

Using our value for $a(^{119}Sn)$ in $\cdot Sn(CH_3)_3$ and the a_0 value of Mackey and Wood,[6] we calculate the tin 5s orbital character of the unpaired electron to be $\rho_{5s} = 1{,}983/15{,}400 \sim 0.13$. By normalization the 5s character of the tin bonding orbitals s_b is therefore 0.29. The C–Sn–C bond angle θ may then be calculated by use of the equation[3] $\cos(\pi - \theta) = s_b/(1 - s_b)$. The value $s_b = 0.29$ corresponds to $\theta = 114°$, or an out-of-plane angle (the angle between the Sn–C bond and the plane perpendicular to the threefold axis) of 14°. Because of the approximations made in the above analysis we do not claim great absolute accuracy for this angle; we merely state that the radical is definitely nonplanar. Walsh in fact predicted that AH_3 radicals with seven or more valence electrons would be nonplanar[27] and, as we shall show, the $\cdot MH_3$ and $\cdot M(CH_3)_3$ radicals have similar structures.

Using reported values for the central-atom splitting in the $\cdot Si(CH_3)_3$ radical[28] and the $\cdot C(CH_3)_3$ radical[29] and our observed value for $\cdot Ge(CH_3)_3$, we similarly calculated the out-of-plane angles for these radicals (Table II). To obtain the required $a_0(^{73}Ge)$ the method of Hurd and Coodin[30] was used, along with the empirical relativistic correction factor of Mackey and Wood;[26] the value $a_0(^{73}Ge) = 850$ G was estimated by this method. The relative accuracy of the results for the different radicals should be reasonably good since we used atomic hyperfine interactions (a_0) calculated in a consistent manner for all of the atoms involved.[30] The calculated geometries suggest that carbon radicals are qualitatively different but that the other radicals have essentially the same geometry. Comparison of the central atom splittings for the corresponding $\cdot MH_3$ and $\cdot M(CH_3)_3$ radicals (Table II) shows that they are nearly the same except, of course, for the methyl radical which is known to be planar; also, except for carbon, the g values for corresponding radicals are nearly the same. Therefore, we can state that the substitution of a methyl group for a proton does not change the geometry of the silicon-, germanium-, or tin-centered radicals and that these radicals are pyramidal. This is somewhat in disagreement with the conclusion of Hesse, *et al.*,[22] who suggested that in the trimethylsilyl radical the angle ϕ is less than 5°. We have reached conclusions similar to the above concerning the effect of substitution of halogen-containing groups for protons in several other series of halogenated aliphatic radicals.[31]

In the $\cdot MCl_3$ radicals the structure of the carbon radical is again different from the other members of the series. Hesse, Leray, and Roncin[32] obtained a Cl–M–Cl angle of 116° in $\cdot CCl_3$ from analysis of their esr data. We have used the central atom splitting to calculate the corresponding angles in $\cdot SiCl_3$ and $\cdot GeCl_3$ (Table IV) and they are seen to have nearly the tetrahedral values. The $\cdot CCl_3$ radical is known from infrared results,[33] as well as the esr data, to be more planar than the other $\cdot MCl_3$ radicals.[34,35] It also has been shown that in the series of radicals $\cdot CF_nCl_{3-n}$ the chlorine hyperfine splitting increases with increased bending from planarity.[36] Thus, the abrupt increase in chlorine hyperfine splitting in going from $\cdot CCl_3$ to its higher homologs (Table IV) is accounted for by the change in geometry. This change would be expected on the basis of Pauling's arguments that the structures of AX_3 radicals depend on the electronegativity difference between A and X,[37,38] since carbon is more electronegative than its higher homologs and the electronegativity difference increases in going down the IVa group.

In the two chloromethyltin radicals (Table V) we were not able to observe the β proton hyperfine splittings. It is probable that the radicals become more nearly tetrahedral in going from $\cdot Sn(CH_3)_3$ to $\cdot SnCl_3$ (compare Tables II and IV) and that $a(H_\beta)$ decreases in the same order and so is too small to be resolved in $\cdot Sn(CH_3)_2Cl$ and $\cdot Sn(CH_3)Cl_2$. A decrease in the β proton hyperfine splitting with increasing number of chlorine atoms has been observed in the radicals $\cdot Si(CH_3)_nCl_{3-n}$[22] and $\cdot C(CH_3)_nCl_{3-n}$.[36] The magnitudes of a_{iso}(Cl) in the series (Table V) also show that the

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(23) D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, 47, 5146 (1967).

(24) D. E. Milligan and M. E. Jacox, *ibid.*, 52, 2594 (1970).

(25) G. R. Smith and W. A. Guillory, *ibid.*, 56, 1423 (1972).

(26) J. H. Mackey and D. E. Wood, *ibid.*, 52, 1423 (1972).

(27) A. D. Walsh, *J. Chem. Soc.*, 2296 (1953).

(28) S. W. Bennett, C. Eaborn, A. Hudson, R. A. Jackson, and K. D. J. Root, *J. Chem. Soc. A*, 348 (1970).

(29) D. E. Wood, L. F. Williams, R. F. Sprecher, and W. A. Lathan, *J. Amer. Chem. Soc.*, 94, 6241 (1972).

(30) C. M. Hurd and P. Coodin, *J. Phys. Chem. Solids*, 28, 523 (1966).

(31) R. V. Lloyd and M. T. Rogers, unpublished results.

(32) C. Hesse, N. Leray, and J. Roncin, *Mol. Phys.*, 22, 137 (1971).

(33) E. E. Rogers, S. Abramowitz, M. E. Jacox, and D. E. Milligan, *J. Chem. Phys.*, 52, 2198 (1970).

(34) M. E. Jacox and D. E. Milligan, *ibid.*, 49, 3130 (1968).

(35) W. A. Guillory and C. E. Smith, *ibid.*, 53, 1661 (1970).

(36) J. Cooper, A. Hudson, and R. A. Jackson, *Mol. Phys.*, 23, 209 (1972).

(37) L. Pauling, *J. Chem. Phys.*, 51, 2767 (1969).

(38) A. D. Walsh, *J. Chem. Soc.*, 2301 (1953).

presence of even one chlorine atom causes the radical geometry to become much more bent than that of $\cdot Sn(CH_3)_3$. If the small increase in a(Cl) upon going from the $\cdot Sn(CH_3)_2Cl$ and $\cdot Sn(CH_3)Cl_2$ radicals to the $\cdot SnCl_3$ radical has the same significance as the increase in the corresponding silyl radicals,[22] it is consistent with an increasing deviation from planarity in going from $\cdot Sn(CH_3)_3$ to $\cdot SnCl_3$.

***g* Values.** An interesting aspect of this work is the fact that the g values in the two series of radicals $\cdot M(CH_3)_3$ and $\cdot MCl_3$ go in opposite directions. In the former series the g values increase in going from C to Sn (Table IV) while in the latter they decrease (Table II), except for $\cdot GeCl_3$, which anomaly we do not understand. In both cases the changes are not caused by any progressive variation in geometry; we have shown above that the $\cdot M(CH_3)_3$ radicals (M = Si, Ge, Sn) all have nearly the same geometry as do the $\cdot SiCl_3$ and $\cdot GeCl_3$ radicals.

The trend of the g values in the $\cdot M(CH_3)_3$ radicals is what would be expected as M goes to heavier atoms with larger spin–orbit coupling constants. This is shown by eq 1, giving the variation of a g tensor component from the free-spin value[39]

$$\Delta g_{zz} = 2 \sum_{ij} \frac{\xi_i}{E_j - E_0} \langle \psi_0 | \mathbf{L}_z | \psi_j \rangle \langle \psi_j | \mathbf{L}_z | \psi_0 \rangle \qquad (1)$$

where ξ_i is the spin–orbit coupling constant of atom i, E_0 and E_j are the ground state and excited state energies, respectively, ψ_0 and ψ_j are the corresponding molecular orbital wave functions, and $\mathbf{L}_z$ is the angular momentum operator. Thus, if the other factors are the same, we expect the g tensor component to increase as we go to radicals with atoms having larger spin–orbit coupling constants, as is observed for the $\cdot M(CH_3)_3$ radicals.

For pyramidal radicals with sp hybrid bonds we can write eq 1 as[2]

$$\Delta E = E_j - E_0 = -p\xi/(g_\perp - g_\parallel) \qquad (2)$$

where p represents the fractional p character of the unpaired electron orbital, and $g_\perp$ and $g_\parallel$ are the components of the axial g tensor. For the $\cdot MH_3$ radicals the values of $g_\parallel$ were found experimentally to be nearly equal to the free-spin value,[2] which is to be expected from consideration of the orbitals of a pyramidal AH_3 molecule,[40] and we now assume that the same is true for the $\cdot M(CH_3)_3$ radicals (*i.e.*, $g_\parallel \cong 2.0023$). We can then calculate $g_\perp$ from the relationship $g_{iso} = {}^1/_3 \cdot (g_\parallel + 2g_\perp)$, and the excitation energy ΔE from eq 2 above. The results are listed in Table II. The values of ΔE are sufficiently similar to one another to support the conclusions that we reached from the bond angle calculations, namely, that the $\cdot M(CH_3)_3$ radicals (except M = C) have the same structures.

The situation is obviously quite different with the $\cdot MCl_3$ radicals, where the g values decrease even though the radicals are nonplanar and have similar structures. Atkins and Symons,[40] with the use of Walsh's correlation diagram, state that a 25 electron AB_3 radical should have g values of the order $g_\parallel \sim g_\perp \geq 2.0023$, although they suggest that low values of $g_\perp$ would be due to the participation of d orbitals on the ligand in the bonding. The values of $g_\parallel$ and $g_\perp$ observed for the chloromethylstannyl radicals (Table V) show that the low value of g_{iso} in the $\cdot SnCl_3$ radical is caused by the decrease in $g_\perp$ in going from $\cdot Sn(CH_3)_3$ to $\cdot SnCl_3$. Thus, $g_\parallel$ is always larger than the free-spin value as expected, and $g_\perp$ decreases as the number of α chlorine atoms, and therefore the possibility of (d–p)π bonding, increases. Such (d–p)π bonding has been proposed from infrared studies to account for the extra stability of chloromethyl[41] and bromomethyl radicals.[42] The trend of the g values in the $\cdot MCl_3$ radicals seems to show that this interaction becomes more important in going down the series from carbon to tin.

Conclusions

We have studied by means of esr spectroscopy the structures of some group IVa (C, Si, Ge, Sn) methyl and chloro radicals and have compared them with previously observed members of the series. It has been found that, except for carbon-centered radicals, the radicals within each series, $\cdot M(CH_3)_3$ or $\cdot MCl_3$, have nearly the same geometries, with the trichloro radicals being more nonplanar than the trimethyl radicals. The two carbon-centered radicals are also nonplanar but less so than the others. The trends of the g values in the $\cdot MCl_3$ and the $\cdot Sn(CH_3)_nCl_{3-n}$ radicals suggest that a bonding interaction between chlorine d orbitals and the unpaired electron p orbitals on the central atom is important in these radicals.

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(39) A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance," Harper and Row, New York, N. Y., 1967, pp 132ff.

(40) P. W. Atkins and M. C. R. Symons, "The Structure of Inorganic Radicals," Elsevier, Amsterdam, 1967.

(41) T. G. Carver and L. Andrews, *J. Chem. Phys.*, 50, 4235 (1969).

(42) T. G. Carver and L. Andrews, *ibid.*, 50, 4223 (1969).