

## Electron Spin Resonance Spectra and Structure of the Radical Anions of Methyl Derivatives of Halogeno-silanes and -germanes

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Monomethyl and dimethyl derivatives of halogeno-silanes and -germanes were exposed in tetramethylsilane matrices to  $\gamma$ -rays at 77 K and the radical anions formed from them were studied by e.s.r. spectroscopy. In accord with the results from a previous study on  $\text{SiH}_3\text{Br}^-$ , the radical anions of the derivatives of bromosilane were assigned trigonal bipyramidal structures with a bromide atom and a hydrogen atom in the axial positions. However, a different conclusion was obtained for the radical anions of derivatives of iodosilane. Their structure may be better described as having local  $C_{3v}$  symmetry at the central Si atom, in contrast to the trigonal bipyramidal structure of  $\text{SiH}_3\text{I}^-$ . On the other hand, radical anions formed from methyl derivatives of bromogermane and iodogermane were found to have local  $C_{3v}$  symmetry at the central Ge atom, similar to that found for  $\text{GeH}_3\text{X}^-$  ( $\text{X} = \text{Br}$  or  $\text{I}$ ). The structures of these radical anions are compared with one another and with those of ethyl radical-halide ion adducts produced in acetonitrile matrices.

SPRAGUE and WILLIAMS reported from their e.s.r. studies that methyl radical-halide ion adducts are formed by dissociative electron capture from methyl halide in a  $\gamma$ -irradiated solid of acetonitrile.<sup>1</sup> The adducts appeared to be an intermediate stage of the dissociation process of the radical anions of methyl halide,  $\text{CH}_3\text{X}^-$ . In subsequent work, these results were confirmed, and the structure of the adducts was investigated.<sup>2-4</sup> As a result, it was concluded that the C-X bond is effectively broken since the molecular anion  $\text{CH}_3\text{X}^-$  ( $\text{X} = \text{Cl}$ ,  $\text{Br}$ , or  $\text{I}$ ) formed by electron capture is unstable and that the methyl radical with an essentially planar structure interacts weakly with the halide ion in the adduct.<sup>2,3</sup>

On the other hand, the e.s.r. spectra of the radical anions of halogenosilanes,  $\text{SiH}_3\text{X}^-$  ( $\text{X} = \text{Cl}$ ,  $\text{Br}$ , or  $\text{I}$ ), have been observed recently for  $\gamma$ -irradiated solid solutions of tetramethylsilane (TMS) containing halogeno-silane.<sup>5</sup> It was concluded from the assignments exhibiting the presence of non-equivalent hydrogens that the radical anions have trigonal bipyramidal structures and possess the halogen X and one hydrogen with large couplings in the axial positions and two hydrogens in the equatorial positions.

Furthermore, the e.s.r. spectra of another series of radical anions, that is  $\text{GeH}_3\text{X}^-$  ( $\text{X} = \text{Br}$  or  $\text{I}$ ), have recently been detected in TMS matrices.<sup>6</sup> In contrast with the result of  $\text{SiH}_3\text{X}^-$ , the three hydrogens are equivalent. Thus, it was concluded that  $\text{GeH}_3\text{X}^-$  radical anions have  $C_{3v}$  symmetry with the halogen X on the symmetry axis and the three equivalent hydrogens in the trigonal sites.

These results led us to the interesting finding that there are very different types of structures for the species formed by the electron capture of halide congeners  $\text{MH}_3\text{X}$ , where M is a Group IVB element, C, Si, or Ge.

On the other hand, ethyl radical-halide ion adducts, which are very similar to the methyl radical-halide ion adducts, were formed in irradiated solid solutions of acetonitrile containing ethyl halides.<sup>2</sup> Accordingly, this study was undertaken to investigate whether methyl derivatives of halogeno-silanes and -germanes capture

electrons resulting in the formation of radical anions and to compare the structures of the radical anions, if they are produced, with those of  $\text{MH}_3\text{X}$  radical anions.

### EXPERIMENTAL

Methylsilane and dimethylsilane were obtained from the reductions of trichloromethylsilane<sup>7</sup> and dichlorodimethylsilane<sup>8</sup> (Tokyo Kasei), respectively, with lithium aluminium hydride. Bromomethylsilane was prepared by the reaction of methylsilane with mercury(II) bromide<sup>9</sup> and iodomethylsilane with hydrogen iodide in the presence of aluminium tri-iodide as a catalyst. Iododimethylsilane was prepared by a method similar to that used for iodomethylsilane.<sup>8</sup> Some iododimethylsilane was converted into bromodimethylsilane with silver bromide.<sup>10</sup>

Methylgermane and dimethylgermane were yielded from the reactions of trichloromethylgermane<sup>11</sup> (Alfa Products) and dichlorodimethylgermane<sup>12</sup> (Alfa Inorganics), respectively, with lithium aluminium hydride. Bromomethylgermane and iodomethylgermane were synthesized from methylgermane by reactions with bromide<sup>11</sup> and hydrogen iodide over an aluminium tri-iodide catalyst, respectively. Bromodimethylgermane and iododimethylgermane were prepared by similar halogenations of dimethylgermane with bromine and iodine, respectively.<sup>12</sup>

All the compounds prepared were isolated and purified by distillation *in vacuo*, and identified from their i.r. spectra.<sup>7,11-13</sup>

Solid solutions of tetramethylsilane (Merck) containing 5 mol% of the appropriate methyl derivative were irradiated at 77 K with  $\gamma$ -rays to ca. 1.5 Mrad in a <sup>60</sup>Co  $\gamma$ -source.

E.s.r. spectra were measured at 77 K with an X-band JES-3BSX spectrometer after irradiation.

### RESULTS AND DISCUSSION

$\text{CH}_3\text{SiH}_2\text{Br}^-$ .—In the e.s.r. spectrum observed at 77 K for a  $\gamma$ -irradiated solid solution of TMS containing 5 mol% of  $\text{CH}_3\text{SiH}_2\text{Br}$ , many lines with anisotropic features appeared, as shown in Figure 1, in addition to intense central lines originating from the matrix radical,  $\dot{\text{C}}\text{H}_2\text{-Si}(\text{CH}_3)_3$ . Through comparison of this spectrum with that of the  $\text{SiH}_3\text{Br}^-$  radical anion shown in Figure 1 of ref. 5, it was concluded that the observed spectrum

can be interpreted in terms of anisotropic hyperfine interactions with the nuclei of one  $^1\text{H}$  and the two isotopes of  $^{79}\text{Br}$  ( $I$  3/2; 50.6%) and  $^{81}\text{Br}$  ( $I$  3/2; 49.4%).

In order to confirm this assignment, similar experiments were carried out with  $\text{CH}_3\text{SiD}_2\text{Br}$ . As a result, the doublet shown in Figure 1 of this paper disappeared, while the two quartets assigned to the two Br isotopes remained. Therefore, the doublet in Figure 1 was attributed to one of the two hydrogens bonded to the Si atom.

E.s.r. parameters were extracted from the spectra, and stick diagrams were calculated with a matrix diagonalization program for an axially symmetric spin hamiltonian. Excellent fits were obtained between the observed spectrum and the stick diagrams calculated from the e.s.r.

the unpaired electron is in a three-centre antibonding orbital largely composed of the  $p$  orbital of the axial Br atom, the  $s$  orbital of the axial H atom, and the  $s$  and  $p$  orbitals of the central Si atom.

$(\text{CH}_3)_2\text{SiHBr}^-$ .—The e.s.r. spectrum attributable to  $(\text{CH}_3)_2\text{SiHBr}^-$  radical anion was obtained from similar experiments with  $(\text{CH}_3)_2\text{SiHBr}$  in a TMS matrix and interpreted in terms of anisotropic hyperfine interactions with one H and two isotopes of Br in a manner similar to that in the case of  $\text{CH}_3\text{SiH}_2\text{Br}^-$ . The coupling constants and spin densities of Br, obtained therefrom, decrease systematically, and those of H decrease slightly with successive substitution by  $\text{CH}_3$  groups from  $\text{SiH}_3\text{Br}^-$  to  $(\text{CH}_3)_2\text{SiHBr}^-$ , as shown in the Table. Irrespective of the presence of only one H atom bonded to the Si atom, it

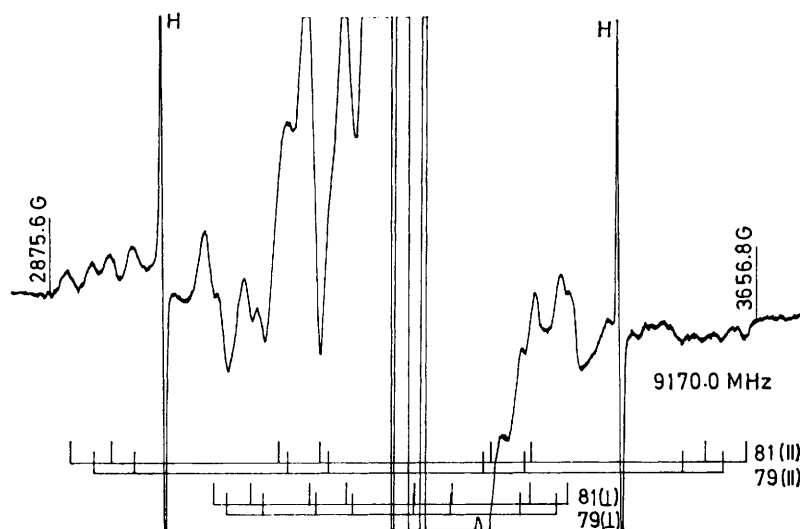


FIGURE 1 First derivative e.s.r. spectrum of a  $\gamma$ -irradiated solid solution of 5 mol % bromomethylsilane in tetramethylsilane, recorded at 77 K. The stick diagrams represent the calculated line positions of the parallel (upper) and the perpendicular (lower) components for  $\text{CH}_3\text{SiH}_2^{79}\text{Br}^-$  and  $\text{CH}_3\text{SiH}_2^{81}\text{Br}^-$  according to the parameters listed in the Table

parameters, listed in the Table for the isotopically normal species.

From the e.s.r. investigation of  $\text{SiF}_4^-$  formed in neopentane<sup>14</sup> and of  $\text{SiH}_3\text{X}^-$ ,<sup>5</sup>  $\text{SiF}_3\text{X}^-$  ( $\text{X} = \text{Cl}, \text{Br}, \text{or I}$ ),<sup>15,16</sup> and  $\text{SiF}_2\text{Cl}_2^-$ <sup>16</sup> formed in TMS, it was established that these radical anions with a central Si atom have trigonal bipyramidal structures and that the hyperfine coupling constants of the axial atoms are much larger than those of the equatorial atoms. Thus, the anisotropic spectrum shown in Figure 1 was assigned to the  $\text{CH}_3\text{SiH}_2\text{Br}^-$  radical anion which has a trigonal bipyramidal structure similar to those of the other radical anions with a central Si atom, *i.e.* the H and Br atoms which give hyperfine splittings in the spectrum occupy the axial (apical) positions of the trigonal bipyramid, and the other H atom and the  $\text{CH}_3$  group are in the equatorial positions.

The spin density distribution calculated from the e.s.r. parameters of the radical anion is given in the Table. Despite the absence of  $^{29}\text{Si}$  data, the results together with those from  $\text{SiF}_4^-$ ,<sup>14</sup>  $\text{SiH}_3\text{Cl}^-$ ,<sup>15</sup> and  $\text{SiF}_3\text{Cl}^-$ <sup>15,16</sup> suggest that

may be therefore reasonable to conclude that the H and Br atoms, which give distinct splittings in the spectrum, occupy the axial positions of the trigonal bipyramid and that the two  $\text{CH}_3$  groups occupy the equatorial positions.

Accordingly, the following results were obtained for successive substitution of  $\text{SiH}_3\text{Br}^-$  by  $\text{CH}_3$  groups. First, the structure of the trigonal bipyramid is preserved in the radical anions of  $\text{SiH}_3\text{Br}^-$ ,  $\text{CH}_3\text{SiH}_2\text{Br}^-$ , and  $(\text{CH}_3)_2\text{SiHBr}^-$ . Second, the  $\text{CH}_3$  groups substituted in these radicals prefer the equatorial to the axial positions of the trigonal bipyramid.

$\text{CH}_3\text{SiH}_2\text{I}^-$ .—Similar experiments with  $\text{CH}_3\text{SiH}_2\text{I}$  in TMS yielded an e.s.r. spectrum attributable to  $\text{CH}_3\text{SiH}_2\text{I}^-$  radical anions. The parallel and perpendicular components of a sextet due to a  $^{127}\text{I}$  nucleus appeared clearly in the spectrum, although every line of the sextet was further split into poorly defined lines. The resolution of these lines was not increased by using dilute samples irradiated with lower doses. The linewidth decreased with increasing temperature up to 123 K without any other significant spectral change. It be-

came obvious from the spectrum at 123 K that every line in the sextet was split into a 1 : 2 : 1 triplet. When stick diagrams for the spectrum at 77 K were made by using the splitting of the triplet observed at 123 K, they satisfactorily explained the poorly defined features of the sextet observed at 77 K. The 1 : 2 : 1 triplet is evidence that two practically equivalent hydrogens are present in  $\text{CH}_3\text{SiH}_2\text{I}^-$ . The spin density of these hydrogens is almost equal to one half that of the axial hydrogen of  $\text{SiH}_3\text{I}^-$  in a trigonal bipyramidal structure. Thus, the

structure of the  $(\text{CH}_3)_2\text{SiHI}^-$  radical anion cannot be determined directly because only one hydrogen is bonded to the Si atom, it may be possible that the radical anion has local  $\text{C}_{3v}$  symmetry similar to that proposed for  $\text{CH}_3\text{SiH}_2\text{I}^-$  and has the H atom and the two  $\text{CH}_3$  groups in the trigonal sites.

$\text{CH}_3\text{GeH}_2\text{Br}^-$ .—The spectrum attributable to  $\text{CH}_3\text{GeH}_2\text{Br}^-$  radical anion changed with the rotation of the sample in the applied magnetic field owing to the partial orientation of the radical anions, as shown in Figure 3.

E.s.r. parameters, spin densities, and structure for the radical anions of halogenosilanes, halogengermanes, and their methyl derivatives

Radical	g Values		Nucleus <sup>a</sup>	Hyperfine couplings (G) <sup>b</sup>		Spin densities <sup>c</sup>		Structure <sup>d</sup>	Reference
	$g_{\perp}$	$g_{\parallel}$		$A_{\perp}$	$A_{\parallel}$	$\rho_s$	$\rho_p$		
$\text{SiH}_3\text{Br}^-$	2.004	2.002	$^{79}\text{Br}$	128	254	0.022	0.183	T	5
			$^{81}\text{Br}$	138	274	0.022	0.183		
$\text{CH}_3\text{SiH}_2\text{Br}^-$	2.005	2.001	$^1\text{H}(1)$	43.4	45.6	0.087		T	This work
			$^{79}\text{Br}$	109	220	0.019	0.160		
$(\text{CH}_3)_2\text{SiHBr}^-$	2.006	2.001	$^{81}\text{Br}$	118	237	0.019	0.160	T	This work
			$^1\text{H}(1)$	41.5	45.3	0.084			
$\text{SiH}_3\text{I}^-$	2.009	1.994	$^{79}\text{Br}$	91	187	0.016	0.140	T	5
			$^{81}\text{Br}$	98	201	0.016	0.140		
$\text{CH}_3\text{SiH}_2\text{I}^-$	2.009	1.997	$^{127}\text{I}$	165	328	0.030	0.238	T	5
			$^1\text{H}(1)$	35.6	35.6	0.070			
$(\text{CH}_3)_2\text{SiHI}^-$	2.012	2.000	$^{127}\text{I}$	148	276	0.026	0.188	C	This work
			$^1\text{H}(2)$	20	22	0.041			
$\text{GeH}_3\text{Br}^-$	2.013	2.005	$^{127}\text{I}$	120	233	0.022	0.166	C	This work
			$^1\text{H}(1)$	39.6	43.1	0.080			
$\text{CH}_3\text{GeH}_2\text{Br}^-$	2.013	2.005	$^{79}\text{Br}$	139	264	0.023	0.182	C	6
			$^{81}\text{Br}$	150	285	0.023	0.182		
$(\text{CH}_3)_2\text{GeHBr}^-$	2.013	2.005	$^1\text{H}(3)$	22.4	23.9	0.045		C	This work
			$^{79}\text{Br}$	111	227	0.019	0.168		
$(\text{CH}_3)_2\text{GeHI}^-$	2.014	2.006	$^{81}\text{Br}$	120	245	0.019	0.168	C	This work
			$^1\text{H}(2)$	31.4	34.5	0.064			
$\text{GeH}_3\text{I}^-$	2.019	1.994	$^{79}\text{Br}$	85	192	0.016	0.155	C	This work
			$^{81}\text{Br}$	92	207	0.016	0.155		
$\text{CH}_3\text{GeH}_2\text{I}^-$	2.024	1.999	$^{127}\text{I}$	214	358	0.036	0.211	C	6
			$^1\text{H}(1)$	21.5	23.2	0.044			
$(\text{CH}_3)_2\text{GeHI}^-$	2.027	2.001	$^{127}\text{I}$	179	318	0.031	0.204	C	This work
			$^1\text{H}(1)$	31.6	33.0	0.063			
$(\text{CH}_3)_2\text{GeH}_2\text{I}^-$	2.027	2.001	$^{127}\text{I}$	121	255	0.023	0.196	C	This work
			$^1\text{H}(1)$	53.3	59.2	0.109			

<sup>a</sup> Number in parentheses indicates the number of equivalent nuclei. <sup>b</sup>  $G = 10^{-4}\text{T}$ . <sup>c</sup> Spin densities were derived using the magnetic parameters listed by B. A. Goodman and J. B. Raynor, *Adv. Inorg. Chem. Radiochem.*, 1970, **13**, 135. <sup>d</sup> T and C mean trigonal bipyramid and  $\text{C}_{3v}$  or local  $\text{C}_{3v}$ , respectively.

radical anion must have a structure different from that of the trigonal bipyramid, and the two equivalent hydrogens seem to suggest that the radical anion has a structure with local  $\text{C}_{3v}$  symmetry at the Si atom and possesses the I atom on the symmetry axis and the two H atoms and the  $\text{CH}_3$  group in the trigonal sites.

$(\text{CH}_3)_2\text{SiHI}^-$ .—The coupling constant of iodine which can be seen in the e.s.r. spectrum (Figure 2) attributable to  $(\text{CH}_3)_2\text{SiHI}^-$  is smaller than that found for  $\text{SiH}_3\text{I}^-$  and  $\text{CH}_3\text{SiH}_2\text{I}^-$ . Nevertheless, the coupling constant observed for hydrogen is approximately twice as large as that of the equivalent hydrogens in  $\text{CH}_3\text{SiH}_2\text{I}^-$  and is considerably larger than that of the axial hydrogen of  $\text{SiH}_3\text{I}^-$ , as shown in the Table. These results for hydrogen coupling are different from those obtained from  $\text{SiH}_3\text{Br}^-$ ,  $\text{CH}_3\text{SiH}_2\text{Br}^-$ , and  $(\text{CH}_3)_2\text{SiHBr}^-$  in trigonal bipyramidal structures. Accordingly, though the struc-

ture of the  $(\text{CH}_3)_2\text{SiHI}^-$  radical anion cannot be determined directly because only one hydrogen is bonded to the Si atom, it may be possible that the radical anion has local  $\text{C}_{3v}$  symmetry similar to that proposed for  $\text{CH}_3\text{SiH}_2\text{I}^-$  and has the H atom and the two  $\text{CH}_3$  groups in the trigonal sites.

Through comparison with the spectrum of  $\text{GeH}_3\text{Br}^-$  assigned to the anisotropic hyperfine structures of two Br isotopes and three equivalent H atoms,<sup>6</sup> the spectrum was interpreted as resulting from the quartets of two Br isotopes and a 1 : 2 : 1 triplet due to two practically equivalent H atoms. The presence of the Br and two equivalent H atoms rules out the possibility of a trigonal bipyramidal structure for the  $\text{CH}_3\text{GeH}_2\text{Br}^-$  radical anion and suggests that it has  $\text{C}_{3v}$  symmetry similar to that proposed for  $\text{GeH}_3\text{Br}^-$ ,<sup>6</sup> *i.e.*, the radical anion has local  $\text{C}_{3v}$  symmetry at the Ge atom, with the Br atom on the symmetry axis and the two equivalent H atoms and the  $\text{CH}_3$  group in the trigonal sites.

In accordance with the results for  $\text{GeH}_3\text{Br}^-$ ,<sup>6</sup> the spin density distribution suggests that the unpaired electron resides in an  $a_1 \sigma^*$  orbital which is composed largely of the *s* and *p* orbitals of the Ge atom and the *p* orbital of the Br

atom, although data for  $^{73}\text{Ge}$  were not obtained, unfortunately. The  $p$  orbital of the Ge atom can be assumed to be directed toward the halogen,<sup>6</sup> in contrast to the  $p$  orbital of the central atom of radical anions with a tri-

methyl groups. A similarly steady decrease was obtained in the spin densities of the Br atom. Hence, it may be reasonably assumed that no substantial structural change from  $C_{3v}$  symmetry occurs upon succes-

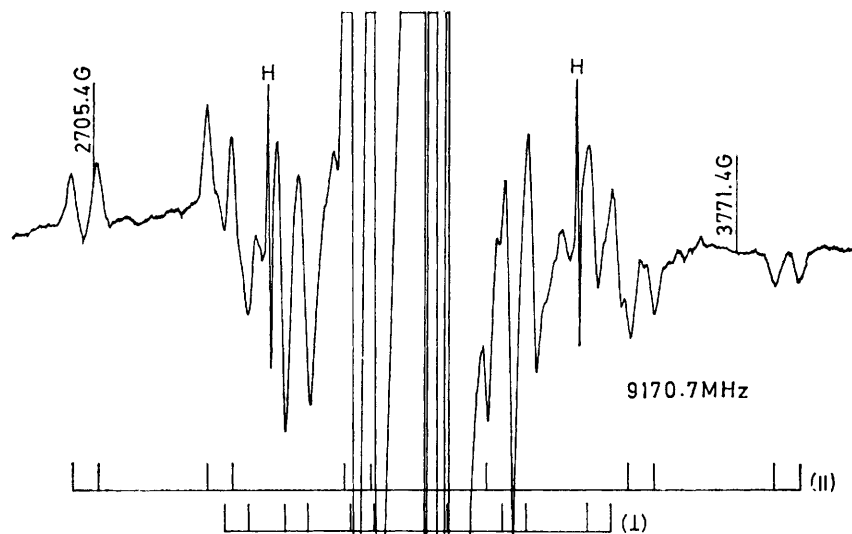


FIGURE 2 E.S.R. spectrum of a  $\gamma$ -irradiated solid solution of 5 mol % iododimethylsilane in tetramethylsilane, recorded at 77 K, and the stick diagrams calculated for  $(\text{CH}_3)_2\text{SiH}_2\text{I}^-$

gonal bipyramidal structure, whose direction is perpendicular to the halogen.<sup>5,6,16</sup>

$(\text{CH}_3)_2\text{GeHBr}^-$ .—The coupling constant of hydrogen in the spectrum assigned to  $(\text{CH}_3)_2\text{GeHBr}^-$  is significantly larger than those for hydrogens in the trigonal

sive substitution of the hydrogens by methyl groups, and therefore the radical anion was postulated to have local  $C_{3v}$  symmetry with the hydrogen and the two  $\text{CH}_3$  groups in the trigonal sites. Returning to the hydrogen coupling of radical anions from  $\text{GeH}_3\text{Br}^-$  to  $(\text{CH}_3)_2\text{GeHBr}^-$ , it

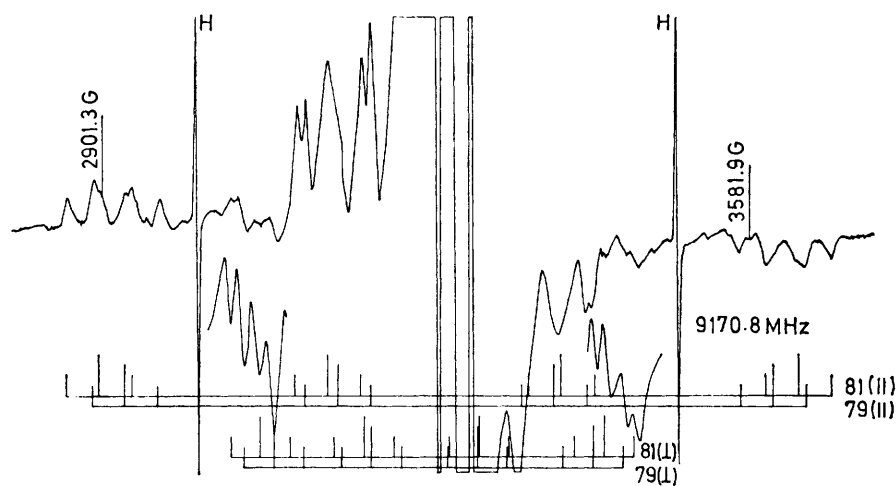


FIGURE 3 E.S.R. spectra of a  $\gamma$ -irradiated solid solution of 5 mol % bromomethylgermane in tetramethylsilane, recorded at 77 K. The lower spectrum was recorded after the rotation of the sample by *ca.*  $90^\circ$  followed by the observation of the upper spectrum. Stick diagrams show the line positions of the parallel components, corresponding to the upper spectrum, and the perpendicular components, for the lower spectrum, of  $\text{CH}_3\text{GeH}_2^{79}\text{Br}^-$  and  $\text{CH}_3\text{GeH}_2^{81}\text{Br}^-$

sites of  $\text{GeH}_3\text{Br}^-$  and  $\text{CH}_3\text{GeH}_2\text{Br}^-$ , as shown in the Table. However, it should be pointed out that the sum of the spin densities on the hydrogens in trigonal sites are 0.135, 0.128, and 0.110 for  $\text{GeH}_3\text{Br}^-$ ,  $\text{CH}_3\text{GeH}_2\text{Br}^-$ , and  $(\text{CH}_3)_2\text{GeHBr}^-$ , respectively, indicating that the sum decreases slightly but steadily with the introduction of

is obviously different from that observed for the radical anions from  $\text{SiH}_3\text{Br}^-$  to  $(\text{CH}_3)_2\text{SiHBr}^-$  which have trigonal bipyramidal structures.

$\text{CH}_3\text{GeH}_2\text{I}^-$ .—The e.s.r. spectrum attributed to  $\text{CH}_3\text{GeH}_2\text{I}^-$  consists of an  $^{127}\text{I}$  sextet and a 1 : 2 : 1 triplet due to two equivalent hydrogens. Although the splitting

due to the hydrogens is larger than in the case of  $\text{CH}_3\text{-SiH}_2\text{I}^-$ , the spectrum is similar to that of  $\text{CH}_3\text{SiH}_2\text{I}^-$ , which supports the analysis for the latter spectrum involving a poorly defined 1 : 2 : 1 triplet.

The presence of the two equivalent H atoms indicates that the radical anion  $\text{CH}_3\text{GeH}_2\text{I}^-$  has local  $C_{3v}$  symmetry similar to that proposed for  $\text{CH}_3\text{GeH}_3\text{Br}^-$  and  $\text{CH}_3\text{SiH}_2\text{I}^-$  and postulated for  $(\text{CH}_3)_2\text{SiHI}^-$ .

$(\text{CH}_3)_2\text{GeHI}^-$ .—An e.s.r. spectrum very similar to that of  $(\text{CH}_3)_2\text{SiHI}^-$  was observed for  $(\text{CH}_3)_2\text{GeHI}$  and assigned to  $(\text{CH}_3)_2\text{GeHI}^-$  radical anion. The coupling constant of the iodine atom decreased in the order  $\text{GeH}_3\text{I}^-$ ,  $\text{CH}_3\text{GeH}_2\text{I}^-$ , and  $(\text{CH}_3)_2\text{GeHI}^-$ . As pointed out for the derivatives of bromogermane, the sum of the spin densities of hydrogen atoms decreased with an increase in the number of substituted  $\text{CH}_3$  groups [0.132, 0.126, and 0.109 for  $\text{GeH}_3\text{I}^-$ ,  $\text{CH}_3\text{GeH}_2\text{I}^-$ , and  $(\text{CH}_3)_2\text{GeHI}^-$ , respectively]. In accord with the results for the derivatives of bromogermane,  $C_{3v}$  symmetry at the Ge atom is retained irrespective of the substitution by  $\text{CH}_3$  groups and therefore the  $(\text{CH}_3)_2\text{SiHI}^-$  radical anion also has local  $C_{3v}$  symmetry.

*Radicals produced from  $(\text{CH}_3)_3\text{SiX}$  and  $(\text{CH}_3)_3\text{GeX}$  ( $X = \text{Br}$  or  $\text{I}$ ).*—Anisotropic e.s.r. spectra consisting of the hyperfine structure of a halogen nucleus with a large coupling were observed for  $(\text{CH}_3)_3\text{SiX}$  and  $(\text{CH}_3)_3\text{GeX}$  ( $X = \text{Br}$  or  $\text{I}$ ) in TMS matrices. The spectra may result from radical anions but such assignments cannot be positively made for the following three reasons. (I) The main purpose of this paper is to clarify the structure of radical anions (trigonal bipyramid or  $C_{3v}$  symmetry). However, since these spectra have a hyperfine structure for only one halogen atom, we cannot differentiate between a trigonal bipyramid and  $C_{3v}$  symmetry from the spectra even if radical anions are produced. (II) The linewidths of the spectra are rather large compared with those of the spectra mentioned earlier. (III) It has been reported recently that radicals assigned to  $(\text{CH}_3)_2\dot{\text{C}}\text{-H}_2\text{Br}$  were formed from  $(\text{CH}_3)_3\text{CBr}$  in a TMS matrix.<sup>17,18</sup> The e.s.r. spectrum of the  $\beta$ -bromo radicals consists of the hyperfine structure of a Br nucleus with a large coupling and is similar to that expected for the radical anions of  $(\text{CH}_3)_3\text{CBr}^-$ . The assignment was, however, confirmed by the photolysis of a system containing tetramethylphenylenediamine and  $(\text{CH}_3)_3\text{CBr}$  in adamantane and by the extraction of hydrogen atoms by  $\text{RO}^\cdot$  radicals.<sup>17</sup> Therefore, special experiments are required for the assignment of radicals formed from  $(\text{CH}_3)_3\text{SiX}$  and  $(\text{CH}_3)_3\text{GeX}$  in TMS matrices, since there are two possibilities, radical anions and  $\beta$ -halogeno radicals  $(\text{CH}_3)_2\dot{\text{M}}\text{CH}_2\text{X}$ . This last reason is the most important.

*Comparison between Radical Anions.*—When similar experiments were carried out with  $\gamma$ -irradiated TMS matrices containing ethyl bromide or ethyl iodide for the purpose of comparison, only ethyl radicals were detected.<sup>19</sup> Therefore, ethyl halides in TMS are easily dissociated by electron capture. On the other hand, ethyl radical-halide ion adducts were formed in acetonitrile matrices.<sup>2</sup> The adduct is well described as a

planar ethyl radical interacting weakly with a halide ion. However, the radical anions of ethyl halides should be compared with those of methyl derivatives of halogeno-silanes and -germanes.

As pointed out by Symons,<sup>2</sup> after the capture of an electron by the  $\sigma^*$  carbon-halogen orbital of ethyl halide the carbon-halogen bond relaxes in order to lower the antibonding character of an extra electron. This results in a flattening of the  $\text{H}_2\text{CCH}_3$  unit, which, in turn, increases the carbon  $2p$  contribution to the orbital. Through a continuous adjusting process, the ethyl radical-halide ion adducts are formed in acetonitrile, while ethyl radicals which are dissociated completely are detected in TMS.

With regard to the silicon-centred radical anions, it was concluded that  $\text{SiH}_3\text{Br}^-$ ,  $\text{CH}_3\text{SiH}_2\text{Br}^-$ ,  $(\text{CH}_3)_2\text{SiHBr}^-$ , and  $\text{SiH}_3\text{I}^-$  have trigonal bipyramidal structures while  $\text{CH}_3\text{SiH}_2\text{I}^-$  and probably  $(\text{CH}_3)_2\text{SiHI}^-$  have a structure with local  $C_{3v}$  symmetry. According to Symons,<sup>18,19</sup> electron addition to phosphorus compounds results in two types of phosphoranyl radical, which are isoelectronic with the silicon-centred radical anions. One is a trigonal bipyramidal structure and the other is a structure with local  $C_{3v}$  symmetry at the phosphorus atom. In the former case (*e.g.*  $\text{PF}_4$ ,<sup>20</sup>  $\text{POCl}_3$ ,<sup>21</sup>  $\text{PCl}_4$ ,<sup>22</sup> and  $\text{PH}_4$ <sup>23</sup>), electron trapping involves a major bending distortion from the initial tetrahedral structure. The latter structure represents the alternative of bond stretching, and is favoured if the parent compound contains a single bond to an electronegative group such as Cl<sup>24</sup> or Br.<sup>25</sup> This argument may be useful for the silicon-centred radical anions. Since only  $\text{CH}_3\text{SiH}_2\text{I}^-$  and  $(\text{CH}_3)_2\text{SiHI}^-$  among the radical anions were revealed to have local  $C_{3v}$  symmetry from the present study, a further investigation is under way using halogenosilanes substituted by other organic groups. Preliminary experiments for  $\text{C}_2\text{H}_5\text{SiH}_2\text{X}$  and  $\text{CH}_2=\text{CH-SiH}_2\text{X}$  ( $X = \text{Br}$  or  $\text{I}$ ) allowed the detection of radical anions in trigonal bipyramidal structures.<sup>26</sup> Therefore, it seems that  $\text{CH}_3\text{SiH}_2\text{I}^-$  and  $(\text{CH}_3)_2\text{SiHI}^-$  have exceptionally local  $C_{3v}$  symmetry, although no reason can be given at present, and that silicon-centred radical anions, in general, favour the trigonal bipyramidal structure brought about by a bending distortion.

On the other hand, the radical anions of halogeno-germanes and their methyl derivatives have  $C_{3v}$  or local  $C_{3v}$  symmetry, which means that bond stretching is important for germanium-centred radical anions.

Accordingly, it was concluded that the stability and structure of the radical anions of methyl derivatives of  $\text{MH}_3\text{X}$  with a central M atom of Group IVB are affected significantly by the nature of M and are very similar in structure to those of  $\text{MH}_3\text{X}^-$  except for  $\text{CH}_3\text{SiH}_2\text{I}^-$  and  $(\text{CH}_3)_2\text{SiHI}^-$ .

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