E.S.R. Spectra of the Hexamethyldisilane and Hexamethyldigermane Radical Cations

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Summary Irradiation of solid solutions of $Me_3Si{-}SiMe_3$ and $Me_3Ge{-}GeMe_3$ in CCl_3F by γ-rays generates the organometallic radical cations whose e.s.r. parameters establish that the unpaired electron is localized in a σ-bonding orbital between the two metal atoms.

Although novel organosilicon radical cations derived from dodecamethylcyclohexasilane and other permethylcyclosilanes have recently been described,[1] no mention was made of the simplest acyclic species $Me_3Si{\cdot}SiMe_3{}^+$. We now report the e.s.r. spectra of this radical cation and its germanium congener which provide new information about the structure of these organometallic radicals.

The radical cations were generated at 77 K by γ-irradiation of solid solutions containing the parent compounds dissolved in trichlorofluoromethane. A similar method was recently used to prepare the hexamethylethane radical cation,[2,3] and the technique appears to be generally applicable when the ionization potential of the solute is well below that of the matrix,[4,5] the mechanism of radical cation formation occurring by positive charge transfer from the matrix molecules.[3–5] After irradiation, the samples were transferred into the variable-temperature accessory of an e.s.r. spectrometer and the spectra recorded at intervals between 77 and 150 K.

As shown in Figure 1, the evenly spaced multiplet spectrum produced from the hexamethyldisilane solution consists of at least 13 lines and fits the intensity distribution for a binomial set of 19 lines, as represented by the stick diagram. This is the expected spectrum for hyperfine interaction with 18 equivalent hydrogens which indicates that the 6 methyl groups are undergoing free rotation in the hexamethyldisilane radical cation, in contrast with the case of the hexamethylethane radical cation where a septet spectrum was obtained and interpreted in terms of a preferred conformation having large hyperfine interactions with only the six axial hydrogens.[2,3] A search for ^{29}Si satellite lines in natural abundance ($^{29}Si = 4{\cdot}7\%$) was unsuccessful, the negative results implying that the ^{29}Si features must be broadened relative to those of the main spectrum by the ^{29}Si hyperfine anisotropy which is very likely to exceed the spectral width from the g anisotropy (*vide infra*).

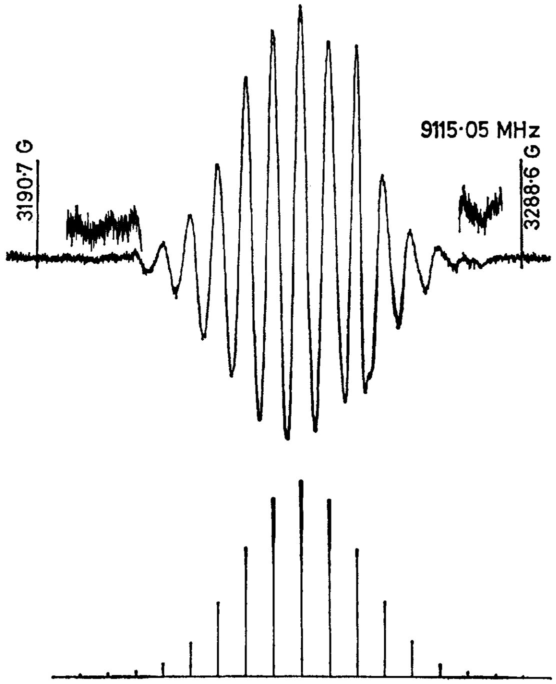

Figure 1. Second derivative e.s.r. spectrum from a γ-irradiated (dose, 1 Mrad) solid solution of 4 mol% hexamethyldisilane in trichlorofluoromethane at 121 K. The stick diagram reconstruction represents the hyperfine pattern from coupling to 18 equivalent ^1H nuclei.

As shown in Figure 2, a large g anisotropy was observed for the hexamethyldigermane radical cation, the spectrum consisting of two clearly separated binomial patterns which could be analysed into perpendicular and parallel sets of features with $g_{\perp} > g_{\parallel}$. Again each pattern consists of at least 13 lines in accord with the intensity distribution for a binomial set of 19 lines. These results for $Me_3Ge{\cdot}GeMe_3^+$ strongly suggest that the observed set of components for $Me_3Si{\cdot}SiMe_3^+$ in Figure 1 are the perpendicular features centred at $g_{\perp} = 2{\cdot}0077$, and that a set of weaker parallel features with $g_{\parallel} = ca.\ 2{\cdot}0023$ is probably masked by the small separation (*ca.* 9 G) between the centres of the two patterns. A summary of the e.s.r. parameters for these organometallic radical cations is given in the Table along with the parameters previously determined for the related $SiMe_3$ and $GeMe_3$ radicals.

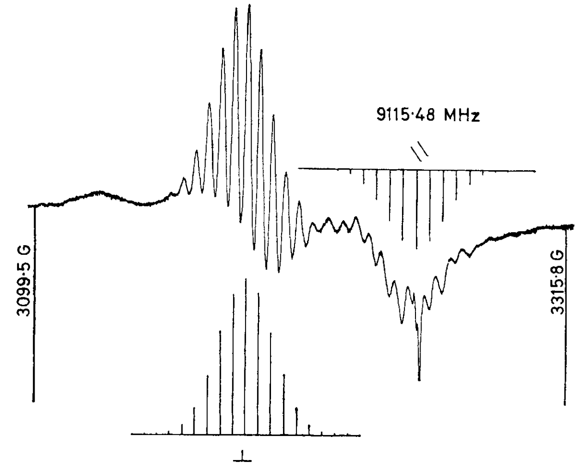

Figure 2. First-derivative e.s.r. spectrum from a γ-irradiated (dose, 1 Mrad) solid solution of 4 mol% hexamethyldigermane in trichlorofluoromethane at 110 K. The stick diagrams represent the 19-line binomial hyperfine patterns associated with the parallel and perpendicular features.

A comparison of the proton hyperfine couplings in the $Me_3M{\cdot}MMe_3^+$ and MMe_3 (M = Si, Ge) radicals (Table) shows that the coupling in the radical cation is only slightly less than that in the corresponding neutral radical, despite the fact that there are twice as many hydrogens in the cation. This remarkable result can be explained, at least qualitatively, in terms of the usual hyperconjugation approach if the unpaired electron is in a *bonding* orbital between the two metal atoms. Although the two coefficients for the admixture of a particular CH_3 group orbital into the two metal atom orbitals are expected to differ according to whether the CH_3 group is bonded directly to the metal atom or not, they will have the same sign for a σ-bonding orbital. Consequently, since the spin density is proportional to the square of the admixture,[6] this additive effect should then

TABLE. E.s.r. parameters for $Me_3M{\cdot}MMe_3^+$ and MMe_3 (M = Si, Ge) radicals.

Radical	^1H Hyperfine coupling (G)	g factor
$Me_3Si{\cdot}SiMe_3^+$	$A_{\perp} = 5{\cdot}55$ (18H)[a]	$g_{\perp} = 2{\cdot}0077$[a]
Me_3Si	$A_{iso} = 6{\cdot}28$ (9H)[b]	
	$A_{iso} = 6{\cdot}42$ (9H)[c]	$g_{iso} = 2{\cdot}0031$[c]
$Me_3Ge{\cdot}GeMe_3^+$	$A_{\parallel} = 5{\cdot}39$ (18H)[a]	$g_{\parallel} = 2{\cdot}0023$[a]
	$A_{\perp} = 5{\cdot}18$ (18H)[a]	$g_{\perp} = 2{\cdot}0441$[a]
	$A_{iso} = 5{\cdot}25$ (18H)[a]	$g_{iso} = 2{\cdot}0302$[a]
Me_3Ge	$A_{iso} = 5{\cdot}5$ (9H)[c]	$g_{iso} = 2{\cdot}0104$[c]
	$A_{iso} = 5{\cdot}28$ (9H)[d]	$g_{iso} = 2{\cdot}0101$[d]
	$A_{iso} = 5{\cdot}31$ (9H)[e]	$g_{iso} = 2{\cdot}0103$[e]

[a] This work. [b] P. J. Krusic and J. K. Kochi, *J. Am. Chem. Soc.*, 1969, **91**, 3938. [c] S. W. Bennett, C. Eaborn, A. Hudson, H. A. Hussain, and R. A. Jackson, *J. Organomet. Chem.*, 1969, **16**, P36. [d] R. V. Lloyd and M. T. Rogers, *J. Am. Chem. Soc.*, 1973, **95**, 2459. [e] H. Sakurai, K. Mochida, and M. Kira, *J. Am. Chem. Soc.*, 1975, **97**, 929.

result in a hydrogen coupling much greater than half of that for the corresponding neutral radical, as observed.

The g anisotropy observed for the hexamethyldigermane radical cation with $g_{\perp} > g_{\parallel}$ is also strongly supportive of a σ-radical, the large positive shift for the $g_{\perp}$ component being expected for the mixing of the singly-occupied σ-orbital with the filled 4p (valence) and 3d orbitals of germanium according to large spin-orbit coupling constants.[7] Whilst smaller positive g shifts were found for the radical cations of hexamethyldisilane (Table) and the permethylcyclosilanes,[1] these results are also consistent with the view that the unpaired electron is largely localized in a σ-orbital between metal atoms.

Consistent with this picture, it follows that the sharp distinction between the 7-line pattern of $Me_3C{\cdot}CMe_3^+$ and the 19-line patterns characteristic of freely rotating methyl groups in $Me_3SiS{\cdot}iMe_3^+$ and $Me_3Ge{\cdot}GeMe_3^+$ can be attributed to the greater ease of σ-spin delocalization along the three coplanar 4-carbon chains to the six axial hydrogens in the former case.[3] In contrast, the much stronger localization of the positive hole between the metal atoms in $Me_3Si{\cdot}SiMe_3^+$ (and $Me_3Ge{\cdot}GeMe_3^+$) implied by the lower ionization potentials of Si–Si bonds[1] allows little spin density to migrate away from the central atoms, and consequently there is no tendency for these two radical cations to adopt a preferred conformation with locked methyl groups.

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