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PRELIMINARY COMMUNICATION

ELECTRON SPIN RESONANCE SPECTRA OF TRIMETHYLSILYL, TRIMETHYLGERMYL AND RELATED FREE RADICALS IN SOLUTION

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The reactions of silicon and germanium containing free-radicals are receiving increasing attention[1], but few ESR studies on neutral radicals of this kind have been made. The flow systems often employed for observing organic radicals are inconvenient for organometallic systems, particularly on account of the large quantities of materials used. However, Hudson and Hussain[2] have recently shown that photolysis of solutions of tert-butyl peroxide in organic solvents at low temperatures gives rise (via hydrogen abstraction by the initially produced tert-butoxy radicals) to radicals derived from the solvent.

We have used this technique to prepare the radicals $Me_3Si^•$, $Me_3Ge^•$, $Me_3SiSiMe_2^•$ and $Me_3SiSiMeH^•$. Solutions of tert-butyl peroxide in the appropriate organometallic solvent at about −70° were photolysed by UV light from a 250 watt Osram lamp, focussed by a quartz lens into the cavity of a Varian E3 spectrometer (Table 3).

TABLE 1
SUMMARY OF ESR DATA

Radical	Coupling constants			Approximate g value	Description
	α-H	β-H	γ-H		
$Me_3Si^•$	6.42	–	–	2.0031	decet
$Me_3Ge^•$	5.5	–	–	2.0104	decet
$Me_3SiSiMe_2^•$	–	8.31	0.47	2.0036	septet of decets
$Me_3SiSiMeH^•$	16.5	8.25	0.30	2.0037	six lines, split into decets

The trimethylsilyl radical (Fig.1) shows a decet with a_H 6.42 gauss. The outside lines are visible under increased gain and the intensities are consistent with the presence of nine equivalent protons. (A small amount of an unidentified radical is also visible). Trimethylgermyl gives rather broader lines than $Me_3Si^•$, probably because of an increase in the anisotropy of the g-tensor coupled with the Brownian motion of the radical; the lowest field line is not sufficiently intense to be visible, and the high field lines are partly obscured by another radical of lower g value. The hyperfine splitting is 5.5 gauss, slightly lower than that of the trimethylsilyl radical. The smallness of the hyperfine splitting in $Me_3Si^•$ and

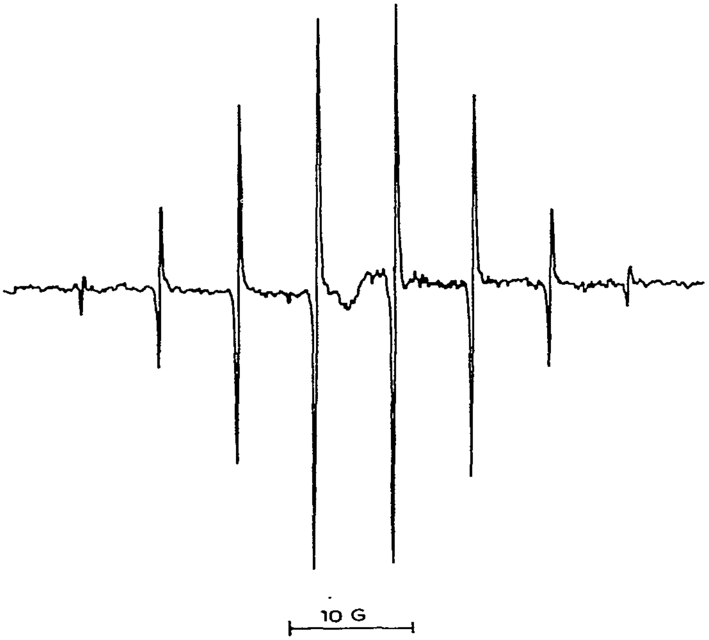

Fig.1. ESR spectrum of the trimethylsilyl radical.

$Me_3Ge^•$ compared with 22.7 gauss for tert-butyl is presumably due (a) to the probable non-planarity of these radicals ($SiH_3^•$ and $GeH_3^•$ are non-planar[3]) and (b) the greater size of silicon and germanium and their reluctance to form multiple bonds, which will reduce the hyperconjugative coupling of β-protons. ^{29}Si studies and MO calculations are in progress to ascertain the relative importance of these effects.

$Me_3SiSiMe_2^•$ gives a heptet (8.31 gauss) split into decets (0.47 gauss). The larger coupling constant, compared with $Me_3Si^•$, possibly indicates a more planar radical. This may be due to conjugative interaction of the free electron with the β-silicon atom, or to an electronegativity effect. Electronegative substituents inductively reduce the charge density in the bonding orbitals of the α-silicon, which results in an increased tendency of the non-bonding electron to occupy a lower energy orbital (*i.e.* with more *s* character), resulting in a non-planar radical. For example in analogous carbon radicals, $CF_3^•$ is non-planar, whereas $CH_3^•$ is essentially planar.

$Me_3SiSiMeH^•$ gives six lines (8.25 gauss separation), split into decets (0.30 gauss). This spectrum is tentatively analysed in terms of a Si—H splitting (16.5 gauss) almost exactly twice as large as the α-methyl proton splitting. This suggests that the more nearly planar structure of this radical (compared with $SiMe_3^•$ or $SiH_3^•$) causes a larger change in the Si—H coupling constant (8.1 gauss in $SiH_3^•$) than in the α-methyl proton coupling constant (6.42 gauss in $SiMe_3^•$). This interpretation supports a negative sign for the Si—H coupling constant, as proposed by Gordy and coworkers[3] for $SiH_3^•$.

The increase in *g* values from Si to Ge follows the same order as for $SiH_3^•$ and $GeH_3^{•3}$. The increase from $Me_3Si^•$ to the disilyl radicals is probably due to the larger and heavier Si substituent.

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