

ELECTRON SPIN RESONANCE SPECTRA OF TRANSIENT TIN-CENTERED RADICALS IN SOLUTION

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Summary

ESR data for short-living stannyl radicals in solution are presented. The radicals are generated in the cavity of the ESR spectrometer by UV irradiation of di-*t*-butyl peroxide with the appropriate tin hydride. The radicals $R_3Sn^\cdot$ ($R = Me, n\text{-}Pr, n\text{-}Bu$) show multiplets caused by interaction with the β -protons ($a_H = 0.30\text{--}0.31$ mT, $g = 2.0160\text{--}2.0163$) and line broadenings depending on $[R_3SnH]$. The radicals $Ph_nMe_{3-n}Sn^\cdot$ ($n = 1, 2$) exhibit only splittings due to the methyl protons ($a_H = 0.30$ mT). The observed linewidths show that $a_{o,p} \leq 0.05$ mT, $a_m \leq 0.03$ mT. The radicals $Ph_nEt_{3-n}Sn^\cdot$ ($n = 0\text{--}2$) show no splittings caused by the methylene protons because of exchange narrowing effects. The g values decrease with increasing n from 2.0163 and 2.015 ($n = 0$) to 2.0023 ($n = 3$) because of increasing deviations from the planar conformation at the radical center. The line broadening and exchange narrowing effects are caused by rapid hydrogen exchange between the radicals and hydride molecules ($k \geq 10^6 M^{-1} s^{-1}$); in Zavitsas' model, the relatively high k values are the consequence of the large Sn—H bond lengths which diminish the repulsive forces between the terminal Sn atoms in the transition state $[R_3Sn\text{--}H\text{--}SnR_3]^\cdot$. The observation of line broadenings in the NMR spectrum of Me_3SnH during irradiation with di-*t*-butyl peroxide confirms the ESR results.

Introduction

Radicals centered at silicon, germanium, tin, and lead are of interest as the homologues of carbon-centered radicals [1]. Whereas many Group IV element centered radicals have been observed by ESR spectroscopy in host matrices, only silicon- and germanium-centered radicals have been thoroughly investigated in solution [1]. Of transient tin-centered radicals, only the trimethylstannyl radical [2] and, very recently, the triphenylstannyl radical [3] have been

studied. In addition, some radicals stabilised by bulky substituents have been described [3–5].

ESR data of some transient alkyl- and aryl-substituted stannyl radicals are considered below. The radicals were generated by hydrogen abstraction from the appropriate tin hydrides according to the following reactions:



In a previous communication it was reported that line broadening and exchange narrowing occur in the ESR spectra of trialkylstannyl radicals [6], indicating a rapid hydrogen exchange between stannyl radicals and hydride molecules. As such effects might complicate the interpretation of the spectra, they will be analysed in detail. Moreover, they give additional information about the nature of hydrogen abstraction reactions.

Results

The ESR data for a few stannyl radicals in *n*-pentane are given in Table 1, in which some data taken from the literature are also included.

The trimethyltin radical shows six or eight signals in the temperature region between -20°C and -100°C , representing the most intense lines of the decet expected from the interaction of the unpaired electron with nine protons. The

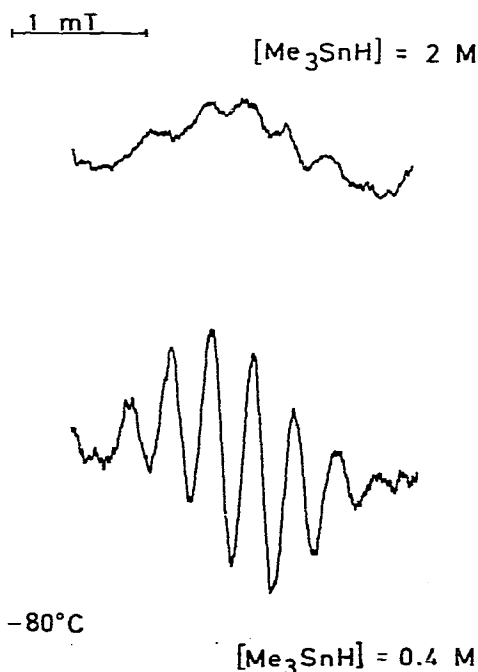


Fig. 1. ESR spectra of $\text{Me}_3\text{Sn}^\cdot$ at various tin hydride concentrations.

TABLE 1
ESR DATA FOR TIN-CENTERED RADICALS IN n-PENTANE

Radical	T ($^{\circ}\text{C}$)		line-width (mT)	hyperfine splitting (mT)	g value	ref.
$\text{Me}_3\text{Sn}^{\cdot}$	25	decet		$a_{\text{H}}^{\text{CH}_3} = 0.275$	2.017	[2] ^a
	-80	decet	0.15-0.3	$a_{\text{H}}^{\text{CH}_3} = 0.31$	2.0163	
$\text{Et}_3\text{Sn}^{\cdot}$	-80	singlet	≈ 1	—	2.015	
$\text{n-Pr}_3\text{Sn}^{\cdot}$	-80	septet	0.3-0.5	$a_{\text{H}}^{\text{CH}_2} = 0.30$	2.0160	
$\text{n-Bu}_3\text{Sn}^{\cdot}$	-110	septet		$a_{\text{H}}^{\text{CH}_2} = 0.3$	2.0158	[7] ^b
	-80	septet	0.25-0.45	$a_{\text{H}}^{\text{CH}_2} = 0.31$	2.0160	
$\text{Ph}_3\text{Sn}^{\cdot}$	110	singlet	0.23	$a_{\text{O,P}} \lesssim 0.05$ $a_m \lesssim 0.03$	2.0023	[3] ^c
	-50	singlet	0.23	$a_{\text{O,P}} \lesssim 0.05$ $a_m \lesssim 0.03$	2.0023	
$\text{Ph}_2\text{MeSn}^{\cdot}$	-70	quartet	0.20	$a_{\text{H}}^{\text{CH}_3} = 0.30$ $a_{\text{O,P}} \lesssim 0.05$ $a_m \lesssim 0.03$	2.0082	
$\text{PhMe}_2\text{Sn}^{\cdot}$	-75	septet	0.15	$a_{\text{H}}^{\text{CH}_3} = 0.30$ $a_{\text{O,P}} \lesssim 0.05$ $a_m \lesssim 0.03$	2.0124	
$\text{Ph}_2\text{EtSn}^{\cdot}$	-60	singlet	≈ 1	—	2.0072	
$\text{PhEt}_2\text{Sn}^{\cdot}$	-90	singlet	≈ 1	—	2.0125	
$(\text{PhMe}_2\text{CCH}_2)_3\text{Sn}$	25	septet	0.125	$a_{\text{H}}^{\text{CH}_2} = 0.31$ $a(^{117}\text{Sn}) = 132.5$ $a(^{119}\text{Sn}) = 138.0$	2.0150	[3,5]
$\text{i-Bu}_3\text{Sn}^{\cdot}$	-70	quartet		$a_{\text{H}}^{\text{CH}} = 0.26$	2.0170	[8] ^d
$(\text{i-Pr}_3\text{Ph})_3\text{Sn}^{\cdot}$	150	singlet	0.24	$a(^{117}\text{Sn}) = 160.2$ $a(^{119}\text{Sn}) = 167.8$	2.0078	[3] ^e

^a In di-*t*-butyl peroxide as solvent. ^b In cyclopropane. ^c Observed during the thermal reaction of azodiisobutyronitrile with triphenyltin hydride in *n*-nonane. ^d In cyclopropane during irradiation of di-*t*-butyl peroxide with tetra-*i*-butyltin. ^e Observed during thermal dissociation of the dimer in 1-methyl naphthalene or *n*-nonane.

line width increases strongly with increasing concentration of the hydride and increases slightly with increasing temperature. Two spectra are given in Fig. 1, and line-width values in Table 2. The intensity of the spectra decreases markedly with increasing temperature, and so line-widths could not be determined over a wide temperature range. The bad signal-to-noise ratio did not allow observation of $^{117,119}\text{Sn}$ satellites, which should have an intensity of less than 5 per cent of that of the main signal.

During irradiation of trimethyltin hydride with di-*t*-butyl peroxide in the probe of a ^1H -NMR spectrometer, the signals belonging to the hydride are broadened. Figure 2 shows part of the NMR spectrum, recorded with and without irradiation. The doublet at $\delta = 0.05$ ppm is due to the methyl groups of the hydride, the singlets at $\delta = 0.00$ ppm to tetramethylsilane added as

TABLE 2

ESR LINEWIDTHS ΔH FOR RADICALS $R_3Sn^\cdot$ IN *n*-PENTANE AT $T = -80^\circ\text{C}$

R	$[R_3SnH]$ (M)	ΔH (mT)	$\Delta H - 0.125$ mT
Me	0.4	0.15	0.025
	1.0	0.20	0.075
	1.5	0.25	0.125
	2.0	0.30	0.175
n-Pr	0.4	0.30	0.175
	0.8	0.45	0.325
n-Bu	0.4	0.25	0.125
	1.0	0.45	0.325

reference, and that at $\delta = 0.22$ ppm to hexamethylditin formed by recombination of trimethylstannyl radicals. The line broadenings depend on the rate of the radical formation r . A few values are plotted against the square root of r in Fig. 3.

During irradiation of triethyltin hydride with di-*t*-butyl peroxide, only a broad singlet was observed ($\Delta H \approx 1$ mT). The g value is similar to that of the trimethylstannyl radical. Therefore it is concluded that the singlet is due to the triethylstannyl radical, although the expected septet splitting could not be detected. The tri-*n*-propyl- and the tri-*n*-butylstannyl radical show five-line spectra, representing the central lines of the expected septets. The linewidths also depend on the tin hydride concentration. ESR spectra of the tri-*n*-butyltin radical are given in Fig. 4 and the linewidth values of both radicals in Table 2.

The triphenylstannyl radical shows a broad singlet ($g = 2.0023$, $\Delta H = 0.23$ mT). This could only be observed at the beginning of the irradiation. Later on, it disappeared, probably because of the formation of coloured reaction products which stop the photochemical decomposition of the peroxide. The thermal reaction of azodiisobutyronitrile with triphenyltin hydride also gives a broad singlet with $g = 2.0023$ [3]. This supports the identification of the radical. $\text{PhMe}_2\text{Sn}^\cdot$ and $\text{Ph}_2\text{MeSn}^\cdot$ show seven- and four-line spectra, respectively (see

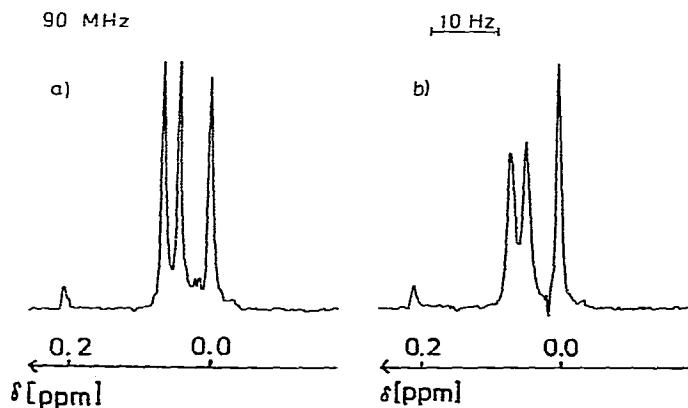


Fig. 2. ^1H NMR spectra a) without and b) with irradiation of di-*t*-butyl peroxide with trimethyltin hydride in cyclohexane- d_{12} at 25°C .

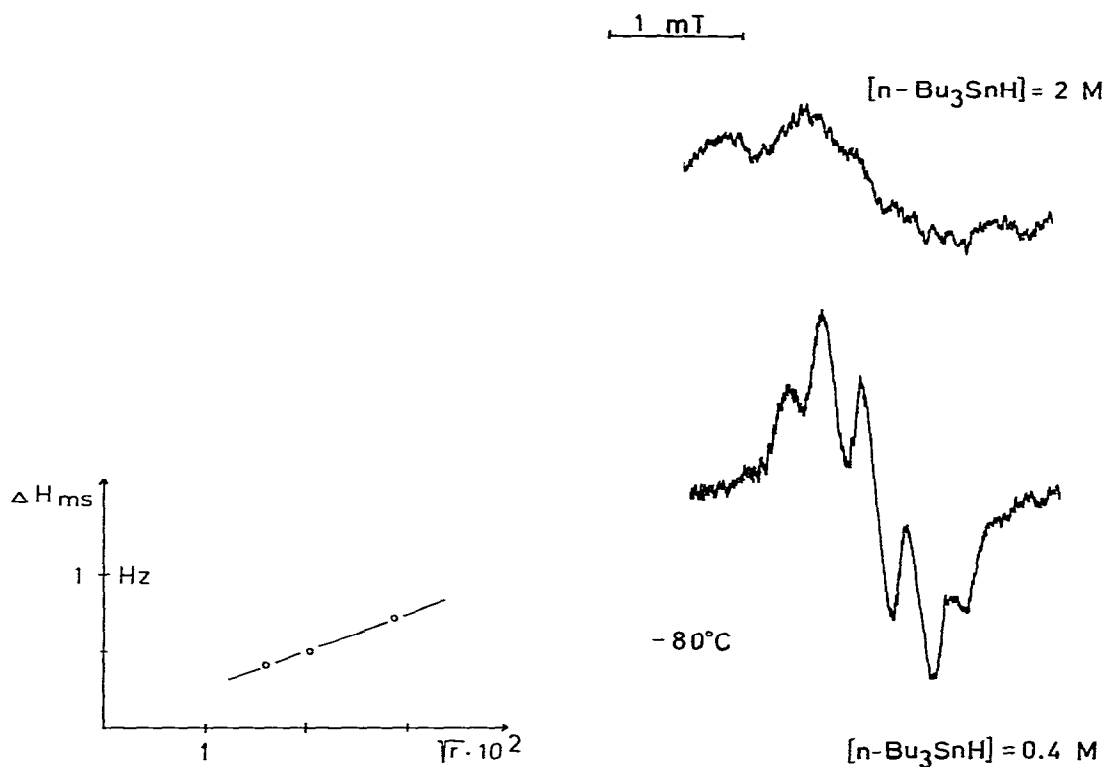


Fig. 3. Line broadenings in the ^1H NMR doublet of trimethyltin hydride during irradiation with di-*t*-butyl peroxide.

Fig. 4. ESR spectra of $n\text{-Bu}_3\text{Sn}^\cdot$ at various tin hydride concentrations.

Fig. 5). The splittings correspond to those observed in $\text{Me}_3\text{Sn}^\cdot$. The g values decrease with increase in the number of phenyl groups on the tin atom. The linewidths do not depend on the hydride concentration. $\text{PhEt}_2\text{Sn}^\cdot$ and $\text{Ph}_2\text{EtSn}^\cdot$ show only broad singlets. The g values are similar to those of $\text{PhMe}_2\text{Sn}^\cdot$ and

TABLE 3

RATE CONSTANTS OF ABSTRACTION REACTIONS INVOLVING STANNYL RADICALS

Reaction	T ($^\circ\text{C}$)	Rate constant ($M^{-1} \text{ s}^{-1}$)
$\text{Me}_3\text{Sn}^\cdot + \text{Me}_3\text{SnH}$	25	4×10^6
	-80	10^7
$\text{Et}_n\text{Ph}_{3-n}\text{Sn}^\cdot + \text{Et}_n\text{Ph}_{3-n}\text{SnH}$ ($n = 1-3$)	-80	$>10^8$
$n\text{-Pr}_3\text{Sn}^\cdot + n\text{-Pr}_3\text{SnH}$	-80	7×10^7
$n\text{-Bu}_3\text{Sn}^\cdot + n\text{-Bu}_3\text{SnH}$	-80	5×10^7
$t\text{-Bu}^\cdot + \text{Me}_3\text{SnH}$	25	2.9×10^5 [12]
$t\text{-Bu}^\cdot + n\text{-Bu}_3\text{SnH}$	25	7.4×10^5 [12]
$\text{Me}_3\text{Sn}^\cdot + t\text{-BuCl}$	25	5.9×10^3 [12]
$n\text{-Bu}_3\text{Sn}^\cdot + t\text{-BuCl}$	25	1.6×10^4 [12]

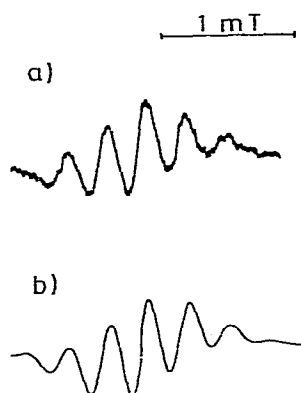
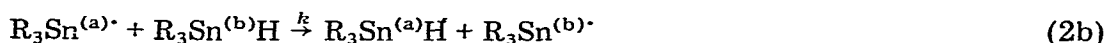


Fig. 5. ESR spectra of $\text{PhMe}_2\text{Sn}\cdot$: a) observed at -80°C ; b) calculated with $a_{\text{H}}^{\text{CH}_3} = 0.30$ mT, $a_{\text{O},\text{P}} = 0.05$ mT, $a_{\text{m}} = 0.03$ mT ($\Delta H = 0.125$ mT).

$\text{Ph}_2\text{MeSn}\cdot$, which supports the identification of the radicals.

Discussion

On comparing the ESR spectra of the alkyl- and aryl-substituted tin centered radicals it is striking that ethyl and phenyl protons do not give hyperfine splittings, whereas the β -protons in the methyl, n-propyl, and n-butyl groups give rise to the expected multiplets. The absence of hyperfine splitting may reflect absence of interaction with the protons. The observation of line broadening effects shows that it might also be due to exchange narrowing. The radicals $\text{PhMe}_2\text{Sn}\cdot$ and $\text{Ph}_2\text{MeSn}\cdot$ show splittings caused by interactions between the unpaired electron and the methyl protons, but do not exhibit hyperfine interactions with the protons of the phenyl groups. It is concluded that the absence of splittings caused by the ring protons is due to the smallness of the conjugation interaction between the unpaired electron and the aromatic systems. The absence of β -proton splitting in the radicals $\text{Et}_3\text{Sn}\cdot$, $\text{PhEt}_2\text{Sn}\cdot$, and $\text{Ph}_2\text{EtSn}\cdot$ is explained by an exchange narrowing process. The process operating is a hydrogen exchange between the radicals and the hydrides. The complete reaction scheme is



In this scheme r is the rate of radical formation, k the rate of the exchange reaction, and $2k_1$ the rate of radical combination. In the case of "slow" exchange between the diamagnetic compound and the radicals, line broadenings occur in the NMR spectra of the diamagnetic compound as well as in the ESR spectra of the radicals [9–11]. They are given by

$$\Delta H_{ms}(\text{NMR}) = \frac{1}{\pi} k \sqrt{\frac{r}{2k_1}} \quad (3a)$$

$$\Delta H_{ms}(\text{ESR}) = \frac{1}{\pi} k [\text{R}_3\text{SnH}] \quad (3b)$$

In the case of "rapid" exchange on the ESR time scale, singlets are observed in the ESR spectra. The linewidth decreases with increasing exchange rate. In the region of intermediate exchange rates, there are no analytical expressions which can be applied.

It follows from eq. 3a that the NMR line broadenings should be proportional to the root of r . Figure 3 shows that this is true for the system di-*t*-butyl peroxide/trimethyltin hydride, giving $k = 4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ with $2k_1 = 3.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ [12].

From eq. 3b it follows that a linear relationship should exist between the line broadenings of ESR signals and the concentration of the tin hydride. As it is seen from Table 2, that is the case for $\text{Me}_3\text{Sn}^\cdot$, $\text{n-Pr}_3\text{Sn}^\cdot$, and $\text{n-Bu}_3\text{Sn}^\cdot$ if the natural linewidth is assumed to be 0.125 mT, a value which has been found for the trineophylstannyl radical, which does not show line broadenings in the ESR spectra caused by hydrogen exchange [3]. In Table 3 are listed k values derived by assuming Lorentzian line shapes ($\Delta H = 0.577 \Delta H_{ms}$ [10]). For $\text{Me}_3\text{Sn}^\cdot$, $k = 10^7 \text{ M}^{-1} \text{ s}^{-1}$ satisfactorily agrees with the NMR value ($4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$) when it is remembered that the NMR value is only approximate, since it involves the quantities r and $2k_1$ which have to be determined independently or taken from the literature. In contrast, the ESR value is determined from the spectra. For the radicals $\text{Et}_n\text{Ph}_{3-n}$, which have medium exchange rates, only the order of magnitude is given in Table 3. Rate constants for the reactions of *t*-butyl radicals with tin hydrides and of stannyl radicals with *t*-butyl chloride are also included [12]. The values show that $\text{Me}_3\text{Sn}^\cdot$ and Me_3SnH are less reactive than $\text{n-Bu}_3\text{Sn}^\cdot$ and $\text{n-Bu}_3\text{SnH}$, which corresponds to the differences in the hydrogen exchange rates.

The values of the hydrogen exchange rates are remarkably high, and show that the activation energy of the reactions is $\lesssim 2$ kcal/mol. This can be understood in terms of the arguments used by Zavitsas [13,14] who represents the energy of the transition state as a combination of three Morse curves: two binding curves for the hydrogen bond formation and breaking and an antibonding curve for the repulsion between the terminal groups in the transition state $[\text{R}_3\text{Sn-H-SnR}_3]^\cdot$. The parameters involved are the bond strength D_e , the bond length r_e , and the bond stretching frequency ω_0 . The activation energy, calculated with $D_e(\text{Sn-H}) = 78 \text{ kcal/mol}$, $r_e(\text{Sn-H}) = 1.68 \text{ \AA}$, and $\omega_0(\text{Sn-H}) = 1810 \text{ cm}^{-1}$ [15], is about 0 kcal, which is in accord with the observation. For comparison, the experimental and the calculated activation energy for the hydrogen exchange reaction between $\text{CH}_3^\cdot$ and CH_4 is $\approx 14 \text{ kcal/mol}$ [13,14]. In Zavitsas' model, the main reason for the high values of k is the large Sn-H bond length, which lowers the repulsive forces between the terminal groups in the transition state $[\text{R}_3\text{Sn-H-SnR}_3]^\cdot$ compared with that in $[\text{H}_3\text{C-H-CH}_3]^\cdot$.

The hyperfine splittings and g values will now be discussed. In Table 4 a few values for carbon, silicon, and germanium centered radicals are shown for purposes of comparison.

TABLE 4

HYPERFINE SPLITTINGS IN mT AND g VALUES OF RADICALS $\text{Me}_3\text{M}^\cdot$ AND $\text{Ph}_3\text{M}^\cdot$ ($\text{M} = \text{C}, \text{Si}, \text{Ge}, \text{Sn}$) IN SOLUTION

		M = C	M = Si	M = Ge	M = Sn
$\text{Me}_3\text{M}^\cdot$:	$a_{\text{H}}^{\text{CH}_3}$	2.274 [20]	0.628 [16–18]	0.55 [18]	0.31
	g	2.0026 [20]	2.0028 [16–18]	2.0104 [18]	2.0163
$\text{Ph}_3\text{M}^\cdot$:	a_o	0.484 [23]	0.095 ^a	0.093 [21,22]	≤ 0.05
	a_m	0.158 [23]	—	0.046 [21,22]	≤ 0.03
	a_p	0.567 [23]	0.117 ^a	0.093 [21,22]	≤ 0.05
	g	2.0026 [24]	2.0027 ^a	2.0054 [21,22]	2.0023

^a The data given are for the tris(3,5-di-*i*-propylphenyl)silyl radical [19].

Hyperfine interactions with CH_3 and CH_2 protons are much smaller in tin-centered radicals than in the other Group IV element-centered radicals, implying that hyperconjugation is about one order of magnitude smaller than in *t*-Bu $^\cdot$ radicals and distinctly smaller than in $\text{Me}_3\text{Si}^\cdot$ and $\text{Me}_3\text{Ge}^\cdot$. Splittings caused by phenyl protons, which are important in $\text{Ph}_3\text{C}^\cdot$, $\text{Ph}_3\text{Si}^\cdot$, and $\text{Ph}_3\text{Ge}^\cdot$, cannot be found in phenyl-substituted stannyl radicals. However, the ESR linewidths of $\text{Ph}_3\text{Sn}^\cdot$, $\text{Ph}_2\text{MeSn}^\cdot$, and $\text{PhMe}_2\text{Sn}^\cdot$ are somewhat larger than in the trineophylstannyl radical, which may be the consequence of unresolved hyperfine interactions. By taking $a_o = a_p = 0.05$ mT, $a_m = 0.03$ mT and a natural linewidth of 0.125 mT, the observed linewidths are reproduced by the calculations (see Table 1 and Fig. 5). The a values given are therefore upper limits.

It follows that the free electron in stannyl radicals is mainly situated on the central tin atom. This agrees with the observation that the methyl proton couplings in the series $\text{Me}_3\text{Sn}^\cdot$, $\text{Me}_2\text{PhSn}^\cdot$, $\text{MePh}_2\text{Sn}^\cdot$ are identical, as found for the analogous germanium-centered radicals [21,22]. In the carbon-centered radicals, however, the couplings decrease from 2.274 mT to 1.56 mT on going from $\text{Me}_3\text{C}^\cdot$ to $\text{MePh}_2\text{C}^\cdot$ [20,22].

The fall in the g values in the series $\text{R}_3\text{Sn}^\cdot$, $\text{R}_2\text{PhSn}^\cdot$, $\text{RPh}_2\text{Sn}^\cdot$, $\text{Ph}_3\text{Sn}^\cdot$ ($\text{R} = \text{Me}, \text{Et}$) is striking; it has also been observed for germanium-centered radicals with $\text{R} = \text{Me}$ [21,22], but not for carbon-centered radicals. A change in the geometry of the radicals is assumed to be the reason for the decreasing g values; the radicals being more pyramidal the greater the number of phenyl substituents. Such a trend was predicted by Pauling [25] provided the electronegativity of the substituents increases, which is the case here. Gordy and coworkers have shown that a decrease in the g value has to be expected with increasing s character of the orbital containing the free electron in radicals with atoms exhibiting an appreciable spin-orbit coupling [26]. As the $^{117,119}\text{Sn}$ couplings are proportional to the s character of the orbital, it follows from Table 1 that the trineophylstannyl radical is more planar than the tris(2,4,6-tri-*i*-propylphenyl)stannyl radical [3]. Furthermore, the ^{119}Sn splitting constants found in matrices increase from 161.1 mT to 186.6 mT on going from $\text{Me}_3\text{Sn}^\cdot$ to $\text{Ph}_3\text{Sn}^\cdot$ [28,29], indicating a more pyramidal structure for $\text{Ph}_3\text{Sn}^\cdot$ in the solid state also.

Pyramidal structures have also been found for silicon- and germanium-centered radicals. The *t*-butyl radical is slightly pyramidal, but the central carbon atom rapidly oscillates through the plane defined by the methyl groups [30]. Such

oscillation does not take place in stannyl radicals, as was shown by Gielen and Tondeur, who found that hydrostannation reactions with chiral tin hydrides lead to optically active products, indicating that chiral stannyl radicals do not racemise [31]. Furthermore, alternating linewidth effects have been observed in the ESR spectrum of the trineophylstannyl radical, and this can most easily be explained by assuming a non-planar structure for the radical combined with restricted rotation around the Sn—C bonds [3].

Experimental

Solutions of di-*t*-butyl peroxide (0.2 *M*) and the appropriate tin hydride (0.4 *M*) in *n*-pentane were irradiated in sealed quartz tubes in the cavity of the ESR spectrometer (Varian E6 or Varian E-109E) with the unfiltered light of a 1000 W Hg/Xe high pressure lamp (HANOVIA 977 B-1). The light was focussed with quartz lenses. The hyperfine splitting constants were taken from the spectra which were calibrated with the field controller. The *g* values were determined by use of DPPH as reference ($g = 2.0036$). The DPPH spectrum was taken after each measurement. The microwave frequencies were determined using a frequency counter (Hewlett-Packard, 5246 L, with frequency converter 5255 A), the field shifts were taken from the spectra. The estimated accuracy in the determination of the coupling constants is about ± 0.01 mT, of the *g* values ± 0.0002 . It was limited by the natural linewidth of the signals (>0.1 mT).

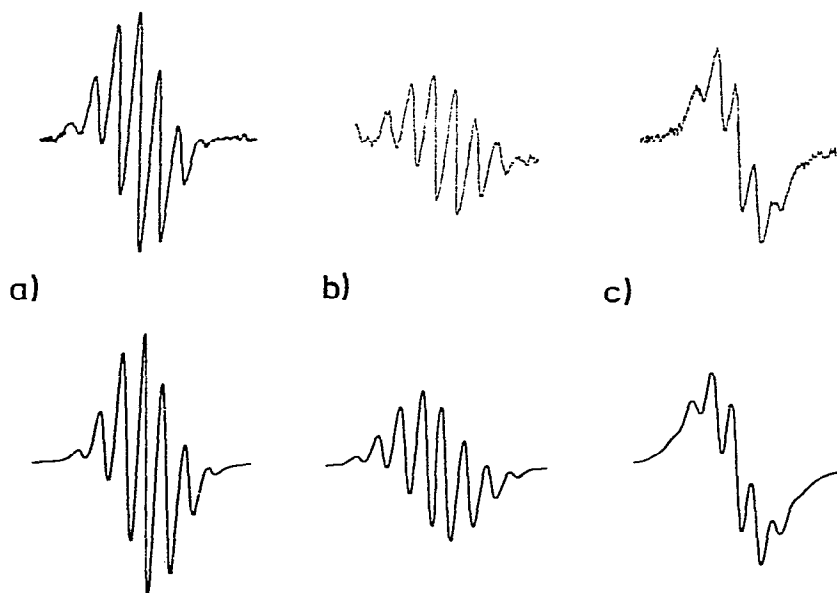


Fig. 6. ESR spectra of tin-centered radicals $R_3Sn^\cdot$ observed (upper portion) and calculated (lower portion). $[R_3SnH] = 0.4$ M. a) $R = \text{neophyl}$ ($T = 40^\circ\text{C}$, $\Delta H = 0.125$ mT). b) $R = \text{methyl}$ ($T = -80^\circ\text{C}$, $\Delta H = 0.15$ mT). c) $R = \text{n-butyl}$ ($T = -80^\circ\text{C}$, $\Delta H = 0.25$ mT). For splitting parameters see Table 1.

Linewidths ΔH were taken from the first derivative spectra by comparing observed and calculated values. Lorentzian line shapes were used. Gaussian line shapes gave a poorer agreement between observed and calculated spectra. The calculations were performed using the Varian E-900-3 data acquisition system. Typical spectra are shown in Fig. 6.

The equipment for recording NMR spectra during irradiation has been described [32]. The filtered light ($\lambda > 305$ nm) of the Hanovia lamp was focussed on to the front rod of a light pipe leading to the sensitive region of the spectrometer. The radiation was passed through an aqueous solution of NiSO_4 (1.14 M), CoSO_4 (0.21 M), and H_2SO_4 (0.01 M), a filter (WG 305, SCHOTT, Mainz) also being used. Under these conditions, homogeneous illumination of the probe was ensured.

Linewidths ΔH_{ms} with and without irradiation of di-*t*-butyl peroxide (0.2 M) and Me_3SnH (0.25 M) in cyclohexane- d_{12} were taken directly from the NMR spectra. The rates of radical formation were determined from rates of the product formation. It is assumed that the tubes were only partially illuminated [32]. The rate of radical formation was varied by partially covering the light source.

Di-*t*-butyl peroxide and *n*-pentane were distilled under argon at reduced pressure prior to use and admitted to the ESR tubes with exclusion of air. Cyclohexane- d_{12} was degassed by freeze-thaw cycles in the NMR tubes before the peroxide and hydride were added.

Tin hydrides were prepared by reduction of the appropriate tin halides with LiAlH_4 [33]. Tin halides R_3SnHal were prepared according to standard methods, while Ph_2MeSnCl , PhMe_2SnCl , Ph_2EtSnCl , and PhEt_2SnCl were synthesised by modified procedures [34,35].

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