CHEMISTRY LETTERS, pp. 611-612, 1980.

ESR SPECTRA AND STRUCTURE OF RADICAL ANIONS OF METHYL DERIVATIVES OF STANNANE

Akinori HASEGAWA, Takatoshi YAMAGUCHI, and Michiro HAYASHI
Department of Chemistry, Faculty of Science, Hiroshima University, Hiroshima 730

ESR spectra of $(CH_3)_xSnH_{4-x}^-$ (x=0∿3) radical anions formed in TMS matrices were observed. These radical anions have trigonal bipyramidal structure and the methyl groups prefer the equatorial positions to the axial positions of the trigonal bipyramid.

The formation of SnH_4^- radical anions was reported by Morton and Preston in their ESR study of the γ-irradiated solid solution of neopentane containing SnH_4.[1] From the analysis of the ESR spectrum observed at 100K, it was concluded that the SnH_4^- radical anions have a trigonal bipyramidal structure similar to that for SiF_4^- [1] and PF_4[2] and that two hydrogen atoms with coupling constants of 143.5G occupy the axial(apical) sites and the other two hydrogen atoms with coupling constants of 8.0G possess the equatorial sites. In the spectrum, weak satellites due to two isotopes of Sn atom were also observed.

On the other hand, $(CH_3)_4Sn^-$ radical anions have been reported by Fieldhouse et al. in their ESR study on γ-irradiated solid of $(CH_3)_4Sn$.[3] Although weak satellites due to the isotopes of the central Sn atom were observed, no h.f.s. of ligand atoms was observed. The detailed structure of the radical anions could not, therefore, be determined from the spectrum.

The present study was undertaken in order to investigate whether the trigonal bipyramidal structure is retained in the radical anions of stannanes successively substituted by methyl groups or not and to determine the structure of $(CH_3)_4Sn^-$.

ESR studies were performed using solid matrix of TMS which is established to be more effective to stabilize radical anions than neopentane. In the ESR spectrum of a γ-irradiated solid solution of TMS containing 5 mol% SnH_4 observed at 77K, anisotropic spectral lines originating from SnH_4^- radical anions were observed: two groups of intense lines attributable to the outer lines of h.f.s. of two axial hydrogens split into 1:2:1 triplet by two equatorial hydrogens and their satellites due to ^{117}Sn(I=1/2, 7.7%) and ^{119}Sn(I=1/2, 8.7%) with very large coupling constants. ESR parameters are listed in Table 1. The spectrum observed at 107K yielded isotropic ESR parameters practically equal to those reported by Morton and Preston.[1] The h.f. coupling constants showed very small temperature dependences.

When the ESR spectrum of irradiated CH_3SnH_3 in TMS matrix was recorded at 77K, two intense lines with g anisotropy and poorly defined features and their satellites were found at positions very close to those for SnH_4^-. The spectrum observed at 103K, although it has still a residual anisotropy, revealed that each of the intense lines splits into a doublet with a splitting of 8G. Thus, it was concluded that

Table 1	T(K)	$g_\perp$	$g_\parallel$	Nucleus[a]	$A_\perp$(G)	$A_\parallel$(G)
SnH_4^-	77	2.000	2.010	$H_{ax}(2)$	138	137
				$H_{eq}(2)$	7.7	7.7
SnH_4^- b)	100	g_0=2.0037		$H_{ax}(2)$	a= 143.5	
				$H_{eq}(2)$	a= 8.0	
				^{117}Sn	a=2129	
$CH_3SnH_3^-$	77	1.997	2.012	$H_{ax}(2)$	132	131
	103			$H_{eq}(1)$	a= 8.0	
$(CH_3)_2SnH_2^-$	77	1.996	2.014	$H_{ax}(2)$	127	126
$(CH_3)_3SnH^-$	77	1.995	2.014	$H_{ax}(1)$	140	139
$(CH_3)_4Sn^-$ c)	77	2.0		Sn	2101	1672

a) Number in parentheses indicates the number of equivalent hydrogen nuclei. b) Ref.1). c) Ref.3).

$CH_3SnH_3^-$ radical anions formed have a trigonal bipyramidal structure similar to that of SnH_4^- and that the substituted CH_3 group occupies one of the two equatorial sites.

In an ESR spectrum obtained with $(CH_3)_2SnH_2$ in TMS, two intense lines attributable to the outer lines of h.f.s. due to two axial hydrogens appeared with a very small line width but with no further splitting, and their satellites were also observed clearly. Thus, the $(CH_3)_2SnH_2^-$ radical anions are concluded to have a trigonal bipyramidal structure and to possess the two CH_3 groups in the equatorial sites.

ESR spectrum of γ-irradiated TMS containing $(CH_3)_3SnH$ yielded two lines near the central intense signals of the matrix radicals, a very intense line with g anisotropic feature behind the signals of the matrix radical, and their satellites. The separation of the two lines is approximately equal to that for the axial hydrogens in SnH_4^-. This fact leads us to the conclusion that the radical anions, $(CH_3)_3SnH^-$, have a trigonal bipyramidal structure and possess the hydrogen and one of the three CH_3 groups in the axial positions. The linewidth is larger than that for $(CH_3)_2SnH_2^-$, reflecting probably the unresolved splittings from the axial CH_3 group. The other intense line and its satellites have ESR parameters approximately close to those of $(CH_3)_3\dot{S}n$ formed in $(CH_3)_4Sn$ reported by Fieldhouse et al.[3]

Analyses of the satellites for these radical anions have not been completed, unfortunately, owing to the partial orientation of radicals in TMS matrices.

As results of the successive substitution of SnH_4^- by CH_3 groups, the following facts were obtained. First, the structure of trigonal bipyramid is preserved in these radical anions. Second, the CH_3 groups prefer the equatorial positions to the axial positions of the trigonal bipyramid. Results obtained recently for the radical anions of methyl derivatives of bromosilane[4] are in accordance with these facts, while the radical anions of methyl derivatives of iodosilane have the structure of local C_{3v} symmetry which is different from the trigonal bipyramidal structure of SiH_3I^-.[4] As for the radical anions of methyl derivatives of halogermane, no substantial structural change from C_{3v} symmetry for GeH_3Br^- resulted from substitution by methyl groups.[4]

As a result of this study, it may be reasonably assumed that $(CH_3)_4Sn^-$ radical anions detected by Fieldhouse et al. have a trigonal bipyramidal structure.

References

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(Received February 18, 1980)