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ESR Spectra and Structure of the Radical Anions of Organo Halosilanes

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The radical anions of ethyl- and vinyl- halosilanes formed in solid matrices of tetramethylsilane and their ESR spectra were investigated to be compared with results obtained from related radical anions. These radical anions have a trigonal bipyramidal structure with two axial and two equatorial positions. Ethyl and methyl groups which are less electronetative than H prefer the equatorial positons. The vinyl group with a single π electron system occupies the equatorial position due to its electron-donating capability, in spite of its larger electronegativity.

We have reported some ESR studies on the radical anions of simple halides whose central atom is a Group IV element; these anions formed in solid matrices of tetramethylsilane (TMS).[1–4] Results for some bromides will be mentioned briefly. In CF_3Br^- radical anions, the three F atoms are equivalent to one another and a large spin density is on the Br atom.[1] It was therefore concluded that the radical anions have C_{3v} symmetry and that the Br atoms are on the symmetry axes. On the other hand, a congeneric SiF_3Br^- radical anion with a central Si atom has larger contributions of spin density on the Br and one F atoms and small contributions on the other two F atoms.[2] This fact led us to the conclusion that the radical anion has trigonal bipyramidal structure with the Br atom and the first F atom in the axial positions and the other two F atoms in the equatorial positions. A similar trigonal bipyramidal structure has also been suggested for SiH_3Br^- radical anion, since hyperfine structure due to the Br and one H nuclei was observed in the ESR spectrum.[3] However, GeH_3Br^- radical anions, which are congeneric to SiH_3Br^-, have been reported to have a structure with C_{3v} symmetry, as in the case of CF_3Br^-, because the hyperfine structure of the Br nucleus in the ESR spectrum is further split by three equivalent H nuclei.[4] Thus, the structure of radical anions is significantly affected by the type of central atom present. Moreover, ESR spectra of methyl-substituted radical anions such as $CH_3SiH_2Br^-$ and $CH_3GeH_2Br^-$ have been investigated in order to confirm the structural difference between trigonal bipyramidal and C_{3v} structures.[5] No substantial change in radical structure resulted from the introduction of methyl groups, and it was therefore concluded that, even in the methyl-substituted radical anions, the silicon-centered radical anions prefer a trigonal bipyramidal structure whereas the germanium-centered radical anions have a local C_{3v} structure. For the silicon-centered radical anions, the methyl groups have been suggested to prefer the equatorial positions to the axial ones of the trigonal bipyramidal structure.

On the basis of these facts, this study was designed. Organo halosilanes $RSiH_2X$ (X=Br or I) containing different kinds of organo group R were prepared; irradiation then produces their radical anions in TMS matrices. Thus we could investigate the effect of substituent groups on radical structure and on the distribution of spin density.

Experimental

Ethylsilane and vinylsilane were prepared by reducing ethyltrichlorosilane and vinyltrichlorosilane (Tokyo Kasei), respectively, with lithium aluminium hydride in dibutyl ether. Ethylbromosilane was prepared by the reaction with mercury(II) bromide[6] and ethyliodosilane with hydrogen iodide in the presence of aluminium triiodide as a catalyst.[7] Vinylbromosilane and vinyliodosilane were similarly obtained.

All of the compounds prepared were isolated and purified by distillation *in vacuo*, and identified from IR spectra.[8]

Solid solutions of tetramethylsilane (Merck) containing 5 mol% of the appropriate silane were irradiated at 77 K with γ-rays to *ca.* 1.5 Mrad in a ^{60}Co γ-source.

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

Results and Discussion

When a solid solution of TMS containing 5 mol% of $C_2H_5SiH_2Br$ was γ-irradiated at 77 K and followed by ESR observations at 77 K, the ESR spectrum shown in Fig. 1 was observed. In addition to the central lines originating from the matrix radical $\cdot CH_2SiMe_3$, one can find an anisotropic spectrum similar to the spectra assigned to the SiH_3Br^-[3] and $CH_3SiH_2Br^-$[5] radical anions, which formed in TMS matrices and have trigonal bipyramidal structures. In accordance with the analyses reported for these radical anions, the observed spectrum is interpreted in terms of hyperfine structure due to one Br (^{79}Br(I=3/2)50.57%, ^{81}Br(I=3/2)49.43%) and one H nuclei. The coupling constant of the H nucleus is similar in magnitude to that of H nucleus in an axial position of SiH_3Br^-[3] and to that of the H nucleus which is bonded to the Si atom and possesses an axial position of $CH_3SiH_2Br^-$.[5] Accordingly, the $C_2H_5SiH_2Br^-$ radical anions formed were concluded to have trigonal bipyramidal structure possessing the Br and H atoms with large spin densities in the axial positions and the other H atom and the C_2H_5 group in the equatorial positions.

Similar experiments were also carried out with $C_2H_5SiH_2I$ in a TMS matrix. The observed ESR spectrum was interpreted in terms of hyperfine splittings due to the axial I and H nuclei of trigonal bipyramidal $C_2H_5SiH_2I^-$ radical anions. This result is in contrast to the fact that the radical anions $CH_3SiH_2I^-$ have been assigned to have, exceptionally, a local C_{3v} struc-

TABLE 1. ESR PARAMETERS AND SPIN DENSITIES OF RADICAL ANIONS OF ORGANO HALOSILANES AND HALOSILANES

Radical	g values		Nucleus	Hyperfine couplings		Spin densities		Structure	Reference
	$g_\perp$	$g_{//}$		$A_\perp/\mathrm{G}^{a)}$	$A_{//}/\mathrm{G}^{a)}$	ρ_s	ρ_p		
$C_2H_5SiH_2Br^-$	2.007	2.003	^{79}Br	110	209	0.018	0.145	Tbp[b)]	This work
			^{81}Br	118	226	0.018	0.145		
			^{1}H	39.3	40.8	0.078			
$CH_3SiH_2Br^-$	2.005	2.001	^{79}Br	109	220	0.019	0.160	Tbp	5
			^{81}Br	118	237	0.019	0.160		
			^{1}H	41.5	45.3	0.084			
SiH_3Br^-	2.004	2.002	^{79}Br	128	254	0.022	0.183	Tbp	3
			^{81}Br	138	274	0.022	0.183		
			^{1}H	43.4	45.6	0.087			
$CH_2{=}CHSiH_2Br^-$	2.004	2.003	^{79}Br	117	239	0.020	0.178	Tbp	This work
			^{81}Br	126	258	0.020	0.178		
			^{1}H	33.7	37.3	0.069			
$C_2H_5SiH_2I^-$	2.022	1.997	^{127}I	142	276	0.026	0.196	Tbp	This work
			^{1}H	33.4	35.6	0.069			
$CH_3SiH_2I^-$	2.009	1.997	^{127}I	148	276	0.026	0.188	C_{3v}	5
			^{1}H	20	22	0.041			
SiH_3I^-	2.009	1.994	^{127}I	165	328	0.030	0.238	Tbp	3
			^{1}H	35.6	35.6	0.070			
$CH_2{=}CHSiH_2I^-$	2.015	1.992	^{127}I	157	291	0.028	0.196	Tbp	This work
			^{1}H	31.0	33.4	0.063			

a) $1\ \mathrm{G} = 1\times10^{-4}\ \mathrm{T}$. b) Tbp means trigonal bipyramidal structure.

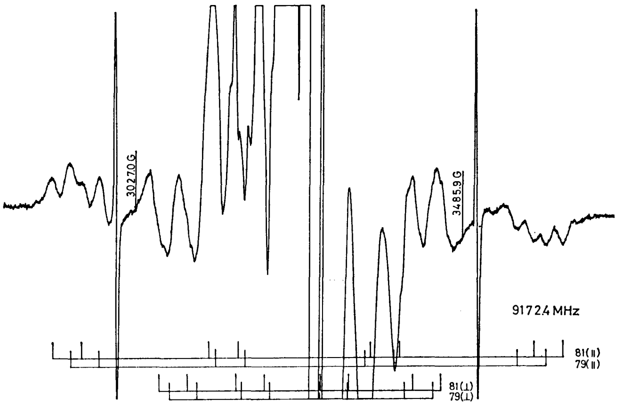

Fig. 1. First derivative ESR spectrum of a γ-irradiated solid solution of 5 mol % ethylbromosilane in tetramethylsilane, recorded at 77 K.
The stick diagrams represent the calculated line positions of the parallel (upper) and the perpendicular (lower) components for $C_2H_5SiH_2{}^{79}Br^-$ and $C_2H_5SiH_2{}^{81}Br^-$ according to the parameters listed in Table 1.

ture rather than a trigonal bipyramidal structure since the ESR spectrum consists of a sextet due to the I nucleus and a 1:2:1 triplet due to three equivalent H nuclei.[5)]

Resonance line positions were calculated by a matrix diagonalization program with the ESR parameters listed in Table 1. In accordance with the above analyses, the stick diagrams calculated show good agreement with the observed spectra assigned to $C_2H_5SiH_2Br^-$ and $C_2H_5SiH_2I^-$. Spin densities were obtained by the use of the atomic values of hyperfine coupling constants[9)] calculated from Froese's wave functions[10)] for comparison with those of related and reported radical anions; the values are listed in Table 1 with ESR parameters. If atomic values calculated recently by Morton and Preston[11)] are used, the values become smaller. In Table 1, results for $CH_3SiH_2X^-$[5)] and SiH_3X^-[3)] (X=Br or I) are given for comparison. Spin densities on the axial H and halogen atoms increase in the order C_2H_5, CH_3, and H for R of $RSiH_2X^-$ (X=Br or I) except for the case $CH_3SiH_2I^-$, where a local C_{3v} structure was suggested.[5)] The group electronegativity of each substituent increases in the same order.

Here, it might be of interest to quote results for the SiF_3Br^-[2)] and SiH_3Br^-[3)] radical anions which have axial Br atoms in their trigonal bipyramidal structure. Since Br is less electronegative than F and more electronegative than H, the less electronegative Br occupies the axial position of SiF_3Br^-. Phosphoranyl radicals are isoelectronic to the silicon-centered radical anions and also have trigonal bipyramidal structures, which are similar to the structure of phosphoranes. Colussi *et al.*[12)] have made INDO calculations for phosphoranyl radicals and phosphoranes. According to their results, electron densities (charge densities) in PH_4 and PH_5 are larger in the axial positions than in the equatorial positions. In the cases of PF_4 and PF_5, however, the equatorial positions have higher electron densities than the axial positions. Therefore, when a group which is more electronegative than H is replaced with an H atom of PH_4 or PH_5, the group prefers an axial position with its higher electron density. Coherently, a less electronegative group possesses an axial position with a lower electron density upon the substitution with an F atom of PF_4 or PF_5. The effect of group electronegativity on the preferential occupation of substituents has also been investigated experimentally for phosphoranyl radicals.[13)] Similar

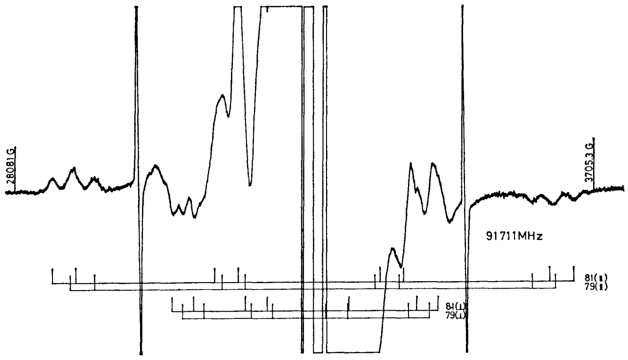

Fig. 2. ESR spectrum of a γ-irradiated solid solution of 5 mol % vinylbromosilane in tetramethylsilane, recorded at 77 K, and the stick diagrams calculated for CH_2=$CHSiH_2{}^{79}Br^-$ and CH_2=$CHSiH_2{}^{81}Br^-$.

results can be expected for the silicon-centered radical anions which are isoelectronic to phosphoranyl radicals. Accordingly, the axial positions of the Br atom in SiH_3Br^- and SiF_3Br^- are well accepted.

In the case of $RSiH_2X^-$, it is thus reasonable to expect that a group R more electronegative than H takes an axial position and that a less electronegative group R occupies an equatorial position. Indeed, as mentioned above, C_2H_5 and CH_3 groups which are less electronegative than H occupy the equatorial positions of the trigonal bipyramidal $RSiH_2X^-$ radical anions. This result is consistent with the result obtained recently for the radical anions of methylstannanes: that methyl groups prefer the equatorial positions of the trigonal bipyramidal structure.[14)]

Since vinyl groups are more electronegative than H and are therefore expected to possess the axial positions of CH_2=$CHSiH_2X^-$ radical anions, a solid solution of TMS containing CH_2=$CHSiH_2Br$ was irradiated. As shown in Fig. 2, the ESR spectrum consists of the anisotropic hyperfine structure of a quartet from one Br atom and a doublet. The doublet may originate from an H atom bonded to the Si atom or from one in the vinyl group. Thus, similar experiments were carried out with CH_2=$CHSiD_2Br$. As a result, the doublet which appeared in the case of CH_2=$CHSiH_2Br$ was removed and the anisotropic quartet spectrum alone was observed. Therefore, the spectrum observed with CH_2=$CHSiH_2Br$ was interpreted to contain hyperfine splittings due to the Br atom and one of the two H atoms bonded to the Si atom. This fact leads us to the conclusion that the CH_2=$CHSiH_2Br^-$ radical anion formed has the vinyl group in the equatorial position of the trigonal bipyramidal structure, although the axial position was the first suggested.

Irrespective of the electronegativity of vinyl group, which is larger than that of H, the value of spin density on the axial Br atom of the CH_2=$CHSiH_2Br^-$ radical anions falls between those obtained for $CH_3SiH_2Br^-$ and SiH_3Br^-, while the value on the axial H atom is smaller than that for $C_2H_5SiH_2Br^-$. Similar trends were obtained between CH_2=$CHSiH_2I^-$ and the related radical anions, although $CH_3SiH_2I^-$ could not be compared because of the different structure.[5)]

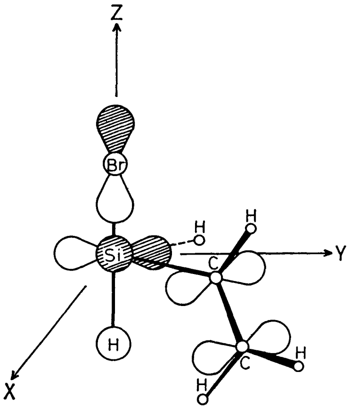

Fig. 3. A structure proposed for CH_2=$CHSiH_2Br^-$. The terminal C atom in the vinyl group is on the upper side or on the lower side of the equatorial plane.

These results may indicate that some other factor than the electronegativity of vinyl groups governs the geometrical and electronic structures of CH_2=$CHSiH_2X^-$ radical anions.

When the effect of substituent groups is considered, electronegativity is important for the inductive effect of σ electrons. However, for the groups with π electrons or nonbonding electron pairs, the more electron attractive for the inductive effect by σ electrons the groups are, the more electron donating are the groups for the π electron mesomeric effect, and the groups behave as π donors. Thus, vinyl groups are considered as electronegative groups and simultaneously as π donors.

As mentioned earlier, the electronic structure of phosphorane PH_5 as well as phosphoranyl radical PH_4 is suggestive of that of the radical anions of halosilane. Therefore, the results for PH_5 derived from extended Hückel calculations by Hoffmann *et al.*[15)] may be helpful for the consideration of the effect of substituent groups in organo halosilane radical anions.

Let us first view the interactions arising between the orbitals of PH_5 and a π donor or a π acceptor.[15)] For a π donor, interaction I with occupied PH_5 skeleton orbitals and interaction II with phosphorus 3d orbitals were considered, while interaction III with unfilled skeleton orbitals was neglected. I is inherently destabilizing, whereas II is inherently stabilizing, and the interaction I is more important than II. On the other hand, there is only one significant interaction (IV) between the acceptor orbital and the occupied skeletal set. Thus, for an acceptor the site with maximum interaction will be favored (IV is stabilizing), and for a donor the site with maximum interaction will be destabilized (I is a repulsive term).

Axial interactions, e_x and e_y, equatorial interactions, b_1 and b_2, and the relation between their magnitudes, $e_x \simeq e_y \simeq b_1 > b_2$, are shown in the paper by Hoffmann *et al.*[15)] According to these results, π acceptors will prefer axial sites in the trigonal bipyramid so as to have the maximum interaction e_x or e_y, while π donors will occupy equatorial positions for b_2 avoiding large interactions. If a substituent has a single π system and is located in the equatorial positions, it will prefer to have its acceptor orbital perpendicular to the equatorial plane, having b_1 interaction, or its donor orbital in that plane, having b_2 interaction.

In the light of these results for PH_5, the vinyl group, which has a single π system in $CH_2{=}CHSiH_2X^-$ radical anion may be expected to occupy the equatorial position and to have its donor orbital in the equatorial plane, as shown in Fig. 3. The π donor orbital of the equatorial vinyl group is shown in Fig. 3 with the a_1 antibonding unpaired electron orbital composed of the p orbital of the axial Br, the s orbital of the axial H and the s and p orbitals of the central Si atom.[2-4] This is accordance with the results obtained from the ESR observations described earlier.

In conclusion, the mesomeric effect as well as the inductive effect of substituent group plays an imporant role in the geometrical preference of the substituent groups in the trigonal bipyramidal structure of organo halosilane radical anions.

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