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SILICON-29 HYPERFINE SPLITTING OF THE SiH_3 RADICAL

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The well defined ESR spectra of the naturally abundant $^{29}SiH_3$ and $^{29}SiD_3$ radicals produced by γ-irradiation of silanes adsorbed on the surface of silica gel are reported. The observed ^{29}Si-hf splitting of 182 G is compared with those obtained previously in the inert-gas matrices.

The remarkably small proton-hf splitting of 7.6 G of the SiH_3 radical observed by Cochran,$^{1)}$ compared with that of 23 G of the CH_3 radical, has been discussed in terms of the deviation from the planarity of the radical.$^{2)}$ Such an argument is to be settled by the determination of the ^{29}Si-hf splitting of the SiH_3 radical since any deviation from the planarity introduces directly an s-character into the orbital occupied by an unpaired electron, which results in a large ^{29}Si-hf splitting.

Gordy and his co-workers first reported the ESR spectrum of the naturally abundant $^{29}SiH_3$ radical formed by γ-irradiation of SiH_4 in the krypton matrix at 4.2 K.$^{3)}$ The large ^{29}Si-hf splitting of 266 G was sufficient to confirm a pyramidal structure of the SiH_3 radical. Subsequently, they also obtained the ^{29}Si-hf splitting of this radical in the xenon matrix$^{4)}$; the value of 190 G, however, markedly differed from that of 266 G obtained previously in the krypton matrix.

Recently, Krusic and Kochi$^{5)}$ and Hudson et al.$^{6)}$ have detected the ^{29}Si species of certain methyl-substituted silyl radicals in fluid solutions by the abstraction of hydrogen atom from the parent silanes by use of the photochemically generated t-butoxy radicals. The observed ^{29}Si-hf splittings of the methyl-substituted silyl radicals show comparatively smaller hf splittings than that of the SiH_3 radical obtained in the krypton matrix. Accordingly, the both research groups have concluded that the silyl radicals become more planar as the hydrogen atom is replaced successively by a methyl group. Shortly thereafter, Sharp and Symons$^{7)}$ have also observed the ^{29}Si-hf splittings of the methyl-substituted silyl radicals produced in solid matrices by γ-irradiation, which differ little among a series of methyl-substituted silyl radicals. Thus, they have suggested that the effect of methyl-substitution is not so significant, and that the result for the SiH_3 radical in the xenon matrix, which is nearly close to those for the methyl-substituted silyl radicals, may be more reliable than that in the krypton matrix. Judging from the variations of α- and β-proton-hf splittings among the series of the radicals, they have tentatively concluded that, on methyl-substitution, there is a slight overall deviation from the planarity but a simultaneous small delocalization of spin density due to hyperconjugation on the methyl groups just offsets this. This is the opposite conclusion to that of the former two groups.

This apparent discrepancy in the argument about the structure of silyl radicals seems to arise entirely from the experimental values of the ^{29}Si-hf splitting of the SiH_3 radical on which values their arguments are based. The ESR spectra of the SiH_3 radical obtained in the inert-gas matrices are poorly resolved, and, moreover, the different values of the isotropic ^{29}Si-hf splitting are estimated in krypton and xenon matrices. Since the matrix environments are so similar, the large matrix effect on the ^{29}Si-hf splitting is difficult to understand. Thus we have reinvestigated the ^{29}Si-hf splitting of the SiH_3 radical to obtain a more reliable value of this hf splitting. In this communication, we will present the well-resolved ESR spectra of $^{29}SiH_3$ and $^{29}SiD_3$ radicals trapped on the surface of silica gel.

The SiH_3 radical was produced on the surface of silica gel by γ-irradiation of adsorbed silane at 77 K. Silane, SiH_4, was synthesized from magnesium silicide and ammonium chloride in liquid ammonia, and deuterated silane, SiD_4, from tetrachlorosilane by reduction with lithium aluminum deuteride in ether. The silica gel was prepared from hydrolysis of distilled ethylorthosilicate, and was pretreated in an oxygen atmosphere for a few hours at 550^{o}C. The surface area determined by the BET method was 580 m^2/g. The silica gel thus obtained was calcined in an oxygen atmosphere for 2-3 hours and evacuated for 4-5 hours at 550^{o}C in a 4 mm o. d. quartz sample tube attached to a conventional high-vacuum system. After about 1/20 of the monolayer amount of silane was introduced into the sample tube at room temperature, the tube was sealed off, and was cooled gradually from room temperature to liquid nitrogen temperature in order to secure a homogeneous adsorption of silane on the surface of silica gel. The samples were then exposed to ^{60}Co γ-rays at 77 K at a nominal dose rate of 0.5 Mrad/hr for 4-8 hours. The paramagnetic centers induced in the quartz sample tube by γ-irradiation were annealed after irradiation. The ESR spectra were recorded with a JEOL PE-1X spectrometer at X-band and with 100 kHz field modulation.

Figure 1 shows the ESR spectrum of the SiH_3 radical at -150^{o}C. The well-resolved ^{29}Si-hf splitting of the naturally abundant $^{29}SiH_3$ radical species was clearly observed at a high gain, and the isotropic hf splitting of 182 G was evaluated from the spectrum. For comparison, SiD_4 adsorbed on the surface of silica gel was γ-irradiated under the same conditions. Although the deuterium-hf splitting of the $^{29}SiD_3$ radical was not resolved as is shown in Figure 2, the ^{29}Si-hf splitting of 182 G was in good agreement with that of the SiH_3 radical. The ESR data for both radicals are listed in Table 1, along with those for SiH_3 and methyl-substituted silyl radicals reported previously. The isotropic ^{29}Si-hf splitting of the SiH_3 radical trapped on the surface of silica gel is close to that in the xenon matrix, supporting the idea that the ^{29}Si-hf splitting in the krypton matrix is less reliable as has been suggested by Sharp and Symons.$^{7)}$

On the basis of our value, a 15 % s-character of the unpaired spin orbital is estimated, using the normal atomic parameter: $A^{o}(^{29}Si) = 1218$ G.$^{8)}$ The large s-character indicates that the SiH_3 radical is not planar like the CH_3 radical but pyramidal in shape. Recently, Pauling$^{9)}$ has pointed out that a non-planar structure is expected for the AX_3-type radical if X is more electronegative than A. Since the difference in the electronegativity between silicon and hydrogen shows just the above trend, a pyramidal structure can be predicted for the SiH_3 radical. The results of theoretical calculations also predict a pyramidal structure, though the bond angle of this radical is a subject of controversy.$^{10-12)}$

It is very interesting that the isotropic ^{29}Si-hf splitting of 182 G of the SiH_3 radical is equal, within experimental errors, to those of the methyl-substituted silyl radicals ($MeSiH_2$, Me_2SiH, and Me_3Si) obtained in both fluid solutions$^{5,6)}$ and solid matrices.$^{7)}$ This implies that the mean bond angles at the silicon atom of these radicals are, to a first approximation, unaffected by the successive methyl-substitution. However, α-proton-hf splittings change significantly from 8 G of SiH_3 to 17 G of Me_2SiH. This change in the proton-hf splitting might possibly be related to a slight change in the average bond angle as has been discussed by Sharp and Symons.$^{7)}$ However, if the bond angle changes slightly with the methyl-substitution, a significant change in the ^{29}Si-hf splitting should also be resulted. Unfortunately, a clear-cut explanation on this point cannot be made at the

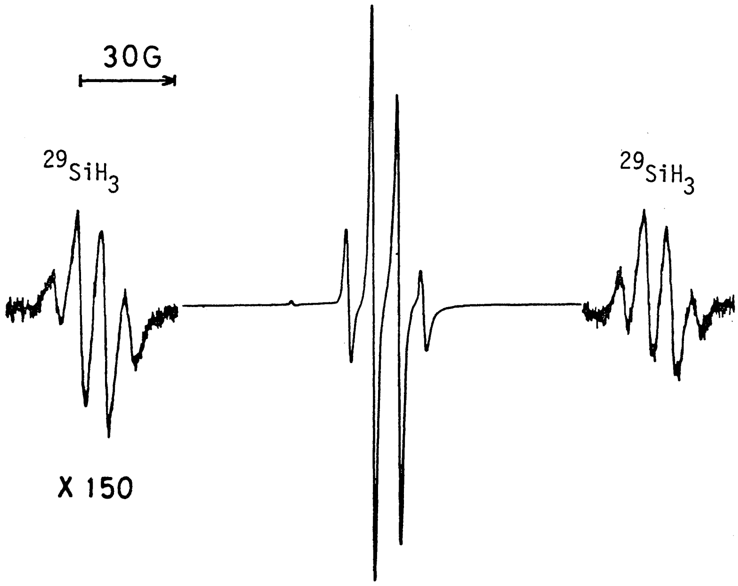

Figure 1. ESR spectrum of the SiH_3 radical on silica gel at -150°C.

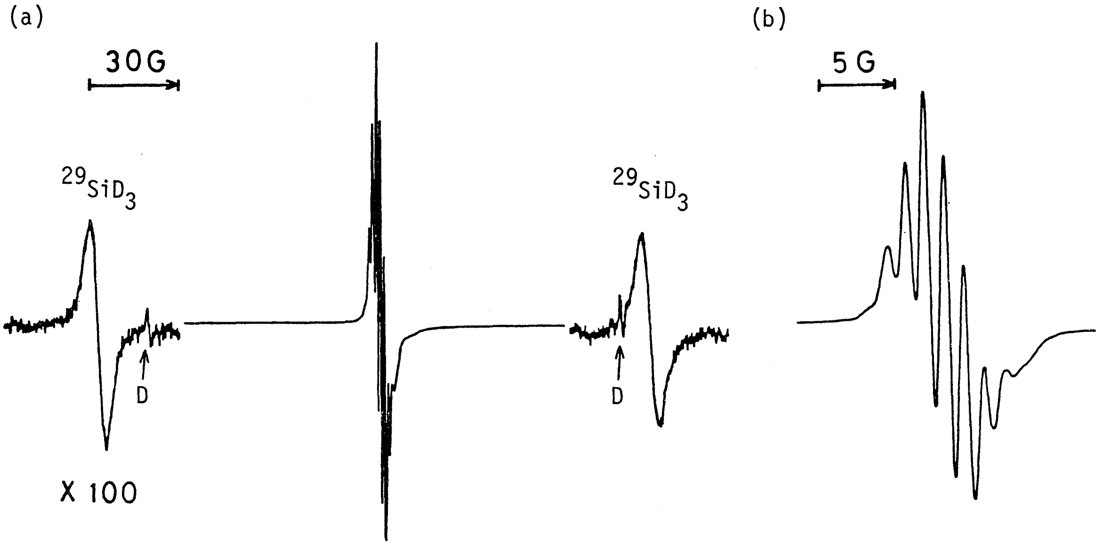

Figure 2. (a) ESR spectrum of the SiD_3 radical on silica gel at -150°C. Arrows: signal of D atom.
(b) Expanded spectrum of the central part of (a).

TABLE 1. ESR Data for Silyl Radicals in Various Matrices

Silyl radical	Matrix	Temp./^{o}C	g-value	A(^{29}Si)/G	A(α-H)/G	A(β-H)/G	Ref.
SiH_3	Argon	-269			7.6		1
	Krypton	-269	2.006	266	8.1		3
	Xenon	-269	2.003	190	unresolved		4
	Solution	-153			7.96		5
	Solution	- 70	2.0032		7.84		6
	Silica gel	-150	2.003	182	7.9		This work
SiD_3	Silica gel	-150	2.003	182	1.2(D)		This work
$MeSiH_2$	Solution	-121			11.82	7.98	5
	Solution	- 70	2.0032		12.11	8.21	6
	Solid	-196	2.0032	181	11.8	8.0	7
Me_2SiH	Solution	-123		183.05	16.99	7.19	5
	Solution	- 70	2.0031		17.29	7.30	6
Me_3Si	Solution	-120		181.14		6.28	5
	Solution	- 70	2.0031	183		6.34	6
	Solid	-196	2.0029	181		6.3	7

present stage.

In order to explain fully this interesting problem, further studies on the relation between the ^{29}Si-hf splitting and the α-proton-hf splitting of variously substituted silyl radicals are now in progress.

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