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MICROWAVE SPECTRA OF ALLYLSILANE

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Microwave spectra of allylsilane and its deuterated species were measured. Their rotational constants determined were predictable by a model having a set of structural parameters transferred from those of 1-butene and ethylsilane and the skeletal dihedral angle of 103°40'. Dipole moment obtained by Stark effect measurements was 0.526 ± 0.022 D for the normal species making an angle of about 36° with the SiC bond. From the observed splittings of the spectra due to the excited silyl torsional state, the barrier to SiH_3 internal rotation was determined to be 2130 ± 70 cal/mol.

Recently, we studied the microwave spectra of allylsilane as a continuation of a series of studies on the molecular structures of organosilicones containing the C=C bond. From the results for the similar molecules such as 1-butene1) and methylvinylsilane,2) we expected two rotational isomers of allylsilane, that is, the cis and skew isomers with the skeletal dihedral angles of 0° and 120°, respectively.

However, in spite of careful searches of the spectra, we could not find any a-type transitions of both isomers in the expected frequency region in appreciable intensities. We found about twenty of fairly strong b-type transitions with $J \leqq 10$ due to the skew isomer. As the centrifugal distortion effect seems to be fairly large, the rotational constants were obtained by a least-square fit of seven observed frequencies with $J \leqq 4$. They are given in Table 1.

In order to estimate the plausible structure, the rotational constants were calculated from a model and compared with the observed. In this model, the structural parameters of the $C\text{-}CH_2SiH_3$ and $H_2C\text{=}CHC\text{-}$ parts of the molecule were transferred from those of ethylsilane3) and of the skew isomer of 1-butene, respectively and the skeletal dihedral angle was taken as an adjustable parameter. The minimum deviations of the calculated rotational constants from the observed for the two species were satisfactorily small (less than 0.15 %) when the skeletal dihedral angle was taken as 103°40'. The skeletal dihedral angle of allylsilane is much smaller than those of the skew isomers of 1-butene(119°54'), methylvinylsilane(120°) and 3-fluoropropene (127°8')4).

The dipole moments were determined by Stark effect measurements of six low J transitions. They are given in Table 1. The dipole moment of allylsilane(0.526 D) is smaller and makes a larger angle with the SiC bond(36°) than those of the similar molecules such as ethylsilane(0.81 D, 1°18') and vinylsilane(0.662 D, 10°).5)

Table 1 Rotational Constants (MHz) and Dipole Moment (D)[a]

Species	State	A	δA[b]	B	δB[b]	C	δC[b]
CH_2=$CHCH_2SiH_3$	Ground	15744.81(26)	0.00	2773.12(13)	-0.13	2655.81(7)	-0.15
	Skeletal torsional	15729.64(53)		2791.97(26)		2663.99(15)	
	SiH_3 torsional	15860.65(23)		2759.87(11)		2646.74(6)	
CH_2=$CHCH_2SiD_3$	Ground	13365.33(17)	0.00	2568.72(8)	-0.03	2468.69(5)	-0.05

	$\|\mu_a\|$	$\|\mu_b\|$	$\|\mu_c\|$	$\|\mu_{total}\|$	$\alpha(\mu \times a)$[c]	$\alpha(\mu \times \overleftarrow{SiC})$[c]	$\alpha(\mu \times \overleftarrow{CH_2{=}CH})$[c]
CH_2=$CHCH_2SiH_3$	0.186(1)	0.489(6)	0.006(144)	0.526(22)	69°17'	36° 4'	79°16'
CH_2=$CHCH_2SiD_3$	0.183(9)	0.477(5)	0.030(60)	0.512(15)	69° 3'	36°30'	78°49'

a) Figures in parentheses indicate the uncertainties attached to the last significant figures calculated from 2.5 times the standard deviations.

b) $\delta R = 100 \times (R_{obsd} - R_{calctd})/R_{obsd}$, R = A, B, and C. R_{calctd} was calculated from the plausible structure.

c) $\alpha(\mu \times a)$, $\alpha(\mu \times \overleftarrow{SiC})$, and $\alpha(\mu \times \overleftarrow{CH_2{=}CH})$ indicate the angles of the dipole moment with the a-inertial axis, the SiC bond and the C=C bond, respectively.

For the normal species, at least two groups of weak spectra exist near the ground state spectra. One of them is stronger than the other and may be attributed to the spectra due to the first excited skeletal torsional state. The other group of the spectra exhibits doublet structures and hence can be attributed to the spectra due to the first excited silyl torsional state. Their rotational constants are given in Table 1. From the splittings of the spectra, the barrier to SiH_3 internal rotation was determined to be 2130 ± 70 cal/mol by the standard principal axis method.[6] The following parameters obtained from the plausible structure were used in the calculation; $I_\alpha = 5.868$ amu·Å^2, $\lambda_a = 0.8236$, $\lambda_b = 0.5526$ and $\lambda_c = 0.1281$. For ethylsilane, the SiH_3 barrier was reported to be 2043 cal/mol neglecting the coupling effect between the silyl and methyl groups. Then the barrier of allylsilane is slightly higher than that of ethylsilane, but is much higher than those of vinylsilane(1500 cal/mol) and methylsilane(1670 cal/mol)[7] and is much lower than that of chloromethylsilane ($ClCH_2SiH_3$, 2550 cal/mol).[8]

We are working on the other isotopic species of allylsilane in order to get more reliable structural parameters.

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