The Vibrational Spectra and Rotational Isomerism of Methylvinylsilane and Allylsilane[1]

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The infrared and Raman spectra have been measured for methylvinylsilane, CH_2=$CHSiH_2(-D_2)CH_3$, and allylsilane, CH_2=$CHCH_2SiH_3(-D_3)$. The fundamental vibrations have been assigned, and the normal coordinate treatment for possible molecular forms has been carried out. For methylvinylsilane, the *cis* and *skew* forms coexist in the gaseous and liquid states, while only the former persists in the solid state. In the liquid state the *cis* form is more stable by 0.66±0.05 kcal/mol than the *skew* form. For allylsilane, the form near the *skew* form predominantly exists in the gaseous, liquid, and solid states.

The ultraviolet absorption maximum of allyltrimethylsilane appears at a wavelength longer than that of trimethylvinylsilane.[2] Previously, the bathochromic effect of the allyl derivative has been commonly cited as evidence of (p-d)π bonding between the double bond and the silicon.[3] Recently, however, this effect has been interpreted in terms of σ-π hyperconjugation[4,5] between the double bond and the Si–C σ bond, whose magnitude may vary with the dihedral angle about the axis between the carbon atoms in the α- and β-positions in allylsilane.

In the present paper, we will, therefore, deal with the molecular vibrations of methylvinylsilane and allylsilane in relation to the rotational isomerism in order to obtain information on the stereospecific effect.

Experimental

The samples of methylvinylsilane, CH_2=$CHSiH_2(-D_2)$-CH_3, and allylsilane, CH_2=$CHCH_2SiH_3(-D_3)$, were prepared by the reduction of commercial products of dichloro(methyl)vinylsilane (K & K Co., U.S.A.) and allyltrichlorosilane (Aldrich Chem. Co., U.S.A.) with lithium aluminium hydride or deuteride in dibutyl ether[6] and were purified by low-temperature bulb-to-bulb distillation in a vacuum. Their purities were checked by means of their nuclear magnetic resonance spectra; CH_2=$CHSiH_2CH_3$ NMR(CCl_4): δ 0.21 (t, 3H, J=4 Hz, Si**C**$\mathbf{H_3}$), 3.94 (dq. 2H, J=1 and 4 Hz, Si**H**$_2$), 5.5—6.5 (m, 3H, **C**$\mathbf{H_2}$=**C**$\mathbf{H}$), CH_2=$CHSiD_2CH_3$ NMR (CCl_4): δ 0.21 (s, 3H, Si**C**$\mathbf{H_3}$), 5.5—6.5 (m, 3H, **C**$\mathbf{H_2}$=**C**$\mathbf{H}$), CH_2=$CHCH_2SiH_3$ NMR(CCl_4): δ 1.69 (sex, 2H, J=4 Hz, **C**$\mathbf{H_2}$Si), 3.53 (t, 3H, J=4 Hz, Si**H**$_3$), 4.8—6.2 (m, 3H, **C**$\mathbf{H_2}$=**C**$\mathbf{H}$), CH_2=$CHCH_2SiD_3$ NMR(CCl_4): δ 1.69 (d, 2H, J=8 Hz, **C**$\mathbf{H_2}$Si), 4.8—6.2 (m, 3H, **C**$\mathbf{H_2}$=**C**$\mathbf{H}$).

The infrared and Raman spectra were recorded on a Perkin-Elmer instrument (Model 621) and a JEOL Raman Spectrometer (Model JRS-400D) with an argon-ion laser respectively. The infrared spectra in the gaseous state were measured using a 10-cm gas cell fitted with CsI windows. The infrared spectra in the liquid state at low temperatures were measured at about 150 K by condensing the gaseous samples on a CsI window cooled with liquid nitrogen. For the Raman spectra in the solid state, the sample in the ampoule was held on a copper block cooled with liquid nitrogen; the solid was obtained by the use of a long period of cooling.

Results

Normal Coordinate Treatment. The normal vibrations were calculated in order to determine the molecular forms and the assignments of the observed spectra to rotational isomers. The valence angles of the CH_2=CH group and the bond lengths used were transferred from those of vinylsilane,[7] dimethylsilane,[8] and 1-butene.[9] The other valence angles were assumed to be tetrahedral, and the dihedral angles were 0° for the *cis* form and 120° for the *skew* form. The modified Urey-Bradley force field was used in the calculation. The force constants of the CH_2=CH group and those of the skeletal torsion were taken so as to predict well the observed frequencies of vinylsilane, CH_2=$CHSiH_3$

Table 1. Force constants for methylvinylsilane and allylsilane[a]

Force const		Force const	
K(C-H), =CH_2	4.651	F(H·C·H), =CH_2	0.0
K(C-H), =CH	4.472	F(C=·C·H)	0.450
K(C-H), CH_3	4.403	F(C·C·H)	0.540
K(C-H), CH_2	4.230	F(Si·C·H)	0.271
K(Si-H), SiH_3	2.578	F(H·Si·H)	0.041
K(Si-H), SiH_2	2.544	F(C·Si·H)	0.149
K(C=C)	7.071	F(C=·C·C)	0.400
K(C-C)	2.800	F(C·C·Si)	0.276
K(C-Si), =C-Si	2.655	F(C·Si·C)	0.040
K(C-Si)	1.991	f(=CH o. p.)	0.252
H(H-C-H), =CH_2	0.360	f(=CH_2 wag.)	0.324
H(H-C-H), CH_3	0.349	Y(C=C)	0.601
H(H-C-H), CH_2	0.331	Y(C-C)	0.088
H(C=C-H)	0.212	Y(C-SiH_3)	0.067
H(C-C-H), =CH	0.123	Y(Si-CH_3)	0.039
H(C-C-H), CH_2	0.278	Y(Si-CH)	0.056
H(Si-C-H), =CH, CH_2	0.123	κ(CH_3)	0.014
H(Si-C-H), CH_3	0.102	κ(CH_2)	−0.040
H(H-Si-H)	0.180	κ(SiH_3)	0.076
H(C-Si-H), =CH	0.123	κ(SiH_2)	0.104
H(C-Si-H), CH_3	0.092	p(C-H), CH_3	−0.084
H(C-Si-H), CH_2	0.094	p(C-H), CH_2	−0.070
H(C=C-C)	0.320	t(C=CH, C=CH)	0.089
H(C=C-Si)	0.090	t(C=CH, C=CY)	0.141
H(C-C-Si)	0.118	t(CSiH_2, SiCH_3)	0.057[b]
H(C-Si-C)	0.133	t(CSiC, SiCH_3)	0.030[b]
F(H·C·H)	0.200	t(CCSi, CSiH_3)	0.053[b]

a) The units of the force constants are mdyn/Å for stretching, K; bending, H; repulsion, F; bond interaction, p; and mdyn Å for out-of-plane bending, f; wagging, f; torsion, Y; intramolecular tension, κ, and *trans* coupling, t. b) The *gauche* coupling constants are assumed to be $g=-0.5\,t$.

TABLE 2. OBSERVED AND CALCULATED FREQUENCIES (cm^{-1}) OF METHYLVINYLSILANE-d_0[a)]

Infrared					Raman[b)]					Calcd			Assignment[c)]
Gas	Int.	Type	Liquid (≈150 K)	Int.	Liquid	Int.	ρ	Solid	Int.	C form		S form	
3064	m	AB(15)	3057	w	3057	vw	dp?	3054	vw	3052	A′	3052	$\nu_a(=CH_2)$
			3013	vvw									1592+1421
2977	m	AB(15)	2972	w	2981	vs	p	2977	vs	2984	A′	2984	$\nu(=CH)$
					2971 sh	vw	p	2974	vs	2964	A″	2964	$\nu_a(CH_3)$
										2964	A′	2964	$\nu_a(CH_3)$
			2951	vw	2953	s	p	2954	vvw	2953	A′	2953	$\nu_s(=CH_2)$
2927	vw							2947	vvw				
2916	vw		2911	vvw	2913	vvw		2907	vw	2900	A′	2900	$\nu_s(CH_3)$
2155	vs				2142	vvs	p	2141		2181	A″	2181	$\nu_a(SiH_2)$
2146	vvs		2138	vs				2133	vvs	2180	A′	2180	$\nu_s(SiH_2)$
								2127					
1920 b	vw		1915	vvw									950×2
1596	vw	AB(15)	1592	vw	1595	vs	p	1595	s	1603	A′	1601	$\nu(C=C)$, $s(=CH_2)$
			1421	vw	1426 sh	vw		1426	vw	1413	A′	1413	$\delta_a(CH_3)$
										1413	A″	1413	$\delta_a(CH_3)$
1408	m	AB(14)	1402	m	1406	m	p	1405	m	1383	A′	1382	$s(=CH_2)$
					1273	s	p	1273	m	1264	A′	1264	$\delta(=CH$ i. p.)
1258	m	AB(14)	1249	m	1255	w	p	1256	vw	1254	A′	1254	$\delta_s(CH_3)$
1012	m	AB(14)	1008	m	1014	vw		1012	vw	1014	A′	1013	$r(=CH_2)$, $\delta(=CH$ i. p.)
								1008	vw	1008	A″	1008	$t(=CH_2)$, $w(=CH_2)$
954	s	AB(20)	950	s	953	w	dp?	955	vs	959	A′	958	$s(SiH_2)$
951	vs		939	s	944 sh	w		942 sh	vw	952	A″	952	$w(=CH_2)$, $t(=CH_2)$
902	vvs	AB(14)	897 sh	vvs	898 b	vw	dp?	893	vw	884	A′	885	$w(SiH_2)$, $r_s(CH_3)$
			886	vvs									
								869 sh	vw				
			864	m	866	vw	dp	865	w	841	A″	840	$r_a(CH_3)$
756	s	AB(14)	751	s	753	w	p	753	m	768	A′	774	$r_s(CH_3)$, $w(SiH_2)$
								731	w				
728	s	C	725	m	726	w	dp?	729	w	721	A′	725	ν(Me-Si), ν(C-Si)
700 sh	w		702	w	700	vs	p	702	vs	704	A″	692	$t(SiH_2)$
629	w	AB(14)	633	w	632	vvs	p	640	vvs	655	A′	662	ν(C-Si), ν(Me-Si)
			527	vw	535 sh	vw		534	w	549	A″		$r(SiH_2)$, $\delta(=CH$ o. p.)
								527	w				
517 b	w		516	vw	522	vw	dp	—				527	$r(SiH_2)$, $\delta(=CH$ o. p.)
477 sh	vw		479	vvw	474	vw		—				499	$\delta(=CH$ o. p.), $r(SiH_2)$
			406	vvw	405	vvw	dp	411	w	462	A″		$\delta(=CH$ o. p.), $r(SiH_2)$
356	vvw	AB(15)	357	vw	357	vw		360	w	330	A′		δ(CCSi), δ(CSiC)
					297	w	p	—				279	δ(CCSi)
					205*	m		—				214	δ(CSiC)
					185	m		176	m	157	A′		δ(CSiC), δ(CCSi)
								145	vw	152	A″	145	τ(Si-Me)
					112*sh	w		118	vs	107	A″	92	τ(C-Si)
								90	m				lattice vibrations
								81	m				
								63	vs				
								57	vs				
								45	vs				
								25	vs				

a) Int.=intensity, s, m, w=strong, medium, weak, v=very, b=broad, sh=shoulder; AB, B, C=*ab*-, *b*-, *c*-type infrared band contours in the asymmetric top case (the values in parentheses indicate the P-R spacing); ρ=polarization, p, dp=polarized, depolarized; C, S=*cis*, *skew*; A′,A″=A′,A″ species of the C_s symmetry. b) Asterisks indicate the Raman lines observed at low temperatures (≈150 K). c) Assignments based on the potential-energy distributions greater than 20% are included; *v*, *s*, *w*, *t*, *r*, δ, τ=stretching, scissoring, wagging, twisting, rocking, deformation, torsion, i.p.=in-plane, o.p.=out-of-plane, a, s=asymmetric, symmetric.

Table 3. Observed and calculated frequencies (cm^{-1}) of methylvinylsilane-d_2[a)]

Infrared					Raman[b)]					Calcd			Assignment[c)]
Gas	Int.	Type	Liquid (≈150 K)	Int.	Liquid	Int.	ρ	Solid	Int.	C form		S form	
3065	m	AB(13)	3056	w	3058	vw	dp?	3052	w	3052	A′	3052	$\nu_a(=CH_2)$
			3013	vw									1593+1413
2977	m	AB(13)			2979	m	p	2975	vs	2984	A′	2984	$\nu(=CH)$
			2969	w				2963 sh	m	2964	A″	2964	$\nu_a(CH_3)$
										2964	A′	2964	$\nu_a(CH_3)$
2928	vw		2949	w	2950	vw	p	2945	vw	2953	A′	2954	$\nu_s(=CH_2)$
2918	vw		2908	vw	2911	m	p	2904	s	2900	A′	2900	$\nu_s(CH_3)$
1916 b	vw		1915	vvw									955×2
			1593	w	1594	vs	p	1593	m	1603	A′	1602	$\nu(C=C)$, $s(=CH_2)$
1570	vvs		1562	vvs				1567 sh	s	1576	A″	1576	$\nu_a(SiD_2)$
1560	vvs		1552 1543 sh	vvs vvs	1552 1545 sh	vvs m	p	1558 1548 sh	vvs s	1559	A′	1559	$\nu_s(SiD_2)$
1411	m		1413 sh	w	1414 sh	vw		1414 sh	w	1413	A′	1413	$\delta_a(CH_3)$
										1413	A″	1412	$\delta_a(CH_3)$
1404	m		1403	m	1404	w	p	1405	m	1383	A′	1382	$s(=CH_2)$
								1266 sh	w				
1264	m		1264 sh	vvw	1269	m	p	1262	m	1264	A′	1264	$\delta(=CH$ i. p.)
1255	m	AB(12)	1248	m	1253	w	p	1244	vw	1254	A′	1254	$\delta_s(CH_3)$
								1021	vvw	1013	A′	1012	$r(=CH_2)$, $\delta(=CH$ i. p.)
1009	m	C	1005	m	1008	vw	dp?	1008	w	1007	A″	1007	$t(=CH_2)$, $w(=CH_2)$
955	m	C	955	s	960	vvw	dp	961	w	952	A″	952	**$w(=CH_2)$**, $t(=CH_2)$
812	vvs	AB(12)	805	vvs	814	vvw	p	814	vvw	823	A′	823	$r_s(CH_3)$
										815	A″	815	$r_a(CH_3)$
741	vvs	AB(13)	746	s	745 sh	w		746	m	742	A′		ν(Me-Si), ν(C-Si)
			731	s	732	s	p	—				738	ν(Me-Si)
703 b 688 b	vs vs		689	vs	695	m	p	697 689	m m	706	A′	709	$s(SiD_2)$
			645	w	647	vvs	p	—				648	ν(C-Si), $s(SiD_2)$
			635	vw	637	vs	p	636	vvs	637	A′		ν(C-Si), ν(Me-Si), $s(SiD_2)$
618 b 607 b	s s		609	s	617	w	p	610	vw	587	A′	599	$w(SiD_2)$
557 b	m		563	m	569	w		567	m	565	A″		$\delta(=CH$ o. p.), $t(SiD_2)$
			550	m	556	w		—				536	$\delta(=CH$ o. p.), $t(SiD_2)$
			455	vw	455	m	dp	—				482	$t(SiD_2)$, $\delta(=CH$ o. p.)
443 b	w		439	vw	442 sh	w		444	m	473	A″		$t(SiD_2)$, $\delta(=CH$ o. p.)
			413	vw	415*	w		—				412	$r(SiD_2)$
			361	vw				367	vw	386	A″		$r(SiD_2)$
355 b	vvw		347	vw	353	vw		344	m	327	A′		δ(CCSi), δ(CSiC)
					268	m		—				267	δ(CCSi)
					198*	s		—				212	δ(CSiC)
					186	s		189	m	157	A′		δ(CSiC), δ(CCSi)
										150	A″	144	τ(Me-Si)
					103*	w		129	m	104	A″	91	τ(C-Si)
								100	vs				lattice vibrations
								86	s				
								69	s				
								62	s				
								38	m				

a), b), and c): See Footnotes a), b), and c) of Table 2.

($-D_3$),[10] and those of methylvinylsilane and allylsilane respectively. The other force constants were transferred from those of alkylsilanes[11] and olefins.[12] The force constants used are listed in Table 1. The observed and calculated frequencies are summarized in Tables 2—5, together with the assignments based on the predominant potential-energy distributions. As a fair agreement was obtained between the observed and calculated frequencies, further adjustment was not attempted. The vibrational assignments based on the

TABLE 4. OBSERVED AND CALCULATED FREQUENCIES (cm^{-1}) OF ALLYLSILANE-d_0[a)]

Infrared					Raman[b)]					Calcd S form	Assignment[c)]
Gas	Int.	Type	Liquid (≈150 K)	Int.	Liquid	Int.	ρ	Solid	Int.		
3093	vw	AB(14)	3080	vw	3083	vw	dp?	3083	w	3053	$\nu_a(=CH_2)$
			3063	vw							1632+1418
			3036	vvw							1632+1392
3001	vw		2997	vw	3000	m	p	2998	m	3029	$\nu(=CH)$
2987	vw		2975	vw	2977	vw	p	2975	vw	2955	$\nu_s(=CH_2)$
2939	vw		2932	vw	2931	vw		2931	m	2946	$\nu_a(CH_2)$
2915	vw				2912 sh	vw		2907 sh	vw		
2902	vw		2896	vw	2897	m	p	2897	vs	2913	$\nu_s(CH_2)$
					2835	vvw		2839	vvw		1422×2
								2168		2174	$\nu_a(SiH_3)$
2167	vvs	AB(15)	2157	vs	2160	vvs	p	2156	vvs	2174	$\nu_a(SiH_3)$
								2148		2172	$\nu_s(SiH_3)$
1814	vvw	B (14)	1804	vvw							906×2
1636	w	AB(14)	1632	m	1632	vs	p	1631	s	1627	$\nu(C=C)$, $s(=CH_2)$
								1426 sh	vw		
1426	vw	AB(16)	1418	w	1422	w	p	1423	vw	1416	$s(CH_2)$
1397 sh	vw		1394	vw	1400	w	p	1401	w	1404	$s(=CH_2)$
								1301 sh	w		
1300	vvw	AB(16)	1295	vvw	1299	vs	p	1295	m	1303	$\delta(=CH$ i. p.)
1195	vw	AB(15)	1192	vw	1192	w		1196	w	1223	$t(CH_2)$
1163	w	AB(14)	1157	w	1161	vs	p	1159	vs	1175	$w(CH_2)$, $s(CH_2)$
1039	vw	AB(14)	1041	vw	1043	vw		1039	vw	1108	$r(=CH_2)$, $\nu(C-C)$
995 sh	vw		990	w	989 sh	vw	dp?	991	vw	999	$t(=CH_2)$
979 sh	w									968	$w(=CH_2)$
			942 sh	s	941	m	dp?	949	vs	949	$\delta_a(SiH_3)$
931 b	vvs		936 sh	s				935	m	949	$\delta_a(SiH_3)$
923 b	vvs		928	vs				928	m	917	$\delta_s(SiH_3)$
			909	vvs	904	vw	dp?	909	vw	906	$\nu(C-C)$, $r(=CH_2)$
								901	w		
834	m	AB(12)	829	s	829	vvw	dp?	828	vvw	769	$r(CH_2)$, $t(CH_2)$
772	vw							772 sh	vw		
767	vw		764	m	765	s	p	763	m	733	$\nu(C-Si)$
			597 sh	m	599	vs	p	602	vs	589	$r_s(SiH_3)$
589	m	AB(14)	588	s	590 sh	m	p	589	w	582	$r_a(SiH_3)$
527 b	vvw		524	vw	529	vw	dp?	530	w	521	$\delta(=CH$ o. p.)
407	vvw	AB(15)	407	vw	408	s	p	415	m	402	$\delta(CCC)$
					227	vw	dp?	237	vw	239	$\delta(CCSi)$
								228 sh	vvw		
										147	$\tau(C-SiH_3)$
					112*	w		137	m	112	$\tau(C-C)$
								98	s		
								91	s		
								71	vs		
								58	vs		lattice vibrations
								44	vs		
								37	vs		
								31	vs		

a), b), and c): See Footnotes a), b), and c) of Table 2.

relative intensities of the infrared bands and the Raman lines and the comparison with the spectra of analogous molecules[10,11,15] are consistent with the results of the calculation, except for the assignments of the SiH_2 twisting and Me–Si stretching modes for methylvinylsilane-d_0 and those of the CH_2 wagging and twisting modes for allylsilane-d_0 and -d_3.

Rotational Isomerism. Figures 1 and 2 show the Raman spectra of methylvinylsilane-d_0 and allylsilane-d_0 in the region below 1700 cm^{-1}; the upper and lower spectra are for the liquid state at room temperature and for the solid state at about 100 K respectively. For 1-butene[9] and methylvinylsilane,[13] the stable conformations have been confirmed by means of the microwave spectra to be *cis* and *skew* about the C–C or C–Si axes adjacent to the double bond. For methylvinyl-

Table 5. Observed and calculated frequencies (cm^{-1}) of allylsilane-d_3[a)]

Infrared					Raman[b)]					Calcd	Assignment[c)]
Gas	Int.	Type	Liquid (≈150 K)	Int.	Liquid	Int.	ρ	Solid	Int.	S form	
3092	vw	AB(13)	3081	w	3084	vw	dp?	3077	w	3053	$\nu_a(=CH_2)$
			3064	vw							1632+1417
			3033	vvw							1632+1392
3003	vw		3005	vw	3003	m	p	3006	w	3029	$\nu(=CH)$
					2997 sh	w		2993 sh	vw		
2986	vw		2976	w	2978	vw	p	2975	vw	2955	$\nu_s(=CH_2)$
2935	vw		2936	vw	2932	vw	dp	2937	w	2946	$\nu_a(CH_2)$
2913	vw				2911 sh	vw		2910	vw		
2901	vw		2901	vw	2898	m	p	2900	m	2913	$\nu_s(CH_2)$
					2834	vvw		2833	vvw		
1811	vvw	B (13)	1810	vvw							900×2
1636	m	AB(14)	1632	m	1632	vvs	p	1631	vs	1627	$\nu(C=C)$, $s(=CH_2)$
								1579 sh	m		
1579	vvs	AB(13)	1574	vs	1574	s	dp?	1573	vs	1572	$\nu_a(SiD_3)$
								1568	vs	1572	$\nu_a(SiD_3)$
1558	vvs	AB(14)	1551	vs	1554	vvs	p	1550	vvs	1545	$\nu_s(SiD_3)$
								1422 sh	vvw		
1425	vw	AB(15)	1417	w	1419	w		1417	vw	1416	$s(CH_2)$
1403	vw	AB(12)	1392	w	1397	w		1399 sh	vw	1404	$s(=CH_2)$
								1395	w		
					1310	vvw		1302	vw		
1300	vvw	AB(15)	1293	vvw	1300	vs	p	1298	s	1303	$\delta(=CH$ i. p.)
1194	vvw	AB(12)	1190	w	1191	vw	dp?	1196 sh	vw	1223	$t(CH_2)$
								1191	w		
1167	w	AB(14)	1165	w	1167	s	p	1166	w		677+479, 750+404
			1151	w	1155 sh	m	p	1151	vs	1175	$w(CH_2)$, $s(CH_2)$
1036	vw	AB(13)	1037	w	1040	vvw	p	1039	vvw	1107	$r(=CH_2)$, $\nu(C-C)$
990	vw	AB(11)	990	m	990	vw	dp?	994	vw	999	$t(=CH_2)$
930	w	AB(13)	928	w	926	w		929	vw	968	$w(=CH_2)$
906	s	B (10)	900	s	903	w	dp?	908	w	904	$\nu(C-C)$, $r(=CH_2)$
786 b	m		792	s	788 sh	vw	dp?	790	vw	764	$r(CH_2)$, $t(CH_2)$
755	m	AB(14)	752	s	750	vs	p	752	vs	744	$\nu(C-Si)$, $\delta_s(SiD_3)$
684	vs		677 sh	vs	678	m	dp?	687	w	681	$\delta_a(SiD_3)$
								680	w		
679	vs		669	vvs				674	w	680	$\delta_a(SiD_3)$
								668	w		
580	vvw	AB(12)	579	w	579	vs	p	583	s	657	$\delta_s(SiD_3)$
					493 sh	vw		494	vvw	523	$\delta(=CH$ o. p.)
482 b	vvw		479	m	478	vw	dp?	483	w	454	$r_s(SiD_3)$
								479 sh	w		
422	vvw	AB(12)	416	w	416 sh	vw	dp?	422	vw	445	$r_a(SiD_3)$
410	vvw		405 sh	vw	403	s	p	410	s	393	$\delta(CCC)$
					213	vw	dp?	233	vvw	227	$\delta(CCSi)$
								225 sh	vw		
										112	$\tau(C-SiD_3)$, $\tau(C-C)$
					100*	w		124	m	108	$\tau(C-C)$, $\tau(C-SiD_3)$
								114 sh	w		lattice vibrations
								87	m		
								82 sh	m		
								75 sh	m		
								55	vs		
								40	m		
								30	s		

a), b), and c): See Footnotes a), b), and c) of Table 2.

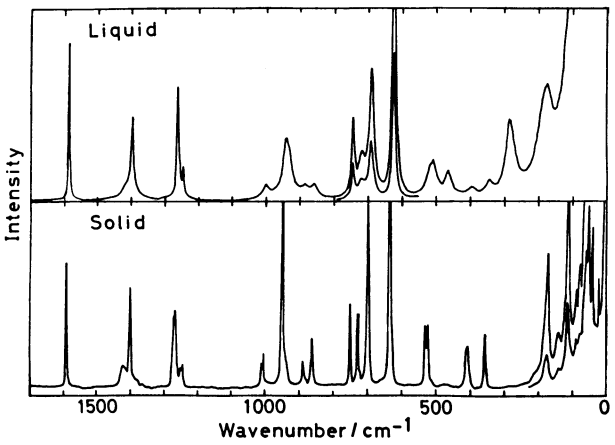

Fig. 1. Raman spectra of methylvinylsilane-d_0.

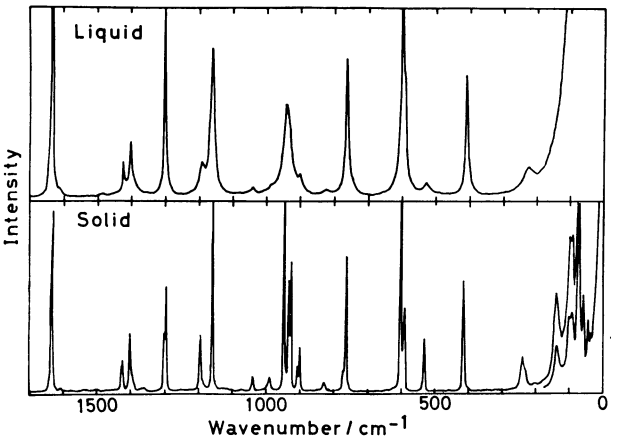

Fig. 2. Raman spectra of allylsilane-d_0.

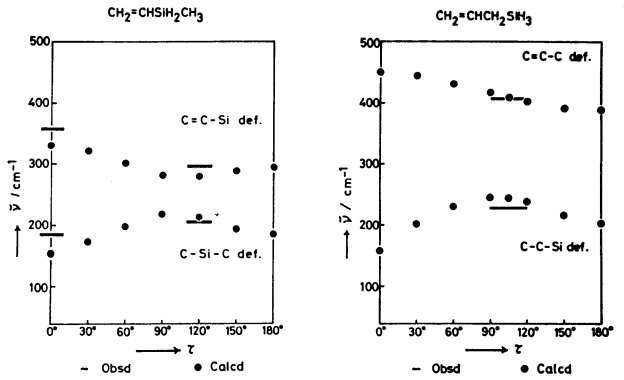

Fig. 3. Dependence of skeletal deformation frequencies on dihedral angle for methylvinylsilane-d_0 and allylsilane-d_0.

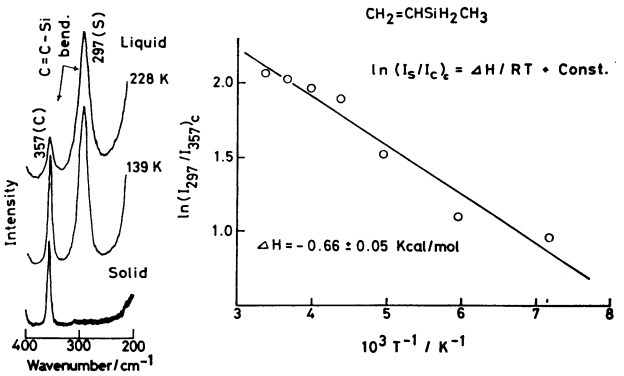

Fig. 4. Raman spectra of methylvinylsilane-d_0 in the 200—400 cm^{-1} region and a plot of $\ln(I_{297}/I_{357})_c$ *vs.* $1/T$.

silane, several Raman lines observed in the liquid state vanish in the solid state, but for allylsilane all the Raman lines observed in the liquid state remain in the solid state. On the other hand, all the vibrational frequencies observed in the solid state for methylvinylsilane and allylsilane are assigned to the fundamental vibrations of one isomer, as Tables 2—5 show. In the 150—450 cm^{-1} region for both the molecules, two skeletal deformation and one torsional vibrations are expected for one isomer; the CH_3 and SiH_3 torsional vibrations may, in general, be very weak in the Raman scattering. For methylvinylsilane-d_0, four Raman lines —at 357, 297, 205, and 185 cm^{-1}—are observed in the liquid state, and two of them remain in the solid state, indicating that two isomers coexist in the liquid state and that one of them persists in the solid state. For allylsilane-d_0, two Raman lines—at 408 and 227 cm^{-1}—are observed in both the liquid and solid states, indicating the existence of only one isomer in both the liquid and solid states. The same results are obtained from methylvinylsilane-d_2 and allylsilane-d_3.

In order to determine the molecular forms, the normal coordinate treatment was carried out for seven possible molecular forms of methylvinylsilane-d_0 and allylsilane-d_0. Figure 3 shows the observed and calculated frequencies of the skeletal deformations. The calculations indicate that, for methylvinylsilane-d_0, *cis* and *skew* forms coexist in the liquid state, while only the *cis* form persists in the solid state, and that for allylsilane-d_0 only the molecular form near the *skew* form exists in both the liquid and solid states.

Enthalpy Difference of the Isomers in Methylvinylsilane. The relative intensities of the Raman lines at 297 and 357 cm^{-1} assigned to the C=C–Si deformation vibrations for the *skew* and *cis* forms of methylvinylsilane-d_0 respectively were measured in the liquid state at temperatures ranging from 297 to 139 K. In the solid state the band at 297 cm^{-1} disappears, but that at 357 cm^{-1} persists. Figure 4 shows some typical examples at 228 and 139 K among seven different temperatures and a plot of $\ln(I_s/I_c)[(1-e^{-h\nu_s/kT})/(1-e^{-h\nu_c/kT})]$ against $1/T$. From the slope of the straight line, the value of the enthalpy difference, $\Delta H(H_{skew}-H_{cis})=0.66\pm0.05$ kcal/mol, is obtained.

Discussion

For allylsilane, the form near the *skew* form is determined on the basis of the normal coordinate treatment to exist predominantly in the liquid and solid states. This result is also supported by the infrared spectra in the gaseous state; no *c*-type bands for the *cis* form were observed, and all the bands were assigned to the fundamental vibrations of only one isomer. On the other hand, for methylvinylsilane, the *cis* and *skew* forms are confirmed to coexist in the gaseous and liquid states; the *cis* form is more stable than the *skew* form by 0.66

±0.05 kcal/mol in the liquid state. For 1-butene, the *skew* form has been reported to be more stable than the *cis* form by only 150±150 cal/mol (from the analysis of microwave spectra[9]) and by −100±50 cal/mol (from the NMR spectra[14]). For allyl halides (X= Cl, Br, I), the *cis* and *skew* forms have been confirmed to coexist in the liquid state, although a larger steric repulsion between the CH_2=CH group and halogen is to be expected.[15]

Recently, Weidner and Schweig have demonstrated, from the photoelectron spectra and CNDO/2 calculations, the importance of σ-π hyperconjugation in trimethylvinylsilane and allyltrimethylsilane.[5] CNDO/2 model calculations have indicated that allyltrimethylsilane has a conformation near the *skew* form as a result of the σ-π hyperconjugation between the Si–C σ bond and the double bond. Thus, the present result on allylsilane is consistent with the conformation of allyltrimethylsilane. Therefore, the form near the *skew* of allylsilane may have a dihedral angle between the 120° of the ordinary *skew* form and the 90° of the maximal σ-π interaction. Actually, Hayashi *et al.* have, from the microwave spectra, reported an estimated dihedral angle of 103°40′ for allylsilane.[16]

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