Journal of Organometallic Chemistry, 226 (1982) 11—19
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

DIRECT SPECTROSCOPIC STUDY OF SILAOLEFINS, Ar-MATRIX STABILIZATION AND IR SPECTRUM OF 1,1-DIMETHYL-1-SILAETHYLENE-d_3

A.K. MALTSEV *, V.N. KHABASHESKU and O.M. NEFEDOV

Institute of Organic Chemistry, Academy of Sciences of the U.S.S.R., Leninsky Prospect 47, Moscow 117913 (U.S.S.R.)

(Received August 20th, 1981)

Summary

The IR spectrum of 1-methyl, 1-trideuteromethyl-1-silaethylene, $CH_3(CD_3)$-$Si{=}CH_2$, formed in the gas phase by vacuum pyrolysis of the corresponding monosilacyclobutane has been recorded in an argon matrix at 10 K. The attribution of the spectral bands to the unstable species was carried out using the dependence of the spectra on temperature and pressure in the pyrolysis zone or on the matrix temperature. A possible assignment of some bands to the ν(Si=C) and $\rho(CH_2)$ vibrations is discussed.

Introduction

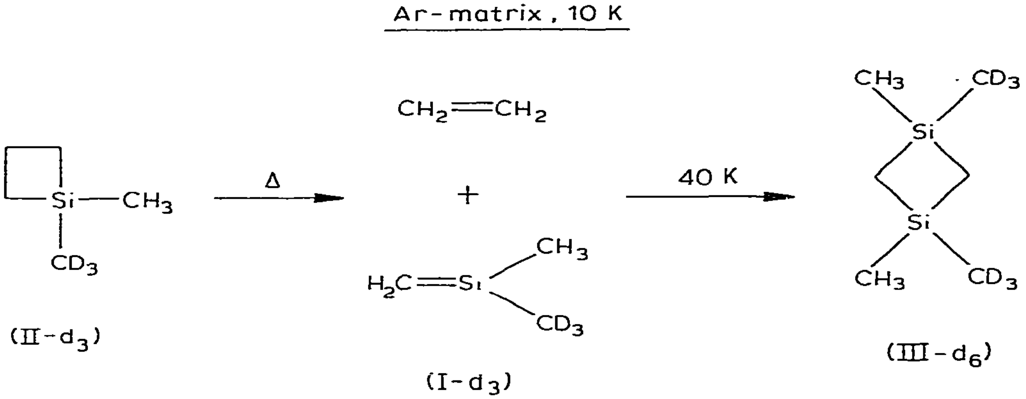
1,1-Dimethyl-1-silaethylene (I) is the first molecule with an unsaturated carbon—silicon bond whose existence has been proved by physical methods: at first for I-d_0 from the infrared spectrum in an inert matrix at 10 K [1,2] and then with mass spectrometry [3] and electron diffraction [4] techniques. The matrix IR spectra of the deuterated derivative $(CD_3)_2Si{=}CH_2$ (I-d_6) were obtained later, simultaneously and independently by us [5—9] and by Gusel'nikov et al. [10—13]. Besides, Auner and Grobe have claimed IR-spectroscopic detection of I-d_0 without a use of an inert matrix at 80 K [14].

The reported vibration frequencies of the I-d_0 and I-d_6 molecules differ substantially in the publications of the three-above-mentioned research groups. In this connection the present study was started to obtain additional information on the vibrational spectrum of I, including frequency shifts due to deuteration for the $CH_3(CD_3)Si{=}CH_2$ (I-d_3) molecule. Another goal was a thorough comparison of all vibrational data for I-d_0 and I-d_6; this problem is of great importance for correct assignment of the frequencies to the normal vibration modes of the molecule I.

Vacuum pyrolysis (10^{-2}—10^{-4} Torr, 650—1000°C) of 1,1-dimethyl-1-sila-

0022-328X/82/0000—0000/$02.75

cyclobutane (II-d_3) was chosen as a source of the I-d_3 species (by analogy with the pyrolysis of II-d_0 [15]), the final products of the reaction being C_2H_4 and 1,1,3,3-tetramethyl-1,3-disilacyclobutane-d_6 (III-d_6). The IR spectrum of the intermediate I-d_3 thus formed may be obtained by its isolation in an Ar-matrix at 10—15 K. A similar technique was used earlier by us to stabilize and investigate I-d_0 and I-d_6 silaolefins [2,9]. Preliminary results of the study were published previously [8].



(II-d_3)

(I-d_3)

(III-d_6)

Experimental

The parent compound II-d_3 was prepared by reaction of CD_3MgI with 1-methyl, 1-chloro-1-silacyclobutane which was synthesized by cyclization of

TABLE 1

THE MASS SPECTRUM OF THE STARTING COMPOUND II-d_3

m/e	Ion type assumed	Relative intensity [a]
105		1.5
104	M^+	2.4
103		16.4
88	$[M-CH_3]^+$	4.5
85	$[M-CD_3]^+$	2.0
77	$[105-C_2H_4]^+$	6.7
76	$[104-C_2H_4]^+$; $[103-C_2H_3]^+$	13.5
75	$[103-C_2H_4]^+$	100.0
74	$[M-29]^+$	5.4
73	$[M-30]^+$	2.9
64	$[M-C_3H_3]^+$	7.7
63	$[M-C_3H_4]^+$	4.8
62	$[M-CH_3-C_2H_2]^+$	19.2
61	$[M-CH_3-C_2HD]^+$	7.7
48	$CSiH_2D_3^+$	7.8
47	$CSiHD_3^+$	19.0
46	$CSiH_2D_2^+$; $CSiD_3^+$	26.7
45	$CSiH_3D^+$; $CSiHD_2^+$	22.2
44	$CSiH_4^+$; $CSiH_2D^+$	19.0
43	$CSiH_3^+$	22.2

[a] The mass spectrum was obtained at an ionizing energy of 70 eV on an Varian MAT CH-6 instrument.

γ-chloropropylmethyldichlorosilane in the presence of Mg. The formal dimer of I-d_3 — disilacyclobutane, III-d_6 — was singled out from the final products of pyrolysis of II-d_3. All the samples were purified by preparative GLC and then by bulb-to-bulb vacuum distillation. Their purity was determined from the GC-MS data to be higher than 99%. The mass spectrum of II-d_3 is given in Table 1.

The pyrolytic products of II-d_3 were trapped at 10 K together with an excess of argon (1000—5000 : 1) on a CsI optical window cooled by a continuous flow of liquid helium. The IR spectra were recorded on a Hitachi-Perkin-Elmer 225 spectrophotometer, wavenumber accuracy being ±0.2 cm^{-1}. Annealing of the matrix and the trapped pyrolysis products was performed by a steady change in a coolant flow. As a result, the temperature of the cold window rose from 10 up to 35—40 K followed by recooling down to 10 K and recording a new IR spectrum.

Results and discussion

The matrix IR spectra of the parent compound II-d_3 (Fig. 1a), those of the final dimeric product III-d_6 (Fig. 1d) and the pyrolysis products of II-d_3 (Fig. 1b) were recorded in the course of the current work. The corresponding wavenumber values are given in Table 2.

The IR spectrum of $CH_3(CD_3)Si{=}CH_2$ (I-d_3)

In the spectrum of the products of the pyrolysis (840°C) one can observe the bands of ethylene and the dimer III-d_6 and those of the initial compound II-d_3, partially converted. The very weak bands belong to the following molecules: CH_4 (1304.5 cm^{-1}), C_2H_2 (736.2 cm^{-1}), C_2HD (682.0 and 518.0 cm^{-1}) and C_2D_2 (541.3 cm^{-1}) [9,16]. The well-known double band of CO_2 at 661.7—663.2 cm^{-1} may also be seen in the matrix spectra.

In addition, we have discovered the bands at 606.0, 755.2, 817.5, 975.5, 1016.5, 1025.0, 1259.5 cm^{-1} and three weaker shoulder-type bands at 749.0, 1003.0 and 1006.0 cm^{-1} in this spectrum (Fig. 1b). All these new features do not belong to the molecules mentioned above.

A steady heating of a matrix up to the diffusion temperatures is often used to distinguish the bands belonging to the unstable intermediates. Earlier, this way the I-d_0 and I-d_6 species were found to form the dimers (corresponding to 1,3-disilacyclobutanes) under the diffusion conditions [9]. The present experiments have demonstrated a synchronous decrease in intensity for seven spectral bands (at 606.0, 755.2, 817.5, 975.5, 1016.5, 1025.0 and 1259.5 cm^{-1}) during the matrix warming from 10 to 35—40 K. Simultaneously, the bands (at 591.0, 674.0, 770.6, 814.9, 841.3, 861.0, 934.6 and 998.5 cm^{-1}) of the compound III-d_6 (the dimer of I-d_3) grew (Fig. 1c). On the other hand, the features at 749.0, 1003.0 and 1006.0 cm^{-1} did not disappear when the matrix was heated.

To verify the assignment of the indicated bands to an unstable species we have studied the effect of pressure and/or temperature changes in the pyrolysis zone on a matrix IR spectrum of the pyrolysis products. The rise in pressure (that is the increased number of the intermolecular collisions) should favour

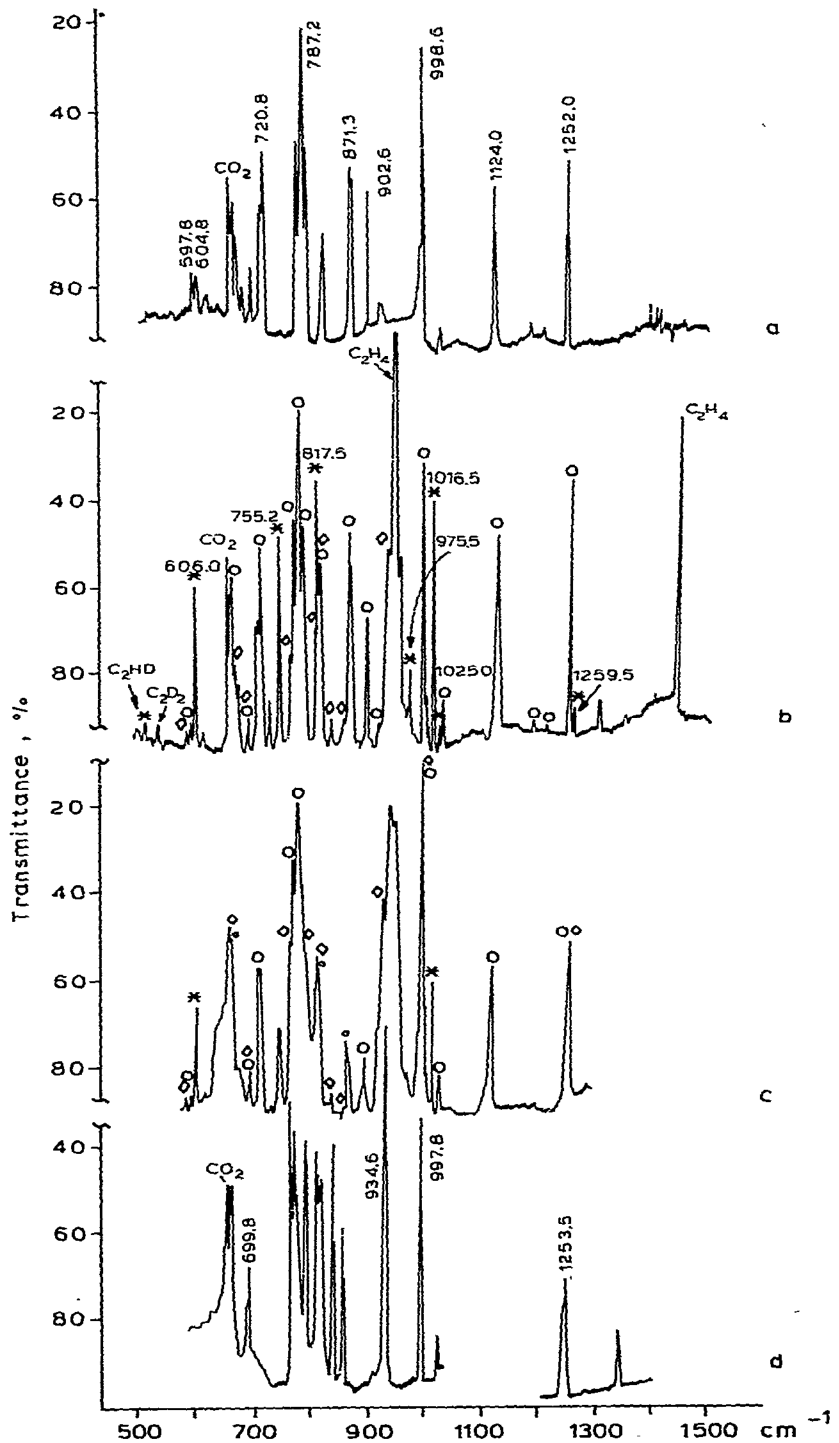


Fig. 1. a) The IR spectrum of II-d_3 in an Ar matrix at 10 K. b) The IR spectrum of the pyrolysis products of II-d_3 (840°C, 5 × 10^{-3} Torr) in an Ar matrix at 10 K. c) The same after warming the matrix up to 35 K and recooling to 10 K. d) The IR spectrum of the cyclodimer III-d_6 in an Ar matrix at 10 K. Here and in Fig. 2: *, I-d_3; ○, II-d_3; ◇, III-d_6.

TABLE 2

THE SPECTRAL BANDS (cm^{-1}) OF THE SILACYCLOBUTANE II-d_3, ITS PYROLYSIS PRODUCTS AND 1,3-DISILACYCLOBUTANE III-d_6 IN AN Ar MATRIX AT 10 K

II-d_3	III-d_6	Pyrolysis products of II-d_3		Assignment
		840°C	970°C	
1460.0				
1444.0				
		1440.0	1440.0	C_2H_4
1418.0				
1411.0				
1398.0		1398.0		II-d_3
	1348.0			
		1304.5	1304.5	CH_4
		1259.5		I-d_3
	1253.5			
1252.0		1252.0	1252.0	II-d_3
1249.0	1249.0			
1215.0		1215.0		II-d_3
1189.0				
1124.0		1124.5	1124.0	II-d_3
	1030.0	1030.0	1030.0	II-d_3 + III-d_6
1029.0				
		1025.0		I-d_3
		1016.5	1016.5	I-d_3
		1006.0	1006.0	?
		1003.0	1003.0	?
998.6		998.5	998.0	II-d_3 + III-d_6
	997.8			
993.5				
989.0				
		975.5		I-d_3
		958.0	957.0	C_2H_4
		946.7	946.5	C_2H_4
	937.5			
	934.6	934.6		III-d_6
924.0				
920.8		920.8		II-d_3
902.0		901.8	901.6	II-d_3
873.6				
871.3		871.2	871.2	II-d_3
	860.9	861.0		III-d_6
	841.9	841.3		III-d_6
	824.7			
824.1		824.2	824.0	II-d_3 + III-d_6
	820.6			
		817.5	817.0	I-d_3
	814.4	814.9		III-d_6
	797.5			
		796.0		II-d_3 + III-d_6
795.2				
787.2		787.0		II-d_3
	779.0			
778.0		777.5	777.0	II-d_3
	770.6	770.6		III-d_6
		755.2		I-d_3
		749.0	749.0	?
		736.2	735.8	C_2H_2
720.8		720.5	720.3	II-d_3
716.0		716.5		II-d_3

TABLE 2 (continued)

II-d_3	III-d_6	Pyrolysis of II-d_3		Assignment
		840°C	970°C	
713.0		713.2		II-d_3
	699.8			
699.1		698.6		II-d_3 + III-d_6
683.2				
		682.0	682.8	C_2HD + II-d_3
	674.0	674.8		III-d_6
	671.0			
670.5		670.3	670.0	II-d_3
666.3		666.4		II-d_3
663.1	663.2	663.0		CO_2
661.7	661.7			CO_2
	656.0			III-d_6
620.6		621.0		II-d_3
		606.0		I-d_3
604.8				
597.8		597.5		II-d_3
	591.0	591.0		III-d_6
		541.3	541.0	C_2D_2
		518.0	518.0	C_2HD

secondary reactions of intermediates in the gas phase. Indeed, the intensities of seven IR bands were significantly lower at pyrolysis pressure of 10^{-1}—1 Torr whereas the intensities of the dimer III-d_6 bands increased considerably. This allows us to assign the seven bands mentioned to silaethylene, $CH_3(CD_3)Si{=}CH_2$ (I-d_3), which reacts with an environment (the parent compound or another I-d_3 species) to form the dimer I-d_6, just as during the matrix warming.

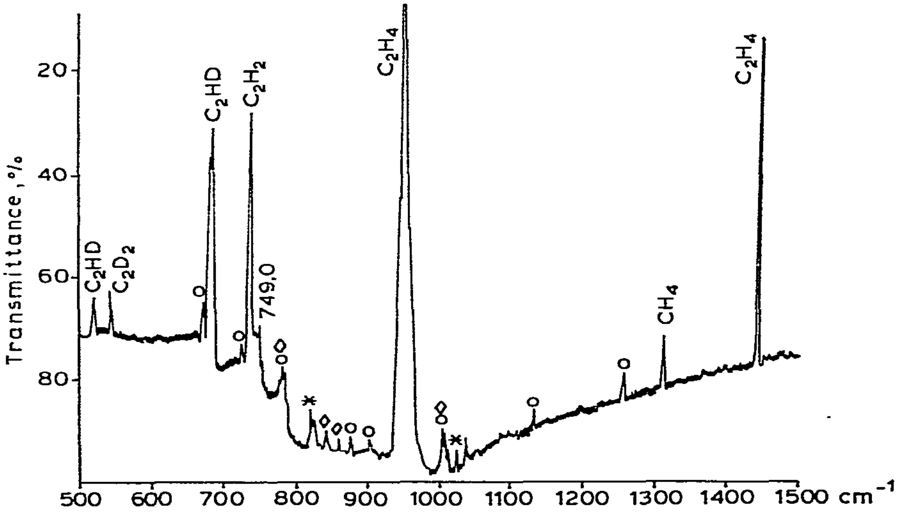


Fig. 2. The IR spectrum of the pyrolysis products of II-d_3 (970°C, 5 × 10^{-3} Torr) in an Ar matrix at 10 K.

The formation of the dimer III-d_6 was found even at 10—15 K in the case of insufficient argon concentration in a matrix which emphasizes the high reactivity of silaethylene I (cf. ref. 9). This observation agrees with the complete absence of the I-d_3 bands in the spectra of the pyrolysis products frozen at 77 K without a matrix. We recorded the bands of the stable compounds II-d_3 and III-d_6 only under such conditions.

The IR bands of silaethylene I-d_3 including the most intensive 755.2, 817.5 and 1016.5 cm^{-1} bands were almost missing in the spectra if the pyrolysis temperature was raised up to 900—1000°C (Fig. 2). We have previously observed similar extensive fragmentation of II-d_0 and II-d_6 silacyclobutanes and probably, I-d_0 and I-d_6 silaethylenes in vacuum pyrolysis at 1000°C [9]. It is worth mentioning that the intensities of the 749, 1003 and 1006 cm^{-1} bands have, on the contrary, increased in the spectrum of Fig. 2 in comparison with Fig. 1b, proving once more their assignment to stable molecules and not to I-d_3. In Fig. 2 the strong bands of C_2H_2, C_2HD, C_2D_2 and CH_4 have appeared. Their growth gives another evidence of nonselective dissociation of II-d_3 at temperatures above 900° C.

A matter of interest is the elimination of C_2HD and C_2D_2 from the parent silacyclobutane II-d_3, which does not contain any C—C bond to a deuterated carbon atom. The intramolecular pyrolitic rearrangement involving formation of C_2HD and C_2D_2 molecules may be compared with the elimination of the neutral acetylenes C_2H_2, C_2HD and C_2D_2 under electron impact fragmentation of II-d_0, II-d_3 and II-d_6 compounds [17].

Analysis of the IR spectra of the I-d_0, I-d_3 and I-d_6

The vibrational frequencies of the I-d_3 molecule obtained in the present study should be correlated with the respective data for I-d_0 and I-d_6 silaethylenes. The differences between the frequency values from three literature sources, however, are rather substantial (Table 3).

TABLE 3

THE VIBRATIONAL FREQUENCIES (cm^{-1}) OF ISOTOPIC 1,1-DIMETHYL-1-SILAETHYLENE MOLECULES

$(CH_3)_2Si{=}CH_2$ (I-d_0)			$(CD_3)_2Si{=}CH_2$ (I-d_6)		$CH_3(CD_3)Si{=}CH_2$ (I-d_3)
[2,9]	[11,13]	[14]	[9]	[13]	Present study
1259.0			1015.5	1012	1259.5
1251.0	1253		1001.4		1025.0
		1156 ^{a}		985 ^{a}	1016.5
1003.5	1001			929 ^{a}	975.5
	992 ^{a}			891 ^{a}	817.5
	932 ^{a}		769.2	768	755.2
825.2	824			722 ^{a}	606.0
817.5	817			718 ^{a}	
	696 ^{a}		687.5		
642.9	644			683 ^{a}	
			579.2	580	
				543 ^{a}	

[a] The frequency values assigned probably by mistake to silaethylene are discussed in the text.

$(CH_3)_2Si{=}CH_2$ (I-d_0). We found six bands of the I-d_0 molecule in the matrix IR spectrum as early as 1976—1977 [1,2]. Later, eight bands were reported for I-d_0 [10—13], five of them agreed well with our data (Table 3).

Three other bands at 696, 932 and 992 cm^{-1} reported [10—13] have been shown to belong to the stable molecules of the dimer III-d_0 and propylene rather than to silaethylene I-d_0 [9]. In particular, this conclusion results from the alteration of the ratio of the mentioned bands intensities in various experiments at 10 K [9,13]. We also observed a similar pattern warming the matrix up to 35—40 K.

Recently, the IR spectrum has been obtained after the pyrolysis products of II-d_0 had been frozen without an inert matrix at 80 K [14]. The band at 1156 cm^{-1} in this spectrum has been assumed to belong to the Si=C stretching vibration of the I-d_0 species. However, a similar band near 1156 cm^{-1} is seen in the IR spectrum of the initial compound II-d_0 [14, Fig. 1]. We observed the 1156 cm^{-1} band at 77 K (1159 cm^{-1} in an Ar matrix at 10 K) in the spectra of an inadequately purified sample of II-d_0 and in those of its pyrolysis products. This spectral band is completely absent when the II-d_0 sample is purified by preparative GLC [9]. Probably the band at 1156 cm^{-1} belongs to an impurity and not to silaethylene I-d_0.

$(CD_3)_2Si{=}CH_2$ (I-d_6). The matrix IR spectra of the I-d_6 molecule have been obtained by us [5—9] and by others [10—13] (Table 3). However, the 543, 683, 718, 722 and 891 cm^{-1} bands given in refs. 10—13 have been shown not to disappear after the matrix warming [9]. What is more, these five bands increase markedly in intensity if the temperature of vacuum pyrolysis approaches 1000°C, just as the strongest bands of I-d_6 species (near 580, 769 and 1015 cm^{-1}) are practically missing in the same spectrum [9]. The other two bands at 929 and 985 cm^{-1} have been assigned [10—13] to the I-d_6 molecule, but they do not disappear on the matrix warming either. These band positions are close to the vibrational frequencies of the stable molecules which can be present in the reaction mixture [10—13]: propylene (931.0 cm^{-1} [18]), the dimer III-d_{12} (932.9 cm^{-1} [9]) and the starting material 1,1,3-trimethyl-1-silacyclobutane-d_6 (of II-d_6). The last two compounds have the corresponding frequency values of 985 and 988 cm^{-1} under a M/R (matrix gas to reagent) ratio less than 500.

Thus one can infer that seven bands out of ten indicated [10—13] for silaethylene I-d_6 (Table 3) belong to stable molecules.

$CH_3(CD_3)Si{=}CH_2$ (I-d_3). For silaethylene I-d_3 we have discovered several IR bands in the present study (Tables 2 and 3). It is of interest to analyse their possible assignments to the normal vibrations of the molecule I-d_3. Earlier, the intense 1003.5 cm^{-1} band had been assigned to the Si=C bond stretching vibration in the I-d_0 molecule [5—9, 10—13]. It is known that the intensity of the C=C stretching vibration band in an IR spectrum of isobutylene does not change much on deuteration of the methyl groups [19]. Analogous deuteration of the methyl groups in the I-d_0 molecule should not cause a very significant shift in the Si=C stretching frequency. Therefore, the corresponding band in the IR spectra of I-d_3 or I-d_6 should be positioned in 950—1150 cm^{-1} region [6,12,13]. In the spectrum of I-d_3 one can see three such bands at 975.5, 1016.5, and 1025.0 cm^{-1}, of which the 1016.5 cm^{-1} band is much stronger than two

others. Probably, this band can be assigned to the stretching Si=C vibration in I-d_3.

The strong band of the out-of-plane vibration of the $=CH_2$ fragment, $\rho(CH_2)$, is characteristic of α-olefines, $CH_3CH=CH_2$, $(CH_3)_2C=CH_2$ and others. The intensity of this band does not vary much on deuteration of a nearby methyl group. Consequently, the most intense 817.5 cm^{-1} band in the spectrum of I-d_3 may belong to the $\rho(CH_2)$ vibrational mode, its counterpart in the I-d_0 molecule being the 825.2 cm^{-1} band [9].

The vibrational frequencies of I-d_3 found in the present work have been used for the force field analysis of the silaethylene I molecule. The basic inferences from the calculations have been published by us previously [5—9,20]. More detailed results of the force field study are described separately [21].

References

1 A.K. Maltsev, V.N. Khabashesku and O.M. Nefedov, Izv. Akad. Nauk SSSR, Ser. Khim., (1976) 1193.
2 A.K. Maltsev, V.N. Khabashesku and O.M. Nefedov, Dokl. Akad. Nauk SSSR, 233 (1977) 421.
3 L.E. Gusel'nikov, K.S. Konobeevsky, V.M. Vdovin and N.S. Nametkin, Dokl. Akad. Nauk SSSR, 235 (1977) 1086.
4 P.G. Mahaffy, P. Gutowsky and L.M. Montgomery, J. Amer. Chem. Soc., 102 (1980) 2854.
5 A.K. Maltsev and O.M. Nefedov, Planary Lecture at 4th International Symposium on Analytical and Applied Pyrolysis. Budapest, Hungary, June 11—15, 1979.
6 V.N. Khabashesku, Dissertation, Institute of Organic Chemistry, Moscow, 1979.
7 V.N. Khabashesku, A.K. Maltsev and O.M. Nefedov, U.S.S.R. Conference on Low Temperature Chemistry, Moscow, U.S.S.R., November 28—29, 1979; Moscow State Univ. Publ., Abstr. p. 53.
8 A.K. Maltsev, V.N. Khabashesku, E.G. Baskir and O.M. Nefedov, Izv. Akad. Nauk SSSR, Ser. Khim., (1980) 222.
9 O.M. Nefedov, A.K. Maltsev, V.N. Khabashesku and V.A. Korolev, J. Organometal. Chem., 201 (1980) 123.
10 L.E. Gusel'nikov, V.V. Volkova and V.G. Avakyan, U.S.S.R. Conference on Low Temperature Chemistry, Moscow, U.S.S.R., November 28—29, 1979; Moscow State Univ. Publ., Abstr. p. 57.
11 L.E. Gusel'nikov and N.S. Nametkin, Chem. Revs., 79 (1979) 529.
12 V.G. Avakyan, L.E. Gusel'nikov, V.V. Volkova and N.S. Nametkin, Dokl. Akad. Nauk SSSR, 254 (1980) 657.
13 L.E. Gusel'nikov, N.S. Nametkin, V.V. Volkova and V.G. Avakyan, J. Organometal. Chem., 201 (1980) 137.
14 N. Auner, J. Grobe, J. Organometal. Chem., 197 (1980) 13.
15 N.S. Nametkin, V.M. Vdovin, L.E. Gusel'nikov and V.I. Zav'yalov, Izv. Akad. Nauk SSSR, Ser. Khim., (1966) 584.
16 L.M. Sverdlov, M.A. Kovner and E.P. Kraynov, Vibrational Spectra of Polyatomic Molecules (in Russian), Nauka, Moscow, 1970.
17 A.K. Maltsev, V.N. Khabashesku and O.M. Nefedov, in preparation.
18 W.A. Guillory and S.G. Thomas, J. Phys. Chem., 79 (1975) 692.
19 V.I. Mochalov, Yu.N. Panchenko, V.I. Pupishev and N.F. Stepanov, Vestn. Mosk. Univ., Khim., 21 (1980) 241.
20 A.K. Maltsev, V.N. Khabashesku, V.A. Korolov, E.G. Baskir and O.M. Nefedov, 2nd U.S.S.R. Conference on Carbene Chemistry, Nauka, Moscow, 1977.
21 A.K. Maltsev, E.G. Baskir, V.N. Khabashesku and O.M. Nefedov, in press.