

DIRECT SPECTROSCOPIC STUDY OF SILAOLEFINS. VIBRATIONAL FREQUENCIES OF $R_2Si=CD_2$ ($R = CH_3, CD_3$) IN AN ARGON MATRIX *

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Summary

As a continuation of studies on Si=C bond species, the silaethenes $(CH_3)_2Si=CD_2$ and $(CD_3)_2Si=CD_2$ have been generated by vacuum pyrolysis of the corresponding silacyclobutanes with totally deuterated rings. The silaethenes are stabilized in argon matrices at 12 K and characterized by IR spectroscopy. The following vibrational bands of the silaethenes have been revealed by using warm-up experiments (to 40 K) and through variations of the pyrolysis conditions: $(CH_3)_2Si=CD_2$ 508.0, 535.3, 617.1, 776.5, 819.8, 895.1, 1117.5, 1251.0, 1259.5 cm^{-1} ; $(CD_3)_2Si=CD_2$ 501.6, 651.2, 732.0, 866.5, 1002.5, 1005.0, 1028.0, 1112.0 cm^{-1} . A comparison of these values with computed vibrational frequencies of the silaethenes indicates that the $\nu(Si=C)$ vibration corresponds to two bands in the spectrum of each silaethene, namely 895.1 and 1117.5 cm^{-1} for $(CH_3)_2Si=CD_2$, 866.5 and 1112.0 cm^{-1} for $(CD_3)_2Si=CD_2$. Within each pair, the band with the higher wave number corresponds to a larger contribution by $\nu(Si=C)$.

Introduction

1,1-Dimethylsilaethene (I), the first silicon-carbon double bond species whose existence was established by a physical method [1], remains a focus of extensive studies [2,3]. Our recent analysis of earlier low-temperature spectroscopic experiments performed by several research teams [1,4–6] has revealed a reliable set of matrix IR bands [7] for the intermediates $(CH_3)_2Si=CH_2$ ($I-d_0$), $CH_3(CD_3)Si=CH_2$ ($I-d_3$) and $(CD_3)_2Si=CH_2$ ($I-d_6$). The isotopic shift of the IR bands on deuteration of the methyl groups was applied to assign the frequencies to the normal vibrations

* Dedicated to Professor Makoto Kumada whose studies on the Si=C bond species and other organosilicon intermediates always encourage the authors.

of the molecule I, particularly for an assignment of the 1003.5 cm^{-1} band to the $\nu(\text{Si}=\text{C})$ vibration in $I-d_0$ [4c,d]. The shifts were also used to determine the force field of silaethenes [4c,8].

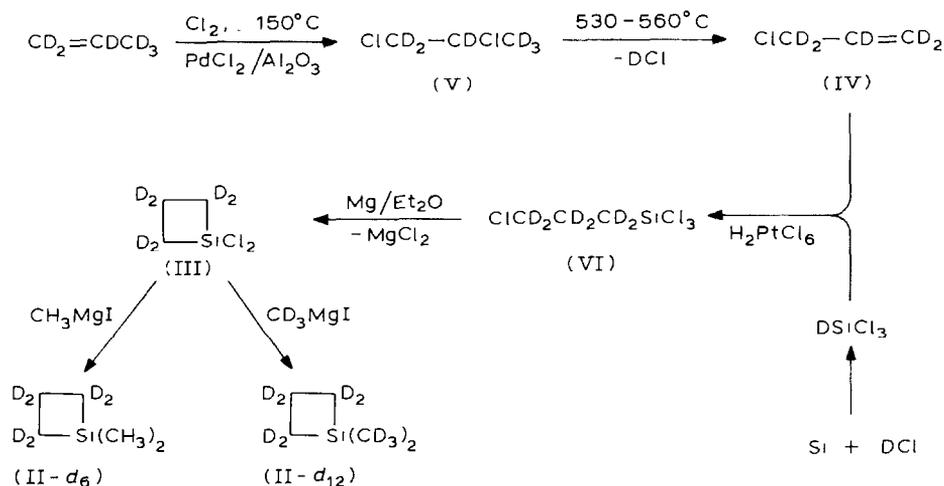
However, these attributions and conclusions require some confirmatory experimental data on silaethenes with the deuterated methylene group at the double $\text{Si}=\text{C}$ bond. Until recently [9] there had been no attempts to study such intermediates, although they are of great value [5b] to confirm unambiguously the assignments of the bands to normal vibrations and to examine the general force field [8] of silaethenes.

As a source of the silaethenes $(\text{CH}_3)_2\text{Si}=\text{CD}_2$ ($I-d_2$) and $(\text{CD}_3)_2\text{Si}=\text{CD}_2$ ($I-d_8$) used in this study, the previously unknown silacyclobutanes $\text{CD}_2\text{CD}_2\text{CD}_2\text{Si}(\text{CH}_3)_2$ ($\text{II}-d_6$) and $\text{CD}_2\text{CD}_2\text{CD}_2\text{Si}(\text{CD}_3)_2$ ($\text{II}-d_{12}$) have been produced and then pyrolyzed in high vacuum. The pyrolysis products, frozen in an inert matrix, have been investigated by IR spectroscopy. A similar technique has been used successfully to detect the silaolefins $I-d_0$, $I-d_3$ and $I-d_6$ [1,4,7].

Experimental

The starting compounds, $\text{II}-d_6$ and $\text{II}-d_{12}$, have been obtained by the reaction of CH_3MgI or CD_3MgI , respectively, with perdeuterated 1,1-dichloro-1-silacyclobutane- d_6 (III) (Scheme 1).

SCHEME 1

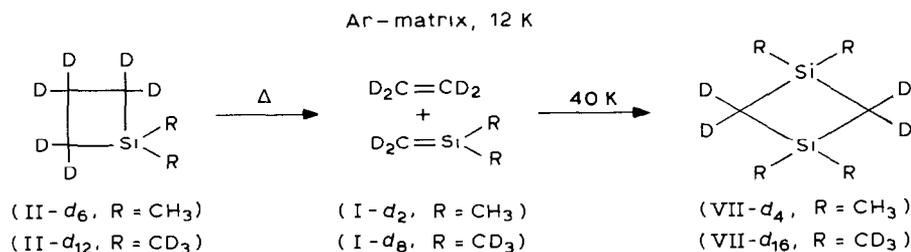


To produce III the following steps are carried out. The first one is a synthesis of chloroallyl- d_5 (IV) by catalytic addition of chlorine to propene- d_6 to form 1,2-dichloropropane- d_6 (V), with subsequent thermolysis of V. Trichlorosilane- d_1 , obtained by a reaction of Si with DCl, was added to IV in the presence of the H_2PtCl_6 catalyst to produce γ -chloropropyltrichlorosilane- d_6 (VI). The latter compound was involved in cyclization with magnesium to give III. The synthesis of $\text{II}-d_6$ and $\text{II}-d_{12}$ will be described in detail elsewhere [10].

The identity of the compounds II-VI was established with NMR (^1H , ^{13}C), MS and IR spectroscopy. The isotopic purity of the samples of $\text{II}-d_6$ and $\text{II}-d_{12}$ appeared

to be higher than 90% from the MS measurements. The mass spectra of II- d_6 and II- d_{12} are presented in [10]. The elemental compositions of these silacyclobutanes are demonstrated by the exact masses of their molecular ions: II- d_6 , m/z 106.1078 (found), 106.1084 (calculated for $\text{SiC}_5\text{H}_6\text{D}_6$); II- d_{12} , m/z 112.1453 (found), 112.1461 (calculated for $\text{SiC}_5\text{D}_{12}$).

The vacuum pyrolysis of the parent silacyclobutanes was accomplished using a flow quartz-tube reactor (diameter 5 mm, length 120 mm) at 700–1000 °C and pressures of 10^{-2} – 10^{-4} Torr. The pyrolysis of II- d_6 and II- d_{12} , performed without the freezing of intermediates, gave the final products: C_2D_4 and 1,1,3,3-tetramethyl-1,3-disilacyclobutanes VII- d_4 and VII- d_{16} , which are cyclodimers of the silaethenes I- d_2 and I- d_8 , respectively. The cyclodimers were isolated and identified by their IR and MS spectra.



To freeze and detect the I- d_2 and I- d_8 intermediates by IR spectroscopy, the thermal reactor was coupled to an optical helium cryostat. The pyrolysis products were trapped with an excess of argon (1000–5000 : 1) at a CsI window cooled down to 12 K with a closed-cycle refrigerator. The IR spectra of the matrix-isolated products were recorded with a Hitachi-Perkin-Elmer-225 spectrophotometer.

Results and discussion

In this study, the IR spectra of the parent compounds II- d_6 and II- d_{12} , the cyclodimers VII- d_4 and VII- d_{16} , and the pyrolysis products of II- d_6 and II- d_{12} have been registered for the first time. The corresponding wave numbers are presented in Tables 1 and 2.

IR spectrum of $(\text{CH}_3)_2\text{Si}=\text{CD}_2$ (I- d_2)

In a matrix IR spectrum obtained from the pyrolysis of II- d_6 (840 °C, 2×10^{-3} Torr), we have found the absorptions of the parent compound II- d_6 and C_2D_4 , as well as a number of new bands (marked with an asterisk in Fig. 1b) at 508.0, 535.3, 617.1, 776.5, 819.8, 895.1, 1117.5, 1251.0, 1259.5 cm^{-1} , as well as a weak band at 2351 cm^{-1} . When the matrix was warmed to 40 K (Fig. 1c), the intensities of these ten bands decrease simultaneously, suggesting they belong to the same transient species. At the same time, one can indicate the growth of absorptions at 636.7, 651.7, 780.7, 858.0 cm^{-1} , all pertaining to the cyclodimer VII- d_4 , a matrix spectrum of which has been recorded in a separate experiment (Fig. 1d). Obviously, the accumulation of VII- d_4 on matrix warming results from the cyclodimerization of the intermediate I- d_2 . Hence, the above ten IR bands should be assigned to I- d_2 . An attribution of 2351 cm^{-1} band is not definite.

TABLE 1

THE VIBRATIONAL FREQUENCIES (cm^{-1}) OF THE SILACYCLOBUTANE II- d_6 , ITS PYROLYSIS PRODUCTS AND 1,3-DISILACYCLOBUTANE VII- d_4 IN AN Ar MATRIX AT 12 K

II- d_6	VII- d_4	Pyrolysis products of II- d_6		Assignment ^a
		At 840 °C	At 930 °C	
511.8	514.4	508.0	508.0	I- d_2 *
		511.0		II- d_6
			518.6	C ₂ HD
		535.3	541.6	I- d_2 * C ₂ D ₂
590.8	551.0	591.5	590.6	II- d_6
		610.0		II- d_6
610.0	636.5	617.1		I- d_2 *
		636.7		VII- d_4 *
		651.8		VII- d_4
		662.0		CO ₂
679.6		680.0		II- d_6
			683.3	C ₂ HD
686.2		686.8		II- d_6
		705.0	705.0	II- d_6
		719.3	719.0	C ₂ D ₄
		736.0	736.2	C ₂ H ₂
		749.6	749.0	
		776.5		I- d_2 *
		780.2		VII- d_4
783.3	780.0	783.4		II- d_6
		792.0		
		803.2	803.4	II- d_6
802.6	809.5	809.0	809.3	II- d_6 + VII- d_4
		819.8		I- d_2 *
		832.8		?
		836.0		?
849.5	847.0	849.5	849.2	II- d_6
		858.0		VII- d_4
		895.1	895.0	I- d_2 *
928.0	915.0	915.4		VII- d_4
		928.0		II- d_6 + VII- d_4
		940.5	940.1	?
958.0		945.0	946.0	?
		958.5		II- d_6
		972.1		II- d_6
976.2	1018.0	977.0	977.3	II- d_6
		1018.0		VII- d_4
		1044.0		II- d_6
		1058.0	1057.0	II- d_6
		1067.5	1066.0	II- d_6
		1074.5	1074.0	C ₂ D ₄
		1105.0		II- d_6
		1117.5	1117.0	I- d_2 *
		1125.5		?
		1249.5	1249.5	II- d_6

TABLE 1 (continued)

II- d_6	VII- d_4	Pyrolysis products of II- d_6		Assignment ^a
		At 840 °C	At 930 °C	
	1250.0			
		1251.1		I- d_2 *
	1252.5			
		1254.5	1254.0	II- d_6
	1256.0			
		1259.5	1259.5	I- d_2 *
		1305.5	1305.0	CH ₄
1323.0		1323.0		II- d_6
2072.0		2073.0		II- d_6
2116.0				
2140		2140		II- d_6
2151		2151		II- d_6
2175		2175		II- d_6
		2195	2195	C ₂ D ₄
		2205	2205	C ₂ D ₄
2214		2214		II- d_6
	2221			
2233		2232		II- d_6
2243	2243			
2257	2257			
		2339	2339	CO ₂
		2344	2344	C ₂ D ₄
		2351		I- d_2 *?
			2580	C ₂ HD
	2910			
2911		2911		II- d_6
	2931	2931		VII- d_4
2968		2968		II- d_6
	2970			
			3285	C ₂ H ₂
			3299	C ₂ H ₂
			3337	C ₂ HD

^a Bands not previously reported are marked *.

Further confirmation of such an interpretation has been provided by our experiments which involve variation of temperature/pressure in the pyrolysis zone or the argon to products ratio. Thus, a pressure increase, multiplying intermolecular collisions in the gas phase, favours cyclodimerization of I- d_2 , giving VII- d_4 . Indeed, on a pressure rise from 10^{-3} to 2×10^{-1} Torr, the intensities of the above-mentioned ten bands are substantially lower, whereas all the dimer absorptions grow in intensity (Fig. 2).

As to the influence of temperature, the silaethenes I- d_0 , I- d_3 and I- d_6 are known to be unstable in vacuum at temperatures higher than 900 °C and to decompose to form methane, acetylene and ethylene [4a,d,e]. Matrix spectra obtained from pyrolysis at high temperatures usually contain only very weak bands of the Si=C intermediates [4d,e]. In full agreement with that pattern, the pyrolysis of II- d_6 at 920–930 °C and 5×10^{-3} Torr has led to intensive bands of C₂H₂, C₂HD, C₂D₂,

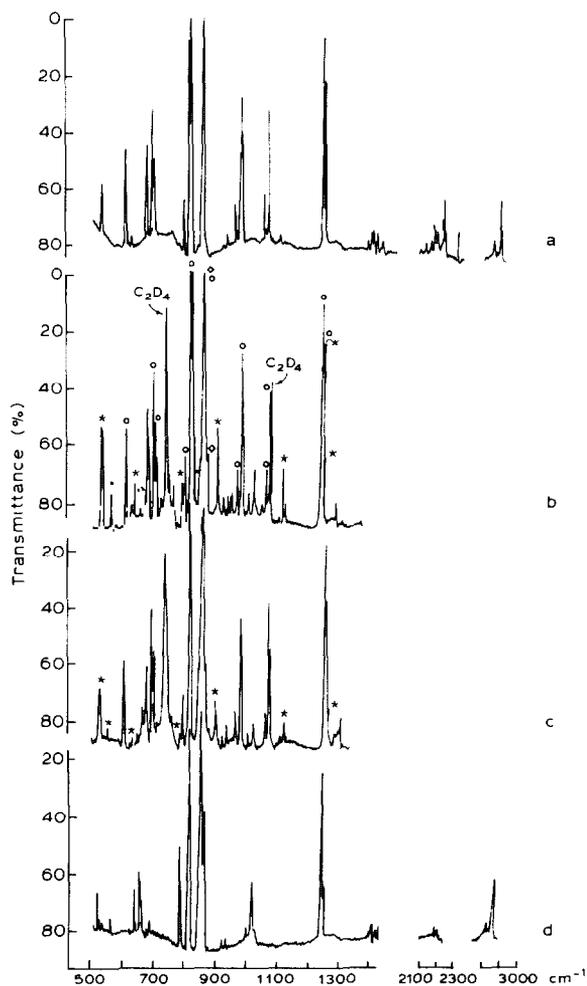


Fig. 1. (a) IR spectrum of II- d_6 in an Ar matrix at 12 K. (b) IR spectrum of the pyrolysis products of II- d_6 (840°C , 2×10^{-3} Torr) in an Ar matrix at 12 K. (c) The same after the matrix had been warmed up to 40 K and recooling to 12 K. (d) IR spectrum of the cyclodimer VII- d_4 in an Ar matrix at 12 K. Here and in Figs. 2-4 the species involved are: I- d_2 \star , II- d_6 \circ , VII- d_4 \diamond .

CH_4 , C_2D_4 and to the complete absence of the ten bands assigned to I- d_2 in matrix spectra (Fig. 3).

The disappearance of the bands of I- d_2 , and formation of its cyclodimer VII- d_4 , have occurred on the decrease from 5000:1 to 100:1 of an argon-to-products ratio and in the absence of argon. The IR spectrum of the pyrolysis products of II- d_6 , frozen at 12 K without an argon matrix, is shown in Fig. 4. Only the bands of the stable molecules II- d_6 , VII- d_4 and C_2D_4 can be seen in the spectrum. Any transient species, particularly I- d_2 , is not observed.

This result demonstrates once again (see earlier [1,4d]) the high reactivity of I at 10-12 K, and throws doubt upon possibility of low-temperature stabilization of simple silaolefines in the absence or in the deficiency of an inert medium [5c,6]. In

TABLE 2

THE VIBRATIONAL FREQUENCIES (cm^{-1}) OF SILACYCLOBUTANE II- d_{12} , ITS PYROLYSIS PRODUCTS, AND 1,3-DISILACYCLOBUTANE VII- d_{16} IN AN Ar MATRIX AT 12 K

II- d_2	VII- d_{16}	Pyrolysis products of II- d_{12}		Assignment ^a
		At 840 °C	At 970 °C	
		501.3		I- d_8 *
524.0		524.6		II- d_{12}
		541.9	542.0	C ₂ D ₂
		546.0		VII- d_{16}
	589.2			
593.2		594.0		II- d_{12}
		613.8	613.1	
		657.2		I- d_8 *
662.8	663.6	663.3	663.0	CO ₂
	667.9	667.2		VII- d_{16}
685.0		685.0		II- d_{12}
693.3		693.6	693.0	II- d_{12}
704.5	704.0	705.0	705.0	II- d_{12}
717.5				
		719.0	719.0	C ₂ D ₄
		723.1	723.1	C ₂ D ₄
		732.0	731.8	I- d_8
741.0		741.6	741.0	II- d_{12}
746.0	746.5	746.3	746.3	II- d_{12} + VII- d_{16}
750.5		750.8	751.0	II- d_{12}
764.3		764.8	764.0	II- d_{12}
	774.5	775.0	774.5	VII- d_{16}
	785.2			
	796.0			
807.6	809.0	807.5	809.0	II- d_{12} + VII- d_{16}
	812.5	812.3	812.5	VII- d_{16}
	841.0			
		866.5		I- d_8 *
928.0		928.0		II- d_{12}
957.6		958.0	957.0	II- d_{12}
971.0		971.6	971.0	II- d_{12}
		987.0	987.0	II- d_{12}
992.0	992.1	993.5	993.0	II- d_{12}
998.1		998.3		II- d_{12}
	1000.0		1000.0	VII- d_{16} + II- d_{12} + CD ₄
		1002.5		I- d_8 *
		1005.0		I- d_8 *
1011.0	1009.0	1010.0		II- d_{12}
1016.0	1015.0	1016.0		II- d_{12}
		1028.0		I- d_8 *
1035.0	1035.0	1035.0		II- d_{12}
			1042.0	
1058.0		1058.5	1058.0	II- d_{12}
1067.0		1067.5	1067.0	II- d_{12}
		1074.5	1074.5	C ₂ D ₄
		1080.0		II- d_{12}
		1112.0		I- d_8 *
		1119.0		?
1130.0		1130.0		II- d_{12}

TABLE 2 (continued)

II- d_2	VII- d_{16}	Pyrolysis products of II- d_{12}		Assignment ^a
		At 840 °C	At 970 °C	
2070		2070		II- d_{12}
	2118.0			
2140		2140		II- d_{12}
2155		2155		II- d_{12}
2166		2166		II- d_{12}
2176		2176		II- d_{12}
		2195	2195	C ₂ D ₄
		2205	2205	C ₂ D ₄
2214		2214		II- d_{12}
	2225		2225	VII- d_{16}
2230		2230		II- d_{12}
			2260	CD ₄
2339		2339	2340	CO ₂
		2344	2344	C ₂ D ₄
		2351		I- d_8 *?
			2441	C ₂ D ₂

^a Bands not reported previously are marked *.

contrast, the data presented in this paper do show that the silaethene I- d_2 is stabilized in argon matrices and can be identified by IR spectroscopy.

IR spectrum of $(CD_3)_2Si=CD_2$ (I- d_8)

The silaethene I- d_8 has been obtained in a similar way by pyrolysis (840 °C, 10^{-3}

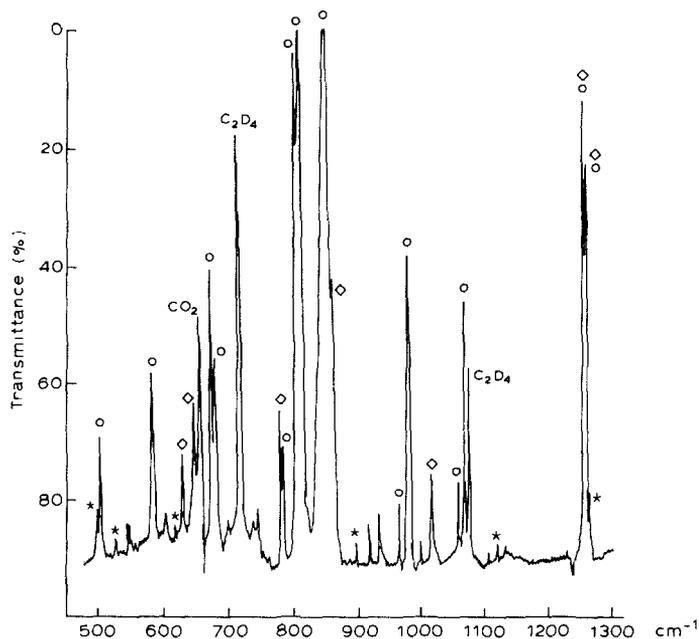


Fig. 2. IR spectrum of the pyrolysis products of II- d_6 (750 °C, 2×10^{-1} Torr) in an Ar matrix at 12 K.

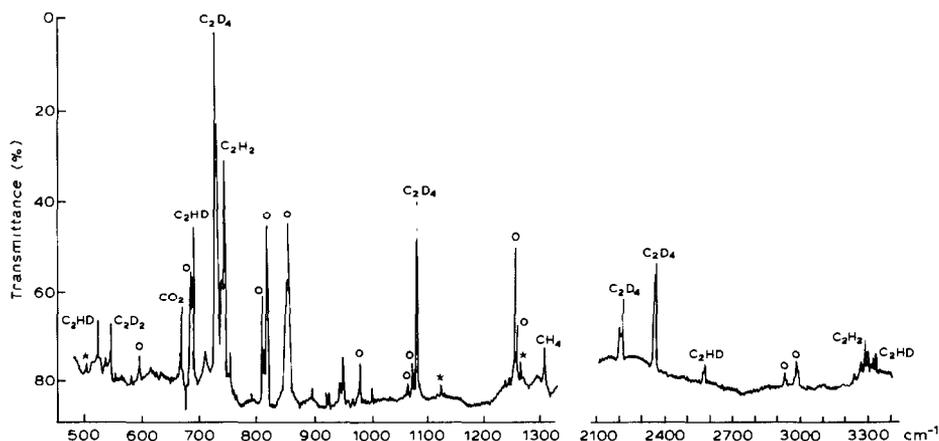


Fig. 3. IR spectrum of the pyrolysis products of II- d_6 (930 °C, 2×10^{-3} Torr) in an Ar matrix at 12 K.

Torr) of the silacyclobutane II- d_{12} . Its spectrum is shown in Fig. 5b, the corresponding wave numbers of II- d_{12} and the pyrolysis products being presented in Table 2. The bands of the intermediate I- d_8 (501.3, 657.2, 732.0, 866.5, 1002.5, 1005.0, 1028.0 and 1112.0 cm^{-1}) are revealed by a technique of matrix warm-up from 12 to 40 K which resulted in cyclodimer, VII- d_{16} , formation (Fig. 5c). The matrix IR spectrum of VII- d_{16} shown in Fig. 5d has been registered separately.

At higher pyrolysis pressure (2×10^{-1} Torr), only the strongest bands of I- d_8 can still be seen in spectra, but the cyclodimer VII- d_{16} , absorptions increase significantly (Fig. 6). The high temperature experiments (up to 970 °C) have confirmed the

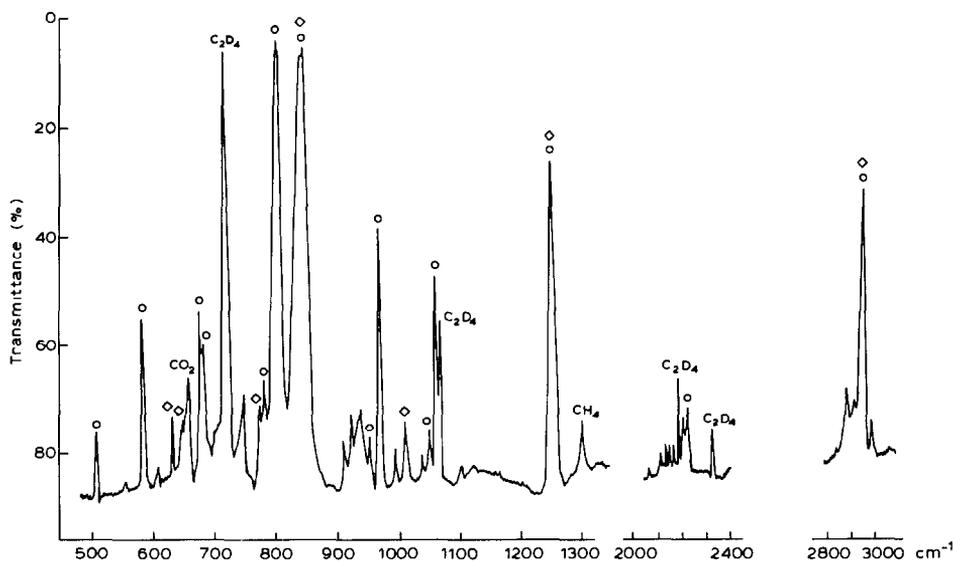


Fig. 4. IR spectrum of the pyrolysis products of II- d_6 (840 °C, 2×10^{-3} Torr) frozen without argon at 12 K.

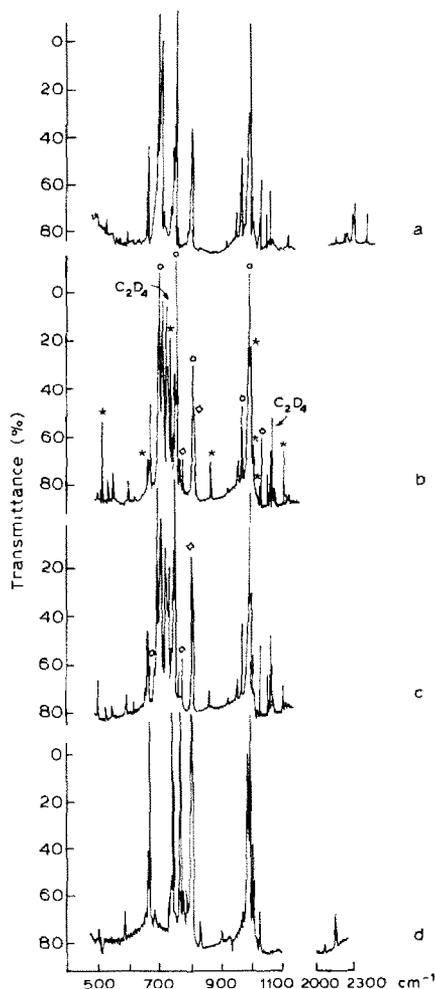


Fig. 5. (a) IR spectrum of II- d_{12} in an Ar matrix at 12 K. (b) IR spectrum of the pyrolysis products of II- d_{12} (840 °C, 2×10^{-3} Torr) in an Ar matrix at 12 K. (c) The same after the matrix had been warmed to 40 K and recooling to 12 K. (d) IR spectrum of the cyclodimer VII- d_{16} in an Ar matrix at 12 K. Here and in Figs. 6–8 the species involved are: I- d_8 ★, II- d_{12} ○, VII- d_{16} ◇.

thermal instability of I- d_8 , being similar to the other isotopic modifications of the silaethene I. Under such conditions, the eight indicated bands were not observed in the spectrum (Fig. 7), while the bands belonging to C_2D_2 , C_2D_4 and CD_4 [11] appeared. As well as for I- d_2 , we could not detect any band of I- d_8 in the spectra of the pyrolysis products frozen without argon at 12 or at about 70 K (Fig. 8).

Beside the spectral features of all the mentioned molecules, one observed some weak bands in spectra from the pyrolysis of II- d_6 or II- d_{12} , at 749.6, 832.8, 836.0, 940.5, 946.0, 1125 cm^{-1} or at 613.8, 1042.0, 1119.0 cm^{-1} , respectively. These unassigned bands do not disappear on heating the matrix to 40 K. They are strong enough in the spectra obtained from the pyrolysis at 930–970 °C, that is under

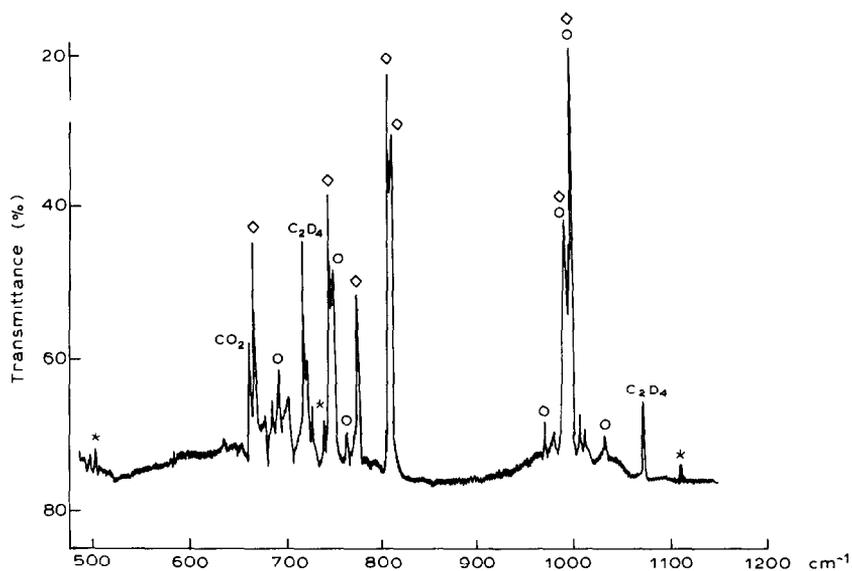


Fig. 6. IR spectrum of the pyrolysis products of II- d_{12} (750 °C, 2×10^{-1} Torr) in an Ar matrix at 12 K.

conditions of the thermal instability of the silaethenes I- d_2 and I- d_8 . Therefore, these bands can not belong to the transient species.

Vibrational frequency of the Si=C bond in the I- d_2 and I- d_8 molecules

The IR bands found in this study for the silaethenes with a deuterated methylene

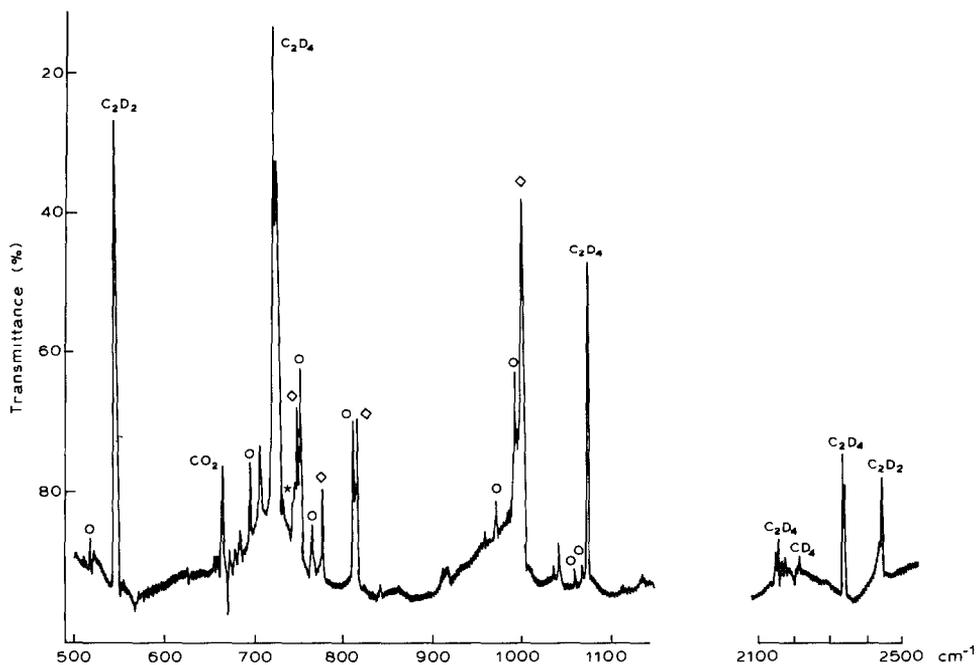


Fig. 7. IR spectrum of the pyrolysis products of II- d_{12} (970 °C, 2×10^{-3} Torr) in an Ar matrix at 12 K.

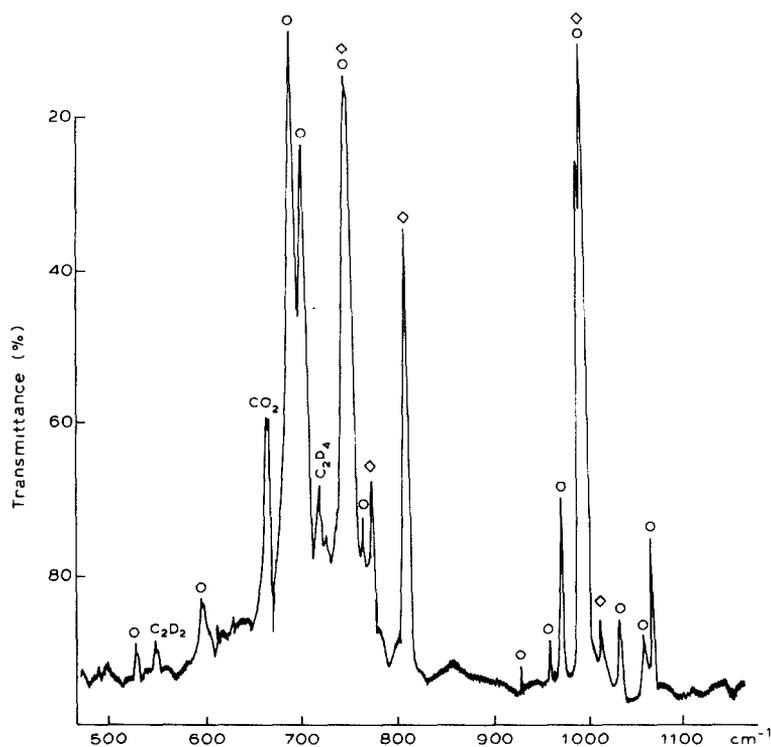


Fig. 8. IR spectrum of the pyrolysis products of II- d_{12} (840 °C, 2×10^{-3} Torr) frozen without argon at 74 K.

group have been assigned to the normal vibrations of I- d_2 and I- d_8 molecules on the basis of force field calculations. The computed vibrational frequencies of I- d_2 and I- d_8 have been obtained using the silaethenes I- d_0 , I- d_3 , I- d_6 force field, particularly the force constant $k_{\text{Si=C}} = 5.6 \text{ m dyn } \text{Å}^{-1}$ [4c].

In the vibrational assignment of the bands of I- d_2 and I- d_8 , the stretching Si=C vibration attracts the greatest attention. For I- d_2 , we could not trace any band in the spectral range 900–1100 cm^{-1} that might be assigned to the Si=C vibration by analogy with I- d_0 (1003.5 cm^{-1}), I- d_3 (1016.5 cm^{-1}) and I- d_6 (1015.5 cm^{-1}). In the spectrum of I- d_8 there is a strong band at 1002.5 cm^{-1} with a shoulder at 1005.0 cm^{-1} . However, intensive IR absorptions of the Si-methyl deformation vibration are known to shift from 1250–1260 cm^{-1} to this quite narrow region near 1000 cm^{-1} when CH_3 is replaced by a CD_3 group. For example, the shift is well documented for the spectra of silaethene I- d_6 [4c,d], $\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{CD}_3)_2$ [12] and $(\text{CH}_3)_2\text{Si}(\text{CD}_3)_2$ [13]. Therefore, the 1002.5 and 1005.0 cm^{-1} bands are assigned by us to these deformation modes of I- d_8 .

On the other hand, both I- d_2 and I- d_8 spectra demonstrate a pair of strong bands within 140 cm^{-1} from 1000 cm^{-1} (895 and 1117 cm^{-1} for I- d_2 , 866 and 1112 cm^{-1} for I- d_8) which are not observed in the spectra of I- d_0 , I- d_3 and I- d_6 . The positions of these bands may be explained by the vibrational mixing-splitting predicted for the simplest silaethene, $\text{H}_2\text{Si}=\text{CD}_2$, from the normal coordinate calculation [8]. This

phenomenon originates in the mixing of the stretching Si=C vibration with the scissoring $\alpha(\text{CD}_2)$ vibration, which shifts from 1386 cm^{-1} for $\text{H}_2\text{Si}=\text{CH}_2$ to $\sim 1000\text{ cm}^{-1}$ for $\text{H}_2\text{Si}=\text{CD}_2$ [8]. This results in a split into two vibrations, each one including.

$\nu(\text{Si}=\text{C})$ and $\alpha(\text{CD}_2)$. A larger contribution of $\nu(\text{Si}=\text{C})$ to the vibration with the higher wavenumber may imply an assignment of the 1117 cm^{-1} band for I- d_2 and the 1112 cm^{-1} band for I- d_8 to the stretching Si=C vibration [14].

From the above standpoint the silaethenes with a deuterated methylene group differ markedly from the species $\text{R}_2\text{Si}=\text{CH}_2$ (I- d_0 , I- d_3 , I- d_6 [1,4,7]), as well as the six-atom silaethenes $\text{H}_2\text{Si}=\text{CH}_2$, $\text{D}_2\text{Si}=\text{CH}_2$ and $\text{Cl}_2\text{Si}=\text{CH}_2$ [8,15]). The latter $\text{R}_2\text{Si}=\text{CH}_2$ type is defined by an IR band of the Si=C vibration near 1000 cm^{-1} , while the former one may be identified by two bands with a substantial contribution of $\nu(\text{Si}=\text{C})$. Within some limits, it is possible to consider a $\nu(\text{Si}=\text{C})$ frequency value increased by $\sim 100\text{ cm}^{-1}$ in $\text{R}_2\text{Si}=\text{CD}_2$ molecules.

Thus, the silaethenes I- d_2 and I- d_8 , obtained and stabilized in a matrix in this study, are characterized by their IR spectra and some chemical properties. A confirmation of the high reactivity of I is its cyclodimerization at extremely low temperatures. At the same time, the silaethene I appears to be quite stable thermally up to 900°C in the absence of intermolecular collisions in high vacuum.

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