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Direct spectroscopic study of unstable molecules with silicon–oxygen multiple bonds: low temperature matrix stabilization of $(CH_3)_2Si{=}O$ and $(CD_3)_2Si{=}O$ in the gas phase *

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Abstract

To continue the IR spectroscopic investigations of intermediates with double-bonded silicon, the silanones $(CH_3)_2Si{=}O$ and $(CD_3)_2Si{=}O$ have been generated by vacuum pyrolysis of the corresponding 6-oxa-3-silabicyclo[3.1.0]hexanes and of Diels–Alder adducts of silapyranes with maleic anhydride. The above silanones have first been stabilized from the gas phase in argon matrices at 12 K and studied by IR spectroscopy. Using the dependence of the spectra on temperature and pressure in the pyrolysis zone or in warming-up experiments (to 35–40 K) the following vibrational bands of silanones have been revealed: $(CH_3)_2Si{=}O$ 1244, 1240, 1210, 822, 798, 770, 657 cm^{-1}; $(CD_3)_2Si{=}O$ 1215, 1032, 1007, 995, 712, 685, 674 cm^{-1}. The limits of thermal ($\sim 850\,°C$) and kinetic (5×10^{-4} torr) stability of dimethylsilanone were determined. By comparison of frequencies found with computed values the band 1210 cm^{-1} in $(CH_3)_2Si{=}O$ (1215 cm^{-1} in $(CD_3)_2Si{=}O$) was assigned to a Si=O stretching vibration. This frequency as well as the calculated force constant (8.32 mdyn/Å) and order (1.45) of the Si=O bond are considered as evidence of significant double bonding in dimethylsilanone.

Introduction

In 1976 the first spectroscopic identification [1] of dimethylsilaethylene, the molecule with a silicon–carbon multiple bond [2], was carried out successfully by us.

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* The results were presented at the 8th International Symposium on Organosilicon Chemistry, 1987, June 7–12, St.-Louis, Missouri, U.S.A.

** Deceased.

Later [3,4], we determined the vibrational frequency, force constant and order of the silicon–carbon multiple bond in the above molecule. To expand spectroscopic studies on the nature of multiple bonding to silicon, direct investigations of the intermediates with silicon–oxygen multiple bonds have been conducted by us during recent years. Recently, the IR bands of the matrix-isolated molecules $F_2Si{=}O$ [5], $Cl_2Si{=}O$ [6], $(CH_3)_2Si{=}O$ (I) [7] * and $H_2Si{=}O$ [10] have been recorded. However, all the above silanones were obtained by the reactions which took place in low-temperature matrices under specific conditions of diffusion of the reagents. In that case formation of different complexes and aggregates of highly-polar silanones can not be excluded. The generation of reactive intermediates in the gas phase at low pressures followed by freezing in an inert matrix gives the possibility of avoiding the undesirable formation of such associates. Besides that, the information on such important and insufficiently known properties of silanones as reactivity and thermal stability can be obtained by the generation of these intermediates by gas phase reactions, i.e. in conditions typical of chemical processes.

Recently, the gas phase thermolysis of 6-oxa-3,3-dimethyl-3-silabicyclo[3.1.0]hexane (II) and its 1,5-dimethyl derivative (III) has been studied. The conclusion on intermediate participation of dimethylsilanone in these reactions was based on formation of octamethylcyclotrisiloxane as the final product [11]. It was shown that the kinetics of this process follows the first order indicating formation of I as an intermediate [12]. Rather earlier, the Diels–Alder adduct of 2,2-dimethylsilapyrane with maleic anhydride (IV), which decomposes at lower temperatures than II, has been considered as another source of silanone I. The isolation of hexamethylcyclotrisiloxane (V), 1,2-dihydrophthalic (VI) and phthalic (VII) anhydrides as the final products of thermolysis as well as chemical trapping of I gave a reason for assuming the intermediate participation of dimethylsilanone in this reaction [13].

To avoid undesirable cyclotrimerization of I under the conditions of its generation we obtained this intermediate in the gas phase at low pressures followed by freezing the pyrolysis products in an argon matrix and their further study by IR spectroscopy. For reliable detection of the IR bands of dimethylsilanone it has been obtained from four independent sources, epoxides II and III, Diels–Alder adducts IV and from 2,2,6-trimethylsilapyrane with maleic anhydride (VIII). For the assignment of the IR bands recorded to vibrational modes of I we also studied the IR spectrum of an intermediate $(CD_3)_2Si{=}O$ (I-d_6), obtained by the vacuum pyrolysis of the bis-trideuteromethyl derivative of epoxide II (II-d_6).

Experimental

Vacuum pyrolysis of the parent compounds II, II-d_6, III, IV and VIII was carried out in a flow quartz reactor at temperatures of 400–1000 °C and pressures of $1{-}1 \times 10^{-4}$ torr. We used a tube reactor with inside diameter 5–8 mm and length 35–90 mm. A flow rate of liquid samples II, II-d_6 and III was regulated by a grease-free valve made from teflon and glass. Solid compounds IV and VIII were evaporated at temperatures of 40–90 °C from a capillary placed in the reactor close to the pyrolysis zone.

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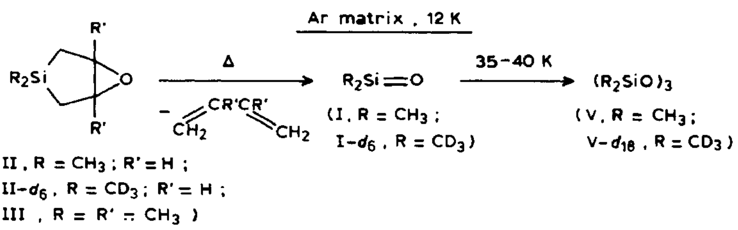
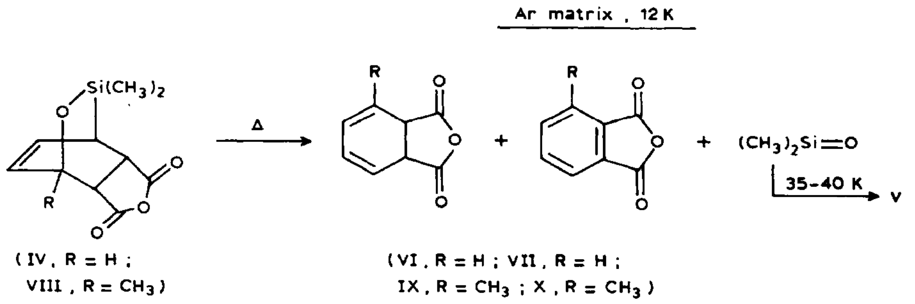
* After publication of the preliminary results of the present work [8] Andrews [9] reported the observation of IR bands of I and $(CH_3)HSi{=}O$, obtained by photochemical oxidation of methylsilanes by means of ozone in an Ar matrix at 17 K.



(1)



(2)

To obtain the matrix IR spectra of the intermediates, the quartz pyrolyzer was coupled to the optical helium cryostat, where the pyrolysis products of the above compounds were frozen out with an excess of argon (1000–5000/1) on a mirror copper plate at 12 K. A closed cycle refrigerator of Air Products CSW 208R was used for cooling the copper plate. A layer of sufficient thickness to obtain high intensity IR spectra was deposited for 0.5–1 h. Spectra were recorded in the range of 400–4000 cm^{-1} by reflecting the IR beam from the mirror plate. In this arrangement, the IR beam passed the solid matrix layer twice and was afterwards directed by the self-made optical system to the monochromator of the LOMO-IKS-24 type IR spectrophotometer. In order to identify the intermediates, controlled warming of the matrix from 12 up to 35–40 K with recooling down to 12 K was carried out.

The final pyrolysis products were analyzed by GLC-MS after their condensation at 77 K into a trap coupled to the cryostat.

The parent epoxides II, II-d_6 and III are synthesised by p-$CH_3OC(O)C_6H_4$-COOOH oxidation of 1,1-dimethyl-3-R-4-R'-1-silacyclopent-3-enes (R = R' = H, CH_3) [14], obtained by the reaction of CH_3MgBr or CH_3MgI with the corresponding 1,1-dichloro-3-R-4-R'-1-silacyclopent-3-enes, or isolated from the reaction products of butadiene or 2,3-dimethylbutadiene with $(CH_3)_2SiCl_2$ and metallic Na [15]. The individual compounds II, II-d_6 and III are isolated by preparative GLC (a column SE-30 on Chromaton with length 2 m, inside diameter 3 mm). The purity of the samples is about 99% from the GLC data. ^1H NMR spectra [11] and MS corresponded to the silabicyclo[3.1.0]hexanes II, II-d_6 and III.

Adducts IV and VIII were obtained by a Diels–Alder reaction from maleic anhydride and 2,2-dimethyl- or 2,2,6-trimethylsilapyrane [13]. The latter are isolated by preparative GLC from a mixture of reaction products of CH_3MgBr with 2,2-dichlorosilapyrane or 2,2-dichloro-6-methylsilapyrane, obtained by gas-phase thermal reaction of $HSiCl_3$ with furan or 2-methylfuran according to [16]. Compounds IV and VIII were purified by recrystallization and sublimation in vacuo. ^1H NMR and MS data are in good agreement with known data [14] for IV and confirm the structure of adduct VIII.

The final product of the pyrolysis of adduct IV, 1,2-dihydrophthalic anhydride VI was prepared by dehydration (boiling in acetic anhydride) of 1,2-dihydrophthalic acid, obtained by reduction of phthalic acid with Na/Hg.

6-Methyl-1,2-dihydrophthalic anhydride (IX) was isolated from the final products of the pyrolysis of adduct VIII by sublimation.

Hexamethylcyclotrisiloxane-d_{18} (V-d_{18}) was isolated from the final products of the pyrolysis of adduct II-d_6 by preparative GLC.

Results and discussion

In this study, matrix IR spectra of the parent epoxides II and III in an Ar matrix at 12 K were recorded (Fig. 1a and 4a). These spectra are in agreement with the data obtained for both compounds in the liquid phase [14]. The matrix IR spectrum of epoxide II-d_6, first synthesized during the present work, is shown in Fig. 7. The bands, recorded in the region 3040–2990 cm^{-1}, belong to C–H stretching vibrations and in the field 940–810 cm^{-1} to C–O, C–C stretching and C–H deformation vibrations, characterizing the epoxide ring [17]. The bands in the region 1256–1248 cm^{-1} in the spectra of II and III obviously belong to Si–CH_3 deformation

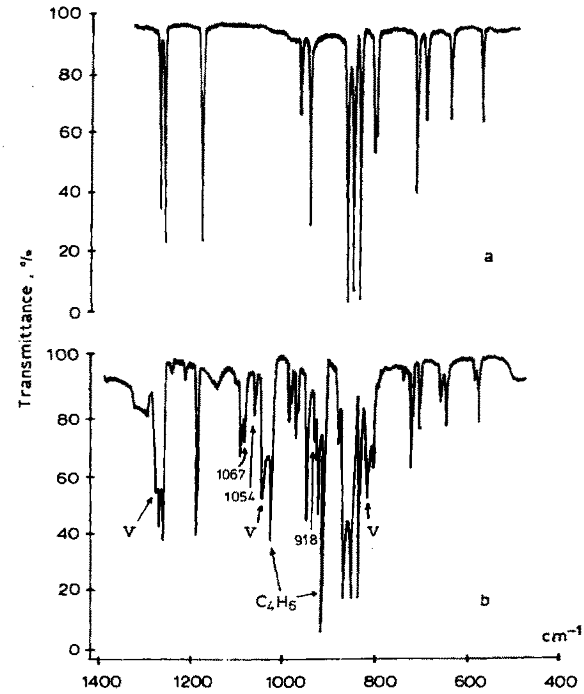
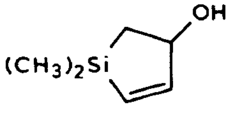


Fig. 1. (a) The IR spectrum of epoxide II in an Ar matrix at 12 K; (b) The IR spectrum of the pyrolysis products of II (750 ° C, 5×10^{-2} torr) in an Ar matrix at 12 K. The bands of the cyclodimer XIII are labelled.

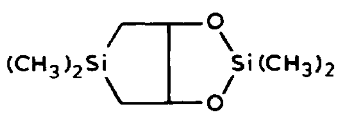
vibrations and on deuteration of the methyl groups are naturally shifted to the region 1010–995 cm^{-1} in the spectrum of II-d_6. The intense bands in the region 1810–1790 cm^{-1} of the adducts IV and VIII belong to stretching vibrations of C=O groups, and intense bands at 1082 and 800 cm^{-1} characterize C–O and Si–O stretching vibrations of the C–O–Si bridge in both compounds. The matrix IR spectra of the parent compounds II, II-d_6, III, IV, VIII, recorded in the present work, as well as of the expected final products of their pyrolysis – butadiene and 2,3-dimethylbutadiene, cyclosiloxanes V and V-d_{18}, 1,2-dihydrophthalic, phthalic and 6-methyl-1,2-dihydrophthalic anhydrides – were used for identification of these molecules in complex mixtures of the products of the pyrolysis reactions (1) and (2).

The IR spectrum of $(CH_3)_2Si{=}O$ (I)

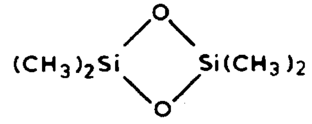
In the IR spectrum of the pyrolysis products of II at 750 °C and 5×10^{-2} torr (Fig. 1b) the intense bands of the two main final products, butadiene and siloxane V, were detected, as follows from the stoichiometry of the reaction (1). Besides that, the bands of the thermal isomerization product of II, 1,1-dimethyl-1-silacyclopent-2-en-3-ol (XI) and the bicyclic compound XII, formed by the insertion of I into the C–O bond of the epoxide ring in the parent compound II, have been observed (Table 1).



(XI)



(XII)



(XIII)

The composition of the final products was additionally confirmed by GLC-MS analysis of the condensate, obtained by re-freezing the pyrolyzate from the matrix, previously warmed slowly up to room temperature, into a trap cooled by liquid nitrogen.

Besides the bands of the above products, three new bands at 1067, 1054 and 918 cm^{-1} were recorded. They disappeared on warming the matrix slowly up to 40 K and were detected in the spectra on freezing the pyrolyzate at 12 K without dilution by argon. According to our mass spectrometric data [18], the cyclodimer of I, 1,1,3,3-tetramethyl-1,3-cyclodisiloxane (XIII), should exist in the gas phase under these conditions. Probably, the three above bands belong to the unstable molecule XIII, which fully agrees with calculations of the vibrational spectrum of cyclodisiloxane $(H_2SiO)_2$ [19].

At lower pressures in the pyrolysis zone (5×10^{-4} torr) the seven new bands at 1244s, 1240m, 1210s, 822w, 798vs, 770w and 657w cm^{-1} in the matrix IR spectrum were detected together with a complete absence of the bands of siloxane V as well as the bands of the cyclodimer XIII. On warming up the Ar matrix over a short period from 12 to 40 K the above bands disappeared simultaneously (Fig. 2b), which indicated that they belonged to the same unstable species. The bands of stable molecules, *trans*-butadiene, the parent compound II, XI and XII, remained in the spectrum. On freezing the pyrolysis products of II at 12 K without argon, the above seven bands were not observed in the spectra; the bands of V and octamethylcyclotetrasiloxane were recorded instead.

(*Continued on p. 284*)

Table 1

The vibrational frequencies (cm^{-1}) of II, III, their pyrolysis products as well as cyclotrisiloxane V, frozen in an Ar matrix at 12 K

II	V	Pyrolysis products of II				Assignment [a]	III	Pyrolysis products of III at 860 °C and ρ 1×10^{-3} torr	
		T 750 °C		ρ 5×10^{-4} torr					
		ρ 5×10^{-2} torr	ρ 5×10^{-3} torr	T 860 °C	T 930 °C				
ν	ν	ν	ν	ν	ν		ν	ν	Assignment [a]
3012									
2999									
	2972								
2968							2967		
2930	2930						2932		
	2970						2913		
	1505						2903		
1469							1458		
1454							1452		
	1440						1435		
1416									
	1415								
1393	1393						1389		
1380			1380	1378		II + C_4H_6	1377		
1322		1322	1322	1322	1322	II + XI	1372		
					1304	CH_4			
	1259	1259	1259			V			
1256				1256	1256	II	1254		
1251		1251	1251	1250	1250	II	1248		
			1244	1244	1244	I*		1244	I*
				1240	1240	I*		1240	I*
					1225	SiO			
1212							1221	1220	III
			1210	1210	1210	I*		1210	I*
		1180	1180	1180	1180	II		1181	
							1166	1166	III
							1134	1135	III
								1094	?

		1078	1078			$[(CH_3)_2SiO]_4$			
		1067				XIII		1075	?
		1054				XIII	1057	1057	III
	1033	1033	1033			V			
						V			
	1028	1028	1028			V			
	1022	1023	1023	1022	1022	*trans*-C_4H_6		1019	C_6H_{10}
		1014	1014	1014	1014	*trans*-C_4H_6			
		996	996	995	995	*cis*-C_4H_6		995	C_6H_{10}
		987	987	987	988	*trans*-C_4H_6			
965				965	964	II			
					948	C_2H_4		947.	C_2H_4
934		935	934	935	935	II		917	C_6H_{10}
		918	918			XIII			
		914	914	914	914	*cis*-C_4H_6	901		
		906	906	906	906	*trans*-C_4H_6		893	C_6H_{10}
	878						869	869	III
		871	871	870	870	XII		864	?
858		857	858	858	858	II + XII		849	?
848		848	848	848	848	II + XII	841	841	III
832		831	831	832	832	II	831	831	III
				822	822	I*		825	?
	818	818	818			V	823	823	III + I *
805		805	806	806	806	II		806	
			798	798	798	I*		789.5	I *
			784	784	784	XI	776		
				770	770	I*		771	I *
			764	764	764	XI			
720		720	720	720	720	II	707	707	III
704		704	704	704	704	II	703	703	III
				657	657	I*		657	I *
643			644	643		II	646	647	III
	605				617	$\cdot CH_3$			
579		580	580	579	579	II			
		534	534	533	534	*trans*-C_4H_6	503	503	III

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[a] Bands not previously reported are marked *

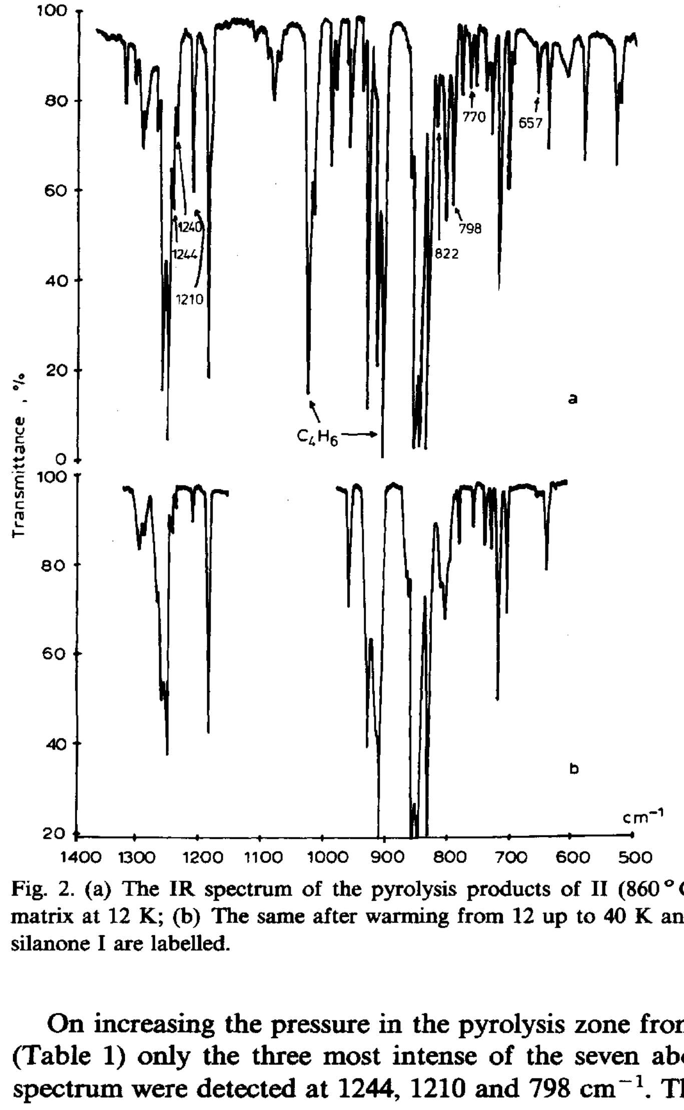

Fig. 2. (a) The IR spectrum of the pyrolysis products of II (860 °C, 5×10^{-4} torr), frozen in an Ar matrix at 12 K; (b) The same after warming from 12 up to 40 K and recooling to 12 K. The bands of silanone I are labelled.

On increasing the pressure in the pyrolysis zone from 5×10^{-4} to 5×10^{-3} torr (Table 1) only the three most intense of the seven above bands in the matrix IR spectrum were detected at 1244, 1210 and 798 cm^{-1}. The rather intense bands of V and the cyclodimer XIII appeared in the spectrum simultaneously. The further increase in pressure up to 2×10^{-1} torr in the pyrolysis zone led to the recording of only the bands of butadiene and siloxane V together with the weak bands of XI and XII in the IR spectrum.

The increase in pyrolysis temperature from 850 to 930 °C (at 5×10^{-4} torr in the pyrolysis zone) resulted in weakening of the intensities of the above seven bands. The bands of the SiO molecule (1225 cm^{-1} [20]), the CH_3 radical (617 cm^{-1}) as well as methane and acetylene appeared in the spectrum instead (Fig. 3). Formation of these products can be explained by silanone I fragmentation under the above reaction conditions:

$$(CH_3)_2Si{=}O \xrightarrow[5\times10^{-4}\ \text{torr}]{930\text{–}950\,^\circ\text{C}} {}^\bullet CH_3 + SiO \qquad (3)$$

On the other hand, the same seven bands were observed in the IR spectrum of the pyrolysis products (1×10^{-3} torr, 860 °C) of another independent source of I,

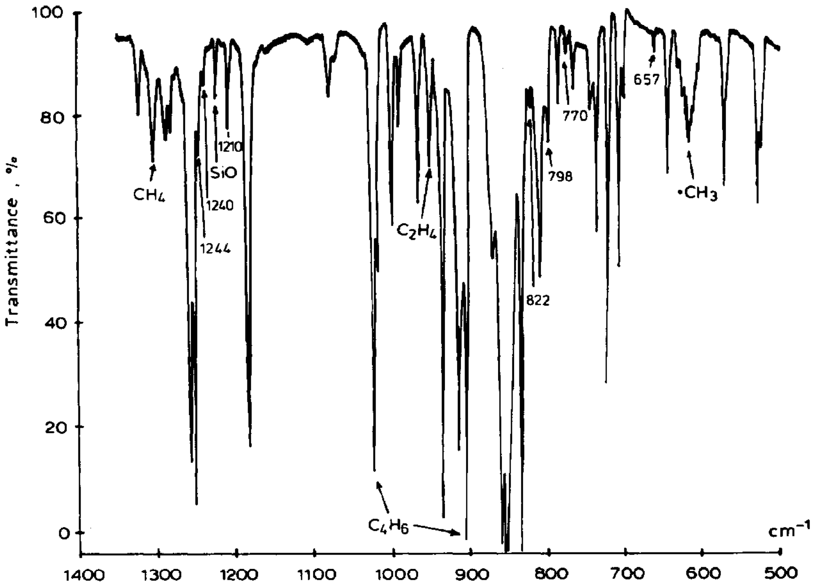

Fig. 3. The IR spectrum of the pyrolysis products of II (930 ° C, 5×10^{-4} torr), frozen in an Ar matrix at 12 K.

epoxide III (Fig. 4a). On warming up the matrix all the above bands disappeared simultaneously (Fig. 4b), the intensities of bands of 2,3-dimethylbutadiene and initial epoxide III remaining the same.

Thus, the results obtained prove that the seven bands 1244, 1240, 1210, 822, 798, 770 and 657 cm^{-1} found belong to dimethylsilanone I, first stabilized from the gas phase *. It was determined that the optimum conditions for the generation of silanone I as a monomer in the gas phase are the lowest pyrolysis temperature of the parent compound in vacuo and the lowest pressure in the reaction zone. The experiments on the pyrolysis of epoxides II and III as well as of other silicon–oxygen-containing sources [21] suggest that the limit of thermal stability of dimethylsilanone in the gas phase is ~ 850 ° C and the limit of kinetic stability is ~ 5×10^{-4} torr. That means that dimethylsilanone has a lower thermal and kinetic stability than 1,1-dimethyl-1-silaethylene, which, according to our data [4], undergoes thermal fragmentation at temperatures higher than 900 ° C and dimerizes in the gas phase at pressures higher than 5×10^{-3} torr.

The conclusion on the conditions of thermal and kinetic stability of I is supported by an IR-spectroscopic study of the vacuum pyrolysis of compounds IV and VIII, Diels–Alder adducts of 2,2-dimethylsilapyrane and 2,2,6-trimethylsilapyrane to maleic anhydride. Pyrolysis of IV at ~ 1×10^{-2} torr and 400–700 ° C shows that complete conversion of the parent compound under these conditions had

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* Only the weak band at 1204 cm^{-1} was assigned in previous work [7] to the monomeric silanone I, prepared by photolysis of a mixture of N_2O and $(CH_3)_{12}Si_6$ in an Ar matrix. In our experiments this band was detected in spectra only after warming up the matrix over a short period to 30 K, leading simultaneously to weakening of the bands of silanone I. This incidates that the bands at 1204 cm^{-1} belong not to monomeric I, but probably to aggregates of I, foregoing the formation of cyclotrisiloxane V on warming the matrix further up.

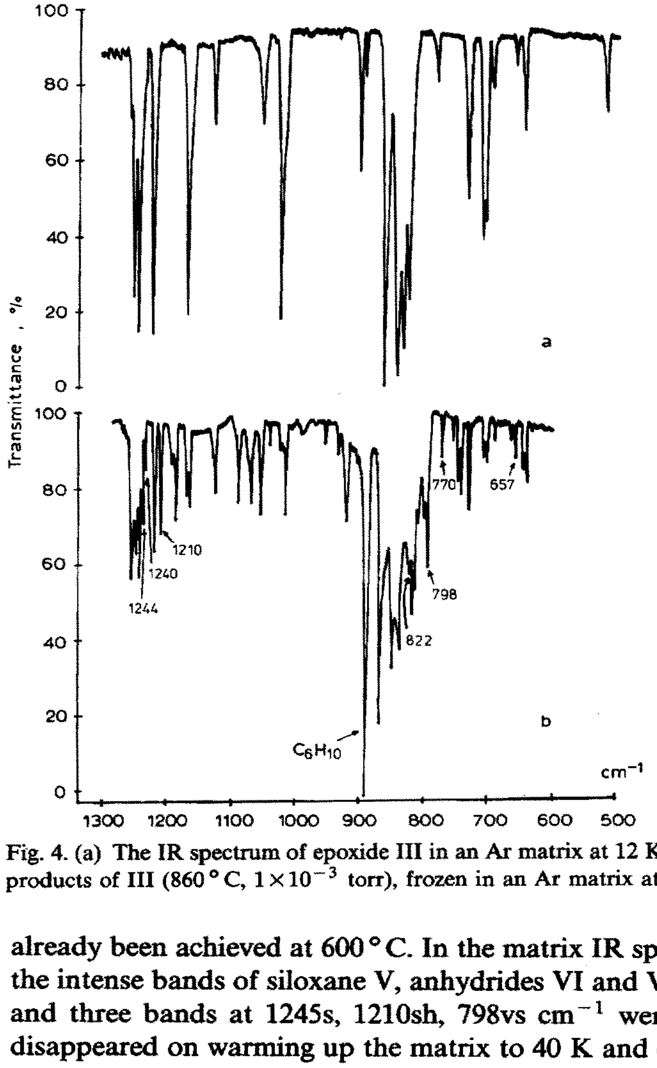


Fig. 4. (a) The IR spectrum of epoxide III in an Ar matrix at 12 K; (b) The IR spectrum of the pyrolysis products of III (860 ° C, 1×10^{-3} torr), frozen in an Ar matrix at 12 K. The bands of I are labelled.

already been achieved at 600 ° C. In the matrix IR spectra of the pyrolyzate (Fig. 5b) the intense bands of siloxane V, anhydrides VI and VII as well as benzene, CO_2, CO and three bands at 1245s, 1210sh, 798vs cm^{-1} were observed. These three bands disappeared on warming up the matrix to 40 K and coincided with the most intense bands of I, generated from epoxides II and III. The observation of its weaker bands was complicated in that case by their overlapping with the intense bands of anhydride VI.

Similar frequencies were recorded in the matrix IR spectrum of the vacuum pyrolysis products of VIII (Fig. 6a,b). Its complete conversion in vacuo was observed at still lower temperatures (500 ° C). However, in these experiments a number of silanone I IR bands also overlapped with intense bands of 6-methyl-1,2-dihydrophthalic anhydride IX, which allowed the identification of only the most intense bands of the above intermediate. It should be noted that in the matrix IR spectra of the pyrolysis products of adducts IV (Fig. 5b) the bands at 1068, 1053 and 919 cm^{-1} were detected. These bands are in agreement with the bands, originally assigned to 1,3-cyclodisiloxane XIII in the spectra of the pyrolysis products of epoxide II (Fig. 1b).

Thus, by taking into account the low thermostability of dimethylsilanone, a vacuum pyrolysis of Diels–Alder adducts is the most suitable method of generating it. For an IR-spectroscopic study of that intermediate the most suitable sources are

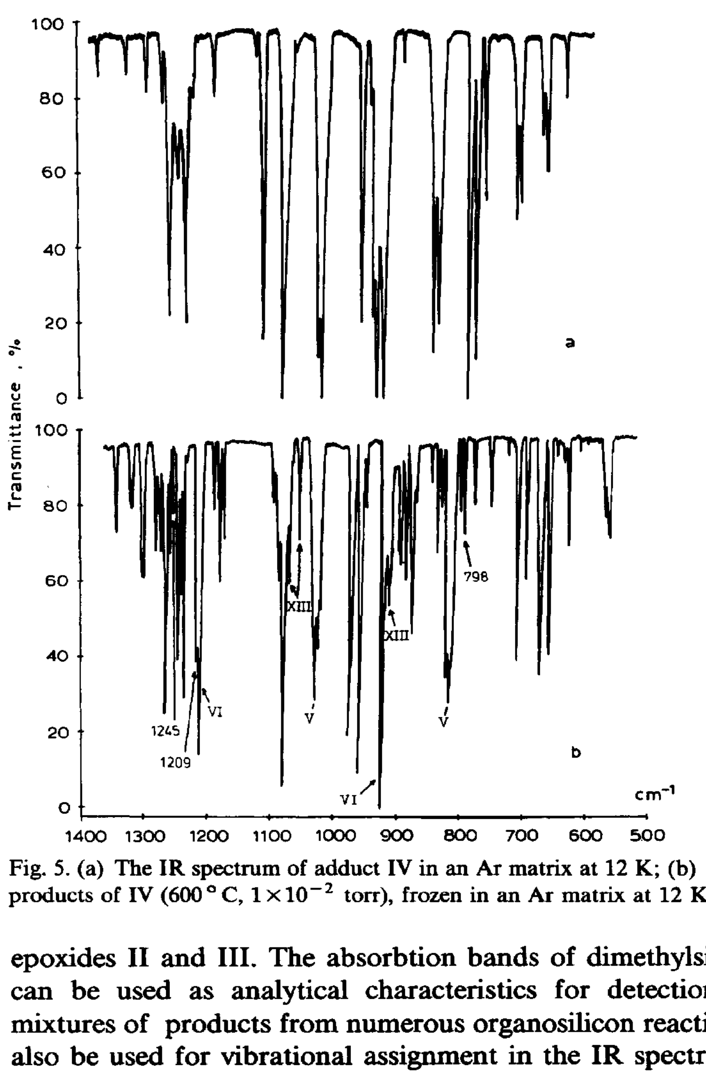
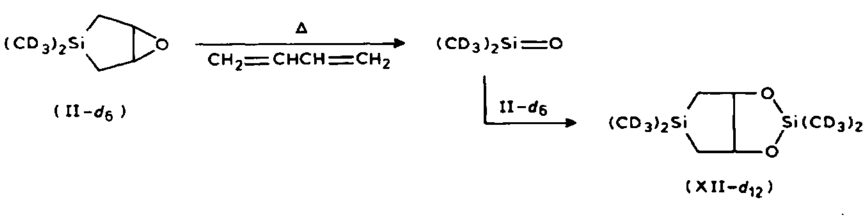


Fig. 5. (a) The IR spectrum of adduct IV in an Ar matrix at 12 K; (b) The IR spectrum of the pyrolysis products of IV (600 °C, 1×10^{-2} torr), frozen in an Ar matrix at 12 K. The bands of I are labelled.

epoxides II and III. The absorbtion bands of dimethylsilanone, determined by us, can be used as analytical characteristics for detection of this intermediate in mixtures of products from numerous organosilicon reactions. These frequencies can also be used for vibrational assignment in the IR spectra of I, involving necessary isotopic shift data. With this aim in view we recorded the matrix IR spectrum of fully deuterated dimethylsilanone $(CD_3)_2Si{=}O$ (I-d_6).

IR spectrum of $(CD_3)_2Si{=}O$ *(I-*d_6*)*

The vacuum pyrolysis of epoxide II-d_6 was used as source of I-d_6. Besides the bands of the parent compound (Fig. 7), butadiene and probably the product of dimethylsilanone insertion into the epoxide C–O bond of II-d_6 (XII-d_{12}), in the matrix IR spectrum of the pyrolysis products of II-d_6 (Fig. 8a) at 880 °C and 5×10^{-4} torr, the new bands at 1215s, 1032m, 1007m, 995s, 712vs, 685m and 674w cm^{-1} were observed.



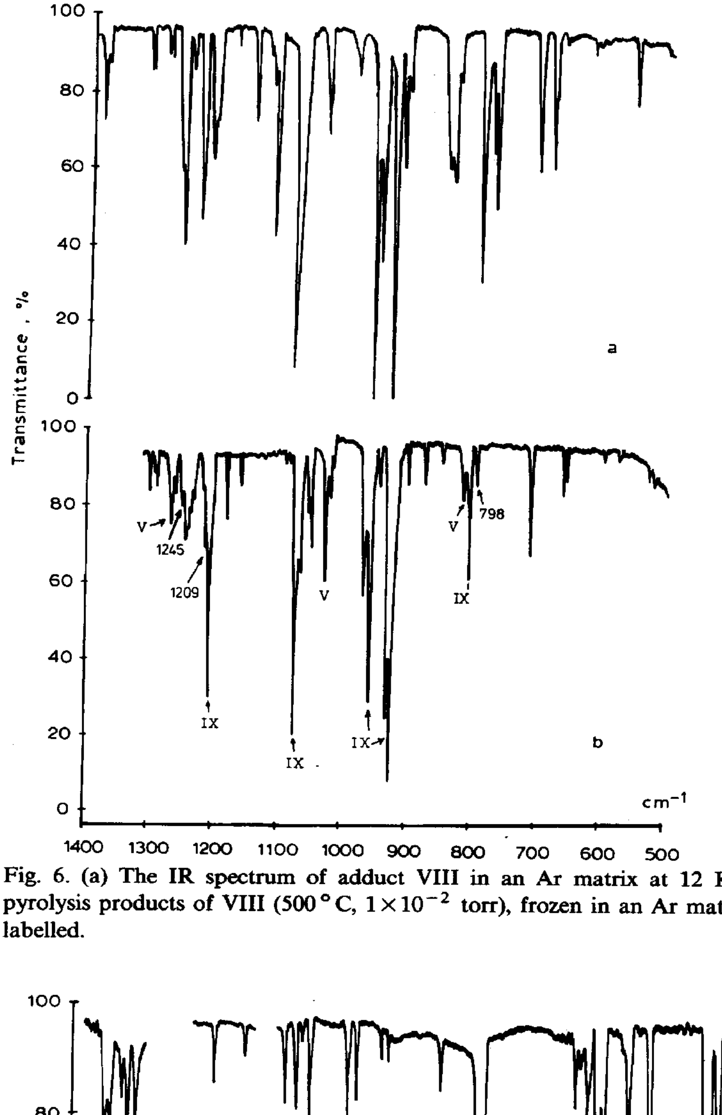


Fig. 6. (a) The IR spectrum of adduct VIII in an Ar matrix at 12 K; (b) The IR spectrum of the pyrolysis products of VIII (500 °C, 1×10^{-2} torr), frozen in an Ar matrix at 12 K. The bands of I are labelled.

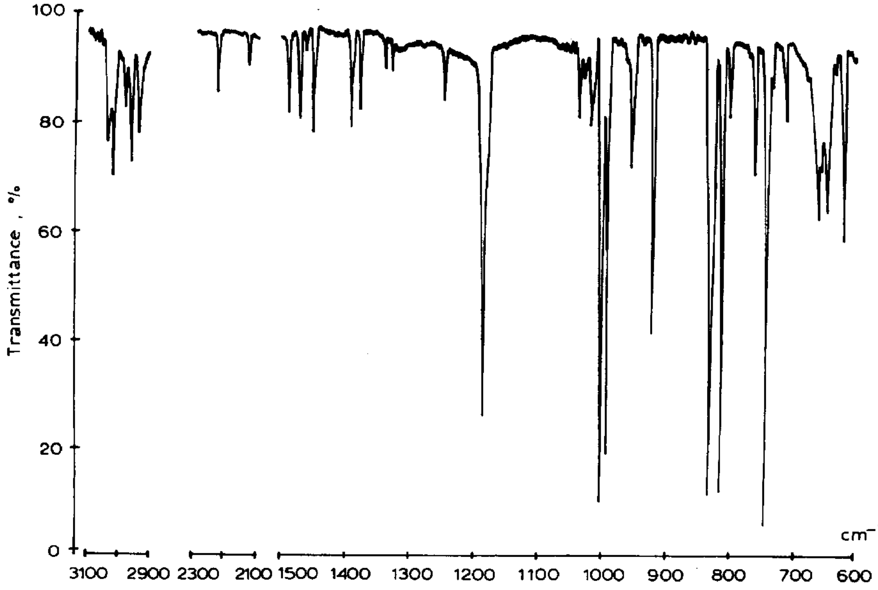


Fig. 7. The IR spectrum of epoxide II-d_6 in an Ar matrix at 12 K.

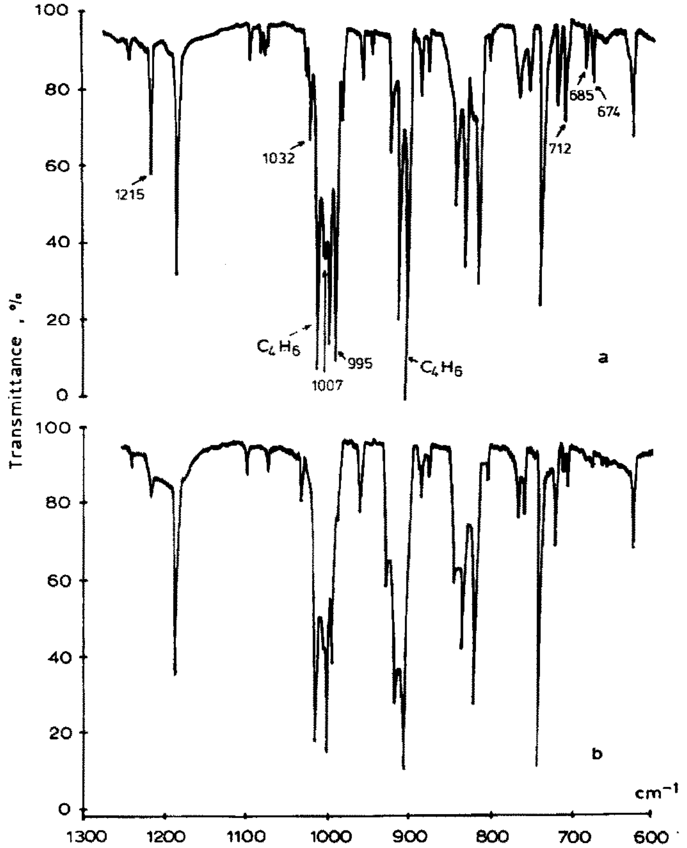


Fig. 8. (a) The IR spectrum of the pyrolysis products of II-d_6 (880 °C, 5×10^{-4} torr), frozen in an Ar matrix at 12 K; (b) The same after warming from 12 to 40 K and recooling to 12 K. The bands of I-d_6 are labelled.

These bands disappeared simultaneously both on warming the matrix up to 40 K (Fig. 8) and on increasing the pressure from 5×10^{-4} to 1×10^{-1} torr in the reaction zone (Table 2).

Increasing the reaction temperature to 900–950 °C (at 5×10^{-4} torr) also brought about the weakening of the silanone bands and intensification of the bands of its decomposition products SiO, CD_3 radical (463 cm^{-1}) as well as C_2D_2, probably facilitated by fragmentation of silanone I-d_6:

$$(CD_3)_2Si{=}O \xrightarrow[5\times10^{-4}\ \text{torr}]{930\text{–}950\,^\circ\text{C}} {\cdot}CD_3 + SiO \qquad (5)$$

These data allowed us to assign the above bands to the intermediate I-d_6. The information on frequency shifts in I caused by deuteration was used to assign the bands to different vibrational modes of the dimethylsilanone molecule.

Vibrational assignment in the spectra of silanones I and I-d_6. The frequency of the stretching vibration, the force constant and order of the Si=O bond

The planar structure of the dimethylsilanone molecule, consisting of 10 atoms, belongs to the C_{2v} symmetry group and has 24 vibrations. Twenty of them are active in the IR spectrum, but only 16 vibrations should be located in the 400–4000

Table 2

The vibrational frequencies (cm^{-1}) of II-d_6, its pyrolysis products as well as cyclotrisiloxane V-d_{18}, frozen in an Ar matrix at 12 K

II-d_6	V-d_{18}	Pyrolysis products of II-d_6			
		ρ 5×10^{-4} torr		ρ 1×10^{-1} torr	Assignment [a]
		T 880 °C	T 930 °C	T 880 °C	
ν	ν	ν	ν	ν	
3024					
3011					
2970					
2941					
2911					
2226					
2131					
1486					
1470					
1454					
1396					
1383					
1237		1236	1237		II-d_6
			1225		SiO
		1215	1215		I-d_6 *
1181		1181	1181	1181	II-d_6
				1077	$[(CD_3)_2SiO]_4$
	1046		1046	1046	V-d_{18}
	1042		1042	1042	V-d_{18}
	1037			1037	V-d_{18}
1036					
		1032	1032		I-d_6^*
1029					
	1026			1026	V-d_{18}
1022		1022	1022	1022	*trans*-C_4H_6
		1014	1014		*trans*-C_4H_6
		1007	1007		I-d_6 *
	1005	1005	1005	1005	V-d_{18}
1003		1002	1002	1002	II-d_6
996		995	995	995	*cis*-C_4H_6, II-d_6 + I-d_6 *
	992			992	V-d_{18}
		987	987	987	*trans*-C_4H_6
965		964	964		II-d_6
		947	947		C_2H_4
927		927	927		II-d_6
		913.5	914	913.5	*cis*-C_4H_6
		905	905	905	*trans*-C_4H_6
		880	879	880	XII-d_{12}
			861		XII-d_{12}
		839	839	839	XII-d_{12}
832		831	832	831	II-d_6
				823	?
814		814	814	814	II-d_6
				810	?
803		803	803.5		II-d_6
	772			771	V-d_{18}
		769	769		XII-d_{12}
		765	765		XII-d_{12}
758		758	758		II-d_6

Table 2 (continued)

II-d_6	V-d_{18}	Pyrolysis products of II-d_6			Assignment [a]
		p 5×10^{-4} torr		p 1×10^{-1} torr	
		T 880 °C	T 930 °C	T 880 °C	
ν	ν	ν	ν	ν	
744		743	744	743	II-d_6
	736			736	V-d_{18}
		722	723	722	V-d_{18}
		712	712		I-d_6 *
708		708	708		II-d_6
		685	685		I-d_6 *
		674	674		I-d_6 *
	672			672	V-d_{18}
667	667	666	666	667	II-d_6; V-d_{18}
		662	662		CO_2
653		653	653		II-d_6
619		619	619		II-d_6
			541		C_2D_2
		533	533.5		C_4H_6
			463		$\cdot CD_3$

[a] Bands not reported previously are marked *.

cm^{-1} range. Most of the frequencies, belonging to stretching and deformation modes of methyl groups, can be predicted from methylsiloxane data [22].

The calculations have been performed by the central force field approximation using a program of Schachtschneider [23]. Bond lengths and valence angles are

Table 3

The vibrational assignment in the IR spectra of silanones $(CH_3)_2Si{=}O$ and $(CD_3)_2Si{=}O$

Vibrational mode	Symmetry type	$(CH_3)_2Si{=}O$			$(CD_3)_2Si{=}O$		
		ν (cm^{-1})		Potential energy distribution (%)	ν (cm^{-1})		Potential energy distribution (%)
		exp.	calc.		exp.	calc.	
$\delta(CH_3)$	A_1		1397	96 $\delta(CH_3)$	1032	1011	97 $\delta(CD_3)$
$\delta(CH_3)$	B_1		1395	96 $\delta(CH_3)$		1008	97 $\delta(CD_3)$
$\delta(CH_3)$	B_2		1395	96 $\delta(CH_3)$		1007	97 $\delta(CD_3)$
$\delta(CH_3)$	A_2		1395	96 $\delta(CH_3)$		1007	97 $\delta(CD)_3$
$\delta(CH_3)$, $\rho(CH_3)$	A_1	1244	1247	54 $\delta(CH_3)$, 46 $\rho(CH_3)$	1007	976	47 $\delta(CD_3)$, 41 $\rho(CD_3)$
$\delta(CH_3)$, $\rho(CH_3)$	B_1	1240	1235	56 $\delta(CH_3)$, 42 $\rho(CH)_3$	995	973	50 $\delta(CD_3)$, 44 $\rho(CD_3)$
$\nu(Si{=}O)$	A_1	1210	1218	89 $\nu(Si{=}O)$	1215	1217	90 $\nu(Si{=}O)$
$\rho(CH_3)$	B_1	822	848	57 $\nu(SiC)$, 41 $\rho(CH_3)$	685	638	63 $\rho(CD_3)$, 16 $\rho(CD_3)$
$\rho(CH_3)$	B_2		810	96 $\rho(CH_3)$	674	611	97 $\rho(CD_3)$
$\rho(CH_3)$	A_1	798	808	96 $\rho(CH_3)$		594	88 $\rho(CD_3)$
$\rho(CH_3)$	A_2		795	96 $\rho(CH_3)$		592	97 $\rho(CD_3)$
$\nu_{as}(SiC)$	B_1	770	772	55 $\rho(CH_3)$, 44 $\nu(SiC)$	712	773	58 $\nu(SiC)$
$\nu_s(SiC)$	A_1	657	657	86 $\nu(SiC)$		581	98 $\rho(CD_3)$

Table 4

Calculated force field of silanones (mdyn/Å)

Force constant	Molecule		
	$(CH_3)_2Si{=}O$ Present work	$F_2Si{=}O$ [5]	$Cl_2Si{=}O$ [6]
$K_{Si{=}O}$	8.32	9.0	9.0
K_{Si-C}	3.22		
K_{C-H}	4.67		
$H_{\delta(CH_3)}$	0.49		
$H_{\rho(CH_3)}$	0.43		
$H_{\delta(SiC_2)}$	0.90		
$H_{\rho(SiC_2)}$	0.90		
F^{C-Si}_{HCSi}	0.20		
F^{C-Si}_{C-Si}	0.18		

borrowed from the work [24] on geometry optimization of methylsilanone. The force constants are transferred from methylsilanes and methylsiloxanes. For a final assignment (shown in Table 3) we have compared the experimental frequencies found for two isotopic molecules with the calculated ones, which are in good agreement within 1% average deviation.

The rather intense band at 1210 cm^{-1} was assigned to the Si=O stretching vibration in the $(CH_3)_2Si{=}O$ molecule [8]. This band is located in spectra significantly higher than the absorption band of the Si–O bond in methylsiloxanes (1020–1080 cm^{-1} [22]). The same kind of assignment was made later by Andrews [9] for a single detected IR band of I at 1209.6 cm^{-1}.

The frequency of the Si=O vibration is slightly increased in I-d_6 and shifted to 1215 cm^{-1}. This agrees with a similar shift of ν(Si=C) from 1003 to 1016 cm^{-1} on transition from $(CH_3)_2Si{=}CH_2$ to $(CD_3)_2Si{=}CH_2$ [25] and with a rise of ν(P=O) from 1161 cm^{-1} for $(CH_3)_3P{=}O$ to 1165 cm^{-1} for $(CD_3)_3P{=}O$ in their IR spectra [26]. According to our calculation the contribution of ν(Si=O) coordinated into the vibration at 1210 cm^{-1} in I (1215 cm^{-1} in I-d_6) is 90%, which indicates a very high degree of specificity of the IR band of the Si=O stretching vibration in dimethylsilanone.

The force field of I is given in Table 4. The best agreement of experimental and calculated frequencies was achieved with an Si=O bond force constant equal to 8.32 mdyn/Å, which agrees with a similar parameter for $F_2Si{=}O$ [5] and $Cl_2Si{=}O$ [6], equal to 9.0 mdyn/Å. This value is considerably higher than the force constant of the Si–O bond in the $(CH_3)_3SiOSi(CH_3)_3$ molecule, equal to 5.3 mdyn/Å. According to Siebert's rule the order of the Si=O multiple bond in I was calculated to be 1.45 taking the order of the Si–O bond to be 1 in the above siloxane, which is close to the order of the Si=C bond in the $(CH_3)_2Si{=}CH_2$ molecule (1.62), estimated by us earlier [3].

Thus, the stretching vibration frequency found experimentally as well as that calculated from spectra, the force constant and order of the Si=O bond constitute direct evidence of considerable double bonding in the $(CH_3)_2Si{=}O$ molecule.

In conclusion, it should be noted that application of vacuum pyrolysis in combination with matrix isolation-IR spectroscopy allowed us for the first time not only to stabilize dimethylsilanone as a monomer from the gas phase but also to observe seven rather intense bands of this intermediate in the IR spectrum. It enabled us to find out both the frequency of the Si=O stretching vibration and the frequencies and modes of other vibrations in dimethylsilanone.

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