Journal of Organometallic Chemistry, 201 (1980) 137—150
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

VERY LOW PRESSURE PYROLYSIS (VLPP) OF MONOSILACYCLOBUTANES. INFRARED ABSORPTIONS OF 1,1-DIMETHYL-1-SILAETHYLENE, $(CH_3)_2Si{=}CH_2$, AND 1,1-DIDEUTERIOMETHYL-1-SILAETHYLENE, $(CD_3)_2Si{=}CH_2$ ISOLATED IN ARGON MATRICES *

L.E. GUSEL'NIKOV*, V.V. VOLKOVA, V.G. AVAKYAN and N.S. NAMETKIN

Topchiev Institute of Petrochemical Synthesis, Academy of Sciences, Moscow (U.S.S.R.)

(Received April 15th, 1980)

Summary

The pyrolysis products of 1,1-dimethyl-1-silacyclobutane (DMSCB) and 1,1,3-trimethyl-1-silacyclobutane (TMSCB), and also of the Si-deuteriomethyl analogs (DMSCB-d_6 and TMSCB-d_6) isolated in argon matrices at 10 K have been studied by IR spectroscopy. Pyrolysis of DMSCB and TMSCB gives rise to an identical set of bands: 644, 696, 817, 824, 932, 992, 1001 and 1253 cm^{-1} which permanently vanish with the increase in temperature. Correspondingly, the bands at 543, 580, 683, 718, 722, 768, 891, 929, 985 and 1012 cm^{-1} are observed in the spectra of pyrolysis products of DMSCB-d_6 and TMSCB-d_6. The appearance of an identical set of bands is attributed to 1,1-dimethyl-1-silaethylene (DMSE) isolated in the argon matrix, but in the case of deuterio analogs, to DMSE-d_6. Based on normal coordinate treatment, the above mentioned bands have been preliminary assigned to certain modes of vibrations of DMSE and DMSE-d_6.

Introduction

The silicon analogs of olefins [1—4] are of significant interest because of the problem of the existence of compounds containing multiple bonds between carbon and the second period elements [4—6]. Among them the silaethylenes, $R_2Si{=}CR_2$, are being extensively studied. They play an important role in a number of transformations of organosilicon compounds, including thermolysis and photolysis processes. A great body of experimental data is now available on the chemistry of silaethylenes: thermodynamically stable but exceedingly

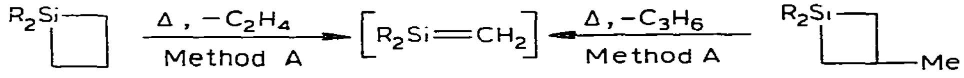
---

* Dedicated to Prof. G.A. Razuvaev on the occasion of his 85th birthday on August 23rd, 1980.

reactive intermediates. However, only few attempts have been made to study silaethylenes isolated under very low pressure or in matrices by direct spectral methods. Thus, 1,1-dimethyl-1-silaethylene (DMSE) has been identified as a molecular ion upon pyrolysis of 1,1-dimethyl-1-silacyclobutane (DMSCB) in an ionic source of a mass spectrometer [7]. The first attempt [8] to detect DMSE in the IR spectrum of the pyrolysis products of DMSCB frozen out from the low pressure gaseous phase onto the target cooled by liquid nitrogen, failed [9]. Subsequently, this technique was improved by isolating pyrolysis products in an argon matrix. The following infrared absorption bands were assigned to DMSE : 642.9 cm^{-1} (stretch vibration $Si—CH_3$), 825.1 cm^{-1} (deformation vibration HCSi) and 1003.5 cm^{-1} (out of plane vibration of CH_2 group) [10]. According to Chapman et al. [9], irradiation of trimethylsilyldiazomethane in an argon matrix at 8 K gave rise to the following infrared absorption bands: 3020 cm^{-1} (stretch vibration CH at the sp^2-hybridized carbon atom), 795 and 646 cm^{-1} (deformation vibrations assigned to 1,1,2-trimethyl-1-silaethylene. Because of the lack of available data on labelled molecules the authors failed to assign any of the observed bands to double bond Si=C stretch vibration. However, the spectrum obtained was found to be similar to the spectrum of trimethylethylene. Therefore it was concluded that the molecule was planar. Chedekel et al. [11] have demonstrated the formation of trimethylsilylcarbene under conditions very similar to those described in ref. 9. The latter is stable at temperatures between 4 and 40 K. Further heating of the matrix results in *trans*-1,2-bis(trimethylsilyl)ethylene. A set of bands assigned to 1,1,2-trimethyl-1-silaethylene was obtained by these authors on irradiation of trimethylsilyldiazomethane by light of wavelength less than 3000 Å. In particular, to 1,1,2-trimethyl-1-silaethylene was assigned the 641 cm^{-1} band which shifted to 510 cm^{-1} in the spectrum of 1,1,2-trimethyl-2-deutero-1-silaethylene (out of plane deformation vibration of H atom at the double bond). In this case also the Si=C stretch vibration band was not isolated. Recently, Brook et al. [12] synthesized the relatively stable 1,1-bis(trimethylsilyl)-2-trimethylsiloxy-2-t-butyl-1,1-silaethylene, in the IR spectrum of which they observed the 8.8 μ (1136 cm^{-1}) band.

In this paper we communicate one more approach for identifying infrared absorption bands produced by matrix isolated silaethylenes generated by methods A and B (see Scheme 1). The present work was undertaken (a) to obtain reproducible absorbtion bands for DMSE in IR spectra of matrix isolated pyrolysis products of DMSCB and TMSCB (1,1,3-trimethyl-1-silacyclobutane) at low pressures; (b) to detect absorption bands of DMSE-d_6; (c) to assign absorption bands of DMSE and DMSE-d_6 based on normal coordinate treatment.

SCHEME 1



R = CH_3 : DMSCB	DMSE	TMSCB
R = CD_3 : DMSCB-d_6	DMSE-d_6	TMSCB-d_6

Experimental

Starting materials

DMSCB and TMSCB were obtained following the procedures described in refs. 13 and 14.

DMSCB-d_6 and TMSCB-d_6 were obtained from 1,1-dichloro-1-silacyclobutane and 1,1-dichloro-3-methyl-1-silacyclobutane by treating them with methyl-d_3 magnesium bromide in ether. Methyl-d_3 bromide (obtained from 10.0 g (0.284 mol) of methanol-d_4, 34.0 g (0.284 mol) potassium bromide, 55 ml of sulfuric acid and 33 ml of D_2O) was bubbled in a reaction flask containing 7.5 g (0.312 g-at) of magnesium stirred in 500 ml of dry ether. To the obtained Grignard reagent was added dropwise dichlorosilacyclobutane (0.142 mol). The volatile products were evaporated from the reaction flask under low pressure, and ether was removed by distillation. The liquid residue was re-condensed and pure deuteriomethylsilacyclobutane sample (yield >90%) was obtained by using preparative GLC (Carbowax 20 M). Isotopic purity of samples was >99%.

DMSCB-d_6. IR spectrum (gas sample) (cm^{-1}) 580vw, 658w, 681m, 689m, 729vs, 735vs, 815vw, 862m, 895vw, 900vw, 924m, 935vw, 993vs, 1002vs, 1031w, 1116m, 1120m, 1123m, 1412m, 1425m, 2135w, 2218m, 2225m, 2808vw, 2880m, 2920s, 2943vs, 2972vs, 2998w. Mass spectrum (m/e 70 eV): 106 (14.5, $M^{+\cdot}$); 78 (100.0, $[M-28]^{+\cdot}$); (m/e, 12 eV) : 106 (45.5, $M^{+\cdot}$); 78 (100.0, $[M-28]^{+\cdot}$).

TMSCB-d_6. IR spectrum (gas sample) (cm^{-1}): 577vw, 581vw, 588vw, 644w, 650w, 668m, 677m, 736vs, 740vs, 745vs, 782w, 785w, 792vw, 819s, 823s, 845m, 878w, 887m, 954w, 957w, 995vs, 1001vs, 1005vs, 1032w, 1039m, 1045m, 1133s, 1137s, 1142s, 1256w, 1330m, 1335m, 1340w, 1386w, 1408m, 1460w, 1467w, 2130vw, 2220s, 2228s, 2733vw, 2810vw, 2865m, 2873m, 2880m, 2910s, 2960vs.

Mass spectrum (m/e 70 eV) : 120 (10.0, $M^{+\cdot}$); 92 (18.5, $[M-28]^{+\cdot}$); 78 (100.0, $[M-42]^{+\cdot}$); (m/e, 12 eV) : 120 (87.5, $M^{+\cdot}$); 92 (100.0, $[M-28]^{+\cdot}$); 78 (92.0, $[M-42]^{+\cdot}$).

Pyrolysis and matrix isolation

Pyrolysis of DMSCB and TMSCB, and also of their deuteroanalogs, DMSCB-d_6 and TMSCB-d_6, was carried out in a flow quartz reactor connected with a liquid helium cryostat FTINT R-47. Studies were made over the range 600 to 850°C. Temperature was maintained to within 0.1°C with a PRT-3M thermoregu lator working with a Pt—Pt/Rh thermocouple. Pyrolysis pressure varied between 2×10^{-2} to 3×10^{-3} Torr. The substance, diluted with argon (in the ratio 1 : 20) was admitted through a fine control inlet valve from the flask, where its vapours were kept in contact with CaH_2 at 50°C. The thermal decomposition products were frozen out on a KBr or NaCl target cooled down to 10 K and located at a distance of 50 mm from the reaction zone. At the same time matrix gas (Ar) was admitted through another fine control inlet valve located also at 45° to the target. The ratio between pyrolysis products and argon was >500. The target temperature was measured with a Au/Fe-Chromel thermocouple.

The IR spectra of gasous samples and matrix isolated DMSCB, DMSCB-d_6, TMSCB-d_6, and TMSCB, and also of their pyrolysis products were recorded on a Unicam SP-1200 spectrophotometer in the 400—4000 cm^{-1} range. Mass spectra were obtained with LKB 2091 GC-MS system.

Results and discussion

As is seen from the comparison of IR spectra of matrix isolated pyrolysis products of DMSCB and TMSCB (Figs. 1b, 2b) with the spectra of starting compounds (Figs. 1a and 2a), new bands are produced due to pyrolysis products. In spectrum 1b these are the absorption bands: 644, 696, 735, 817, 824, 932, 945, 954, 992, 1001, 1253, and 1296 cm^{-1}. Among them the strong band 945 cm^{-1} and the shoulder 954 cm^{-1} occur due to the absorption of ethylene [15] formed in accordance with Scheme 1 (method A).

The decrease in the selectivity of the process (apparently due to the increasing effect of the reactor wall surface [7]) is inherent in low pressure pyrolysis of monosilacyclobutanes. Particularly, in spectra 1b and 2b a 735 cm^{-1} band is observed which is due to acetylene [16]. The latter was observed even at small conversions of silacyclobutane. This is not in good agreement with the data [10] were C_2H_2 formation is associated with profound decomposition processes proceeding at higher temperatures. A weak band at 1296 cm^{-1} indicating methane [17], a minor by-product of DMSCB pyrolysis, was also observed.

Unlike pyrolysis in the static system or in the flow reactor at higher pressures, 1,1,3,3-tetramethyl-1,3-disilacyclobutane (TMDSCB) was not formed. This would have been observed by the following absorption bands: 694, 730, 746, 822, 827, 871, 932, 935, 1245, 1251, and 1260 cm^{-1}. Although some of the bands found in the spectrum (Fig. 1b) (696, 817, 824, 932 and 1253 cm^{-1}) are close to those of TMDSCB, comparison of intensities throughout the whole set of frequencies and the missing characteristic bands (e.g., 871 and 935 cm^{-1}) confirms the absence of TMDSCB among the matrix isolated VLPP products of DMSCB.

In the spectrum of the pyrolysis products of TMSCB (Fig. 2b) are also marked the absorption bands of acetylene (735 cm^{-1}) and methane (1296 cm^{-1}). As would be expected from Scheme 1, characteristic absorption bands of propylene [15] (908, 918, 991, 997 cm^{-1}) are observed in the spectra. A number of bands (766, 893, 897, 903, 1033 and 1145 cm^{-1}) are apparently caused by allyltrimethylsilane formed in small amounts upon pyrolysis of TMSCB [18,19]. Fig. 3 shows the spectrum of the pyrolysis products from TMSCB in the static system isolated in an Ar matrix. Unlike the spectrum shown in Fig. 2b, in this spectrum the absorption bands of TMDSCB are seen as well as those of propylene and allyltrimethylsilane. Thus, in the spectrum shown in Fig. 2b the bands 644, 696, 817, 824, 932, 1001, 1253 cm^{-1} remain unidentified which completely coincide with the unidentified bands in spectrum 1b. According to Scheme 1 these bands may most likely be assigned to 1,1-dimethyl-1-silaethylene.

Apart from the bands of DMSCB-d_6 and TMSCB-d_6 (Figs. 4a and 5a), the spectra of their pyrolysis products (Figs. 4b and 5b) also include the absorption bands of ethylene (945 cm^{-1}) and propylene (908 and 918 cm^{-1}), respectively. Due to overlapping the 991 and 997 cm^{-1} bands of propylene are not seen in

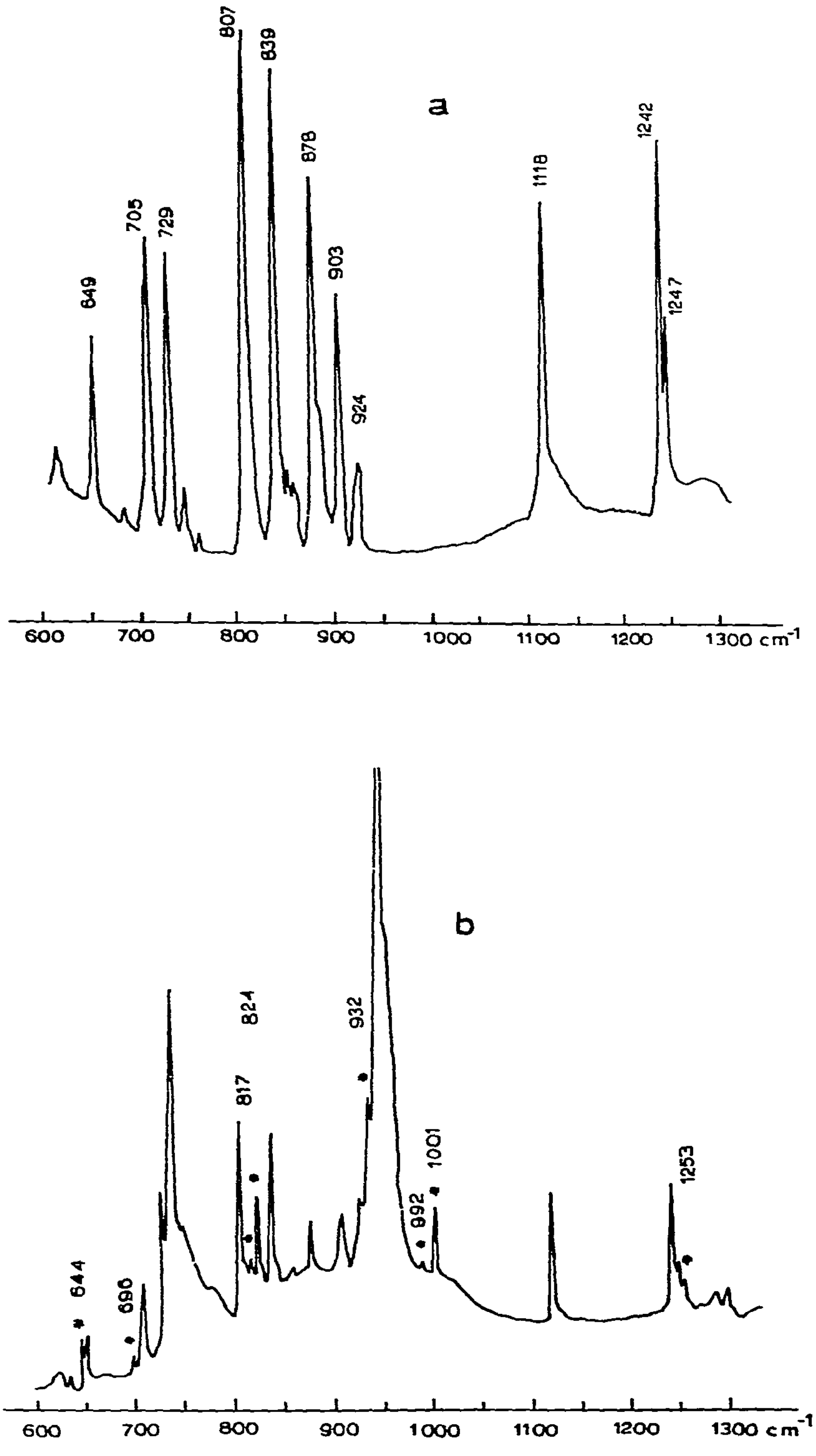


Fig. 1. Infrared spectra of matrix isolated (a) DMSCB, and (b) its VLPP products at 750° C.

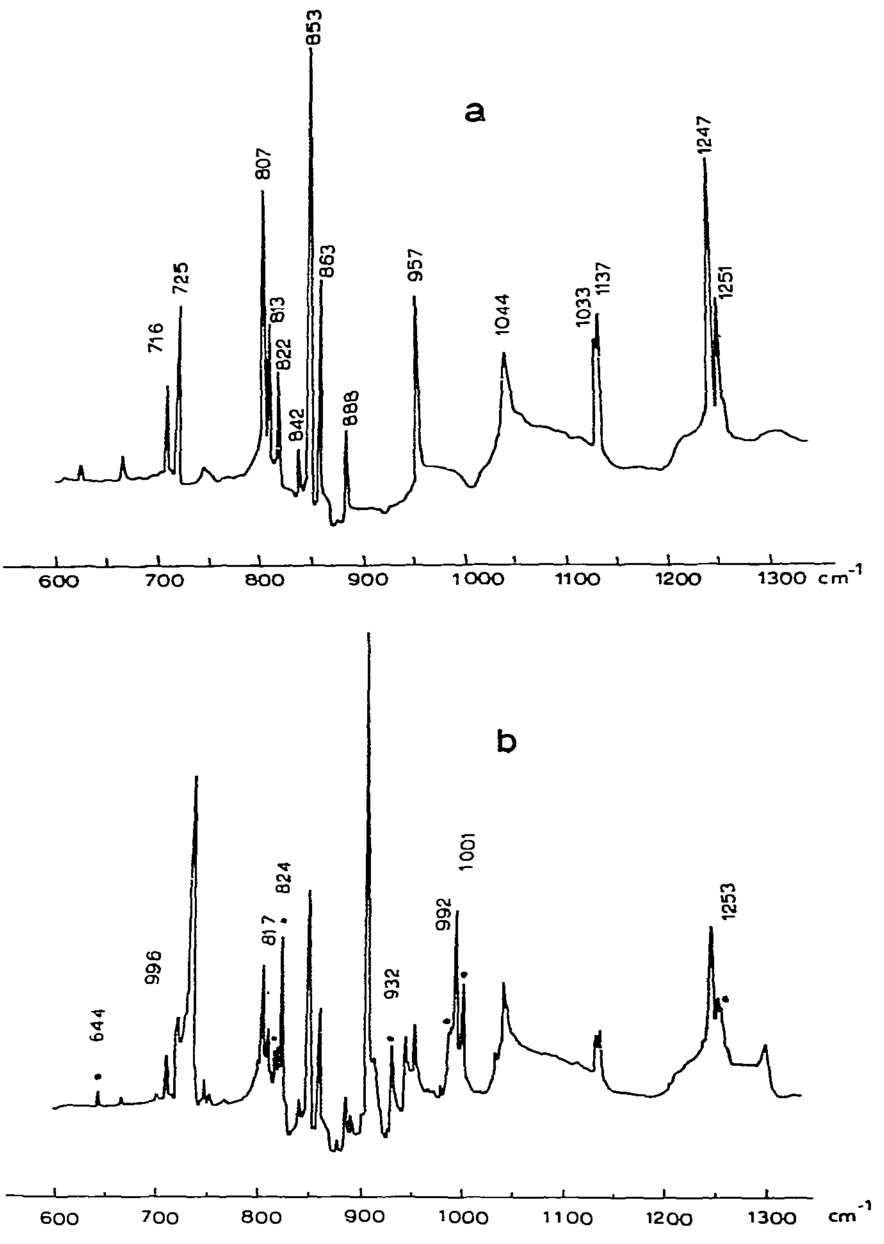


Fig. 2. Infrared spectra of matrix isolated (a) TMSCB, and (b) its VLPP products at 680°C.

the spectrum (Fig. 5b). This data again confirms that the elimination of olefins in the pyrolysis of monosilacyclobutanes is accomplished by destruction of the framework of the four-membered ring. On the contrary, the formation of acetylene is associated mainly with rupture of the Si—CH_3 bond. In the spectra shown in Figs. 4b and 5b the bands at 541 (C_2D_2) [20], 520 and 678 cm^{-1} (C_2HD) [20] are present. The spectrum of VLPP products of DMSCB-d_6, frozen out at the target cooled by solid nitrogen (65 K) (Fig. 6), also resembles the bands of

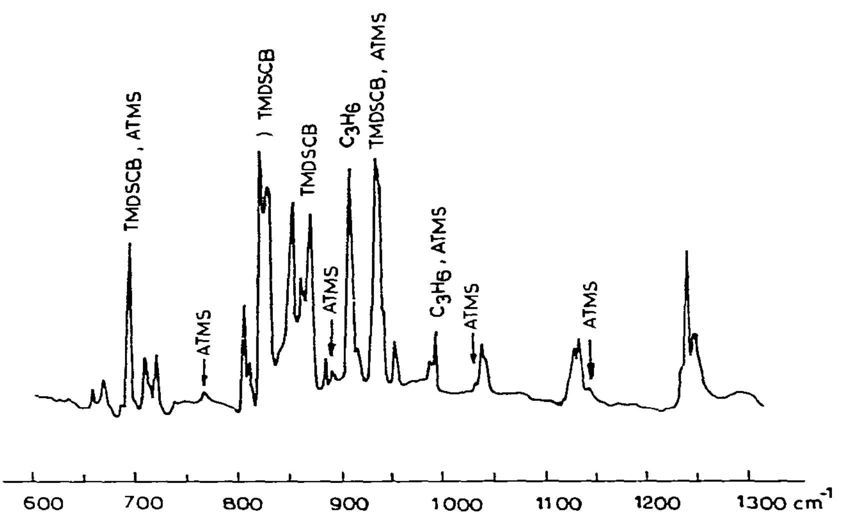


Fig. 3. Infrared spectrum of matrix isolated pyrolysis products of TMSCB in the static system at 440°C.

deuterium labeled acetylenes: 2370 (C_2D_2), 2520 and 3232 cm^{-1} (C_2HD) together with a relatively weak 3180 cm^{-1} band (C_2H_2). Other absorption bands at 543, 580, 683, 718, 722, 768, 891, 929, 985, and 1012 cm^{-1} also occuring in spectra of matrix isolated VLPP products of DMSCB-d_6 and TMSCB-d_6 may most probably be assigned to DMSE-d_6 (1,1-dimethyl-1-silaethylene).

The frequencies of normal vibrations were evaluated in order to assign the bands observed in the IR spectra of DMSE and DMSE-d_6 to the vibrational modes. By normal coordinate analysis we determined (a) the approximate number of bands in the 400—4000 cm^{-1} region of the spectrum; (b) the isotopic shifts of the bands; (c) the dependence of the frequency of the Si=C stretching vibration on the force constant f(Si=C).

Normal coordinate treatment was carried out according to the El'yashevich and Stepanov [21] method, similar to that of Wilson [22]. In accord with the well known expressions, the vibrational frequencies of molecules can be evaluated as eigen values of secular equations of the type $(\mathbf{GF} - \Lambda)\,\mathbf{L} = 0$. Here, **G** is the inverse kinetic energy matrix the elements of which are computed from the geometric parameters of molecules (the bond lengths, the bond and torsional angles) and inverse atomic masses; **F** is the force constants matrix with elements $f_{ij} = \partial^2 E/\partial Q^2$, which are usually unknown; Λ is the diagonal matrix with elements $\lambda = \nu^2$; **L** is the eigen vectors matrix. Thus, for exact normal coordinate treatment it is necessary to know both the molecular geometry and the force constants. The absence of data on f_{ij} is generally substituted by experimental values of ν_{exp} comparable with ν_{calc}. Thereafter the values of f_{ij} are so selected that the difference $\nu_{\text{exp}} - \nu_{\text{calc}}$ is a minimum (solution of inverse vibration problem). Obviously, we do not have data both on the geometry of DMSE molecule and the complete set of absorption bands. Therefore, the calculation is tentative.

According to the theoretical data [23—30], the silaethylene structure containing a silicon—carbon double p_π—p_π bond is energetically more preferred

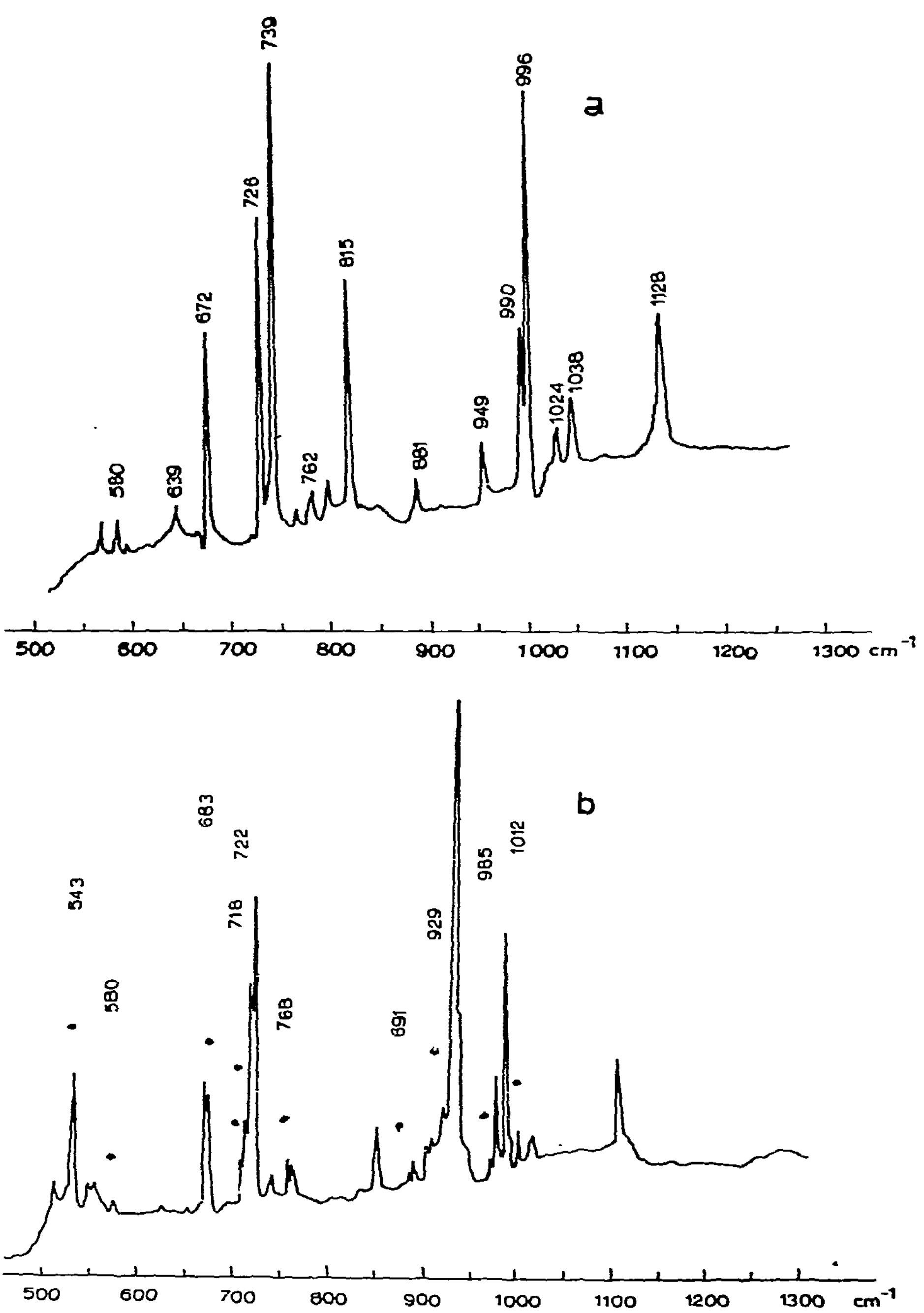


Fig. 4. Infrared spectra of matrix isolated (a) DMSCB-d_6, and (b) its VLPP products at 730°C.

than the biradical structure. Therefore, the model of the DMSE molecule with C_{2v} symmetry formed the basis for the computation. Fig. 7 shows this model together with the types and notations of the vibrational coordinates. Theoretically, such a model has 30 normal modes distributed over irreducible representations of the group C_{2v} in the following manner: 10 A_1, $5A_2$, $9B_1$ and $6B_2$,

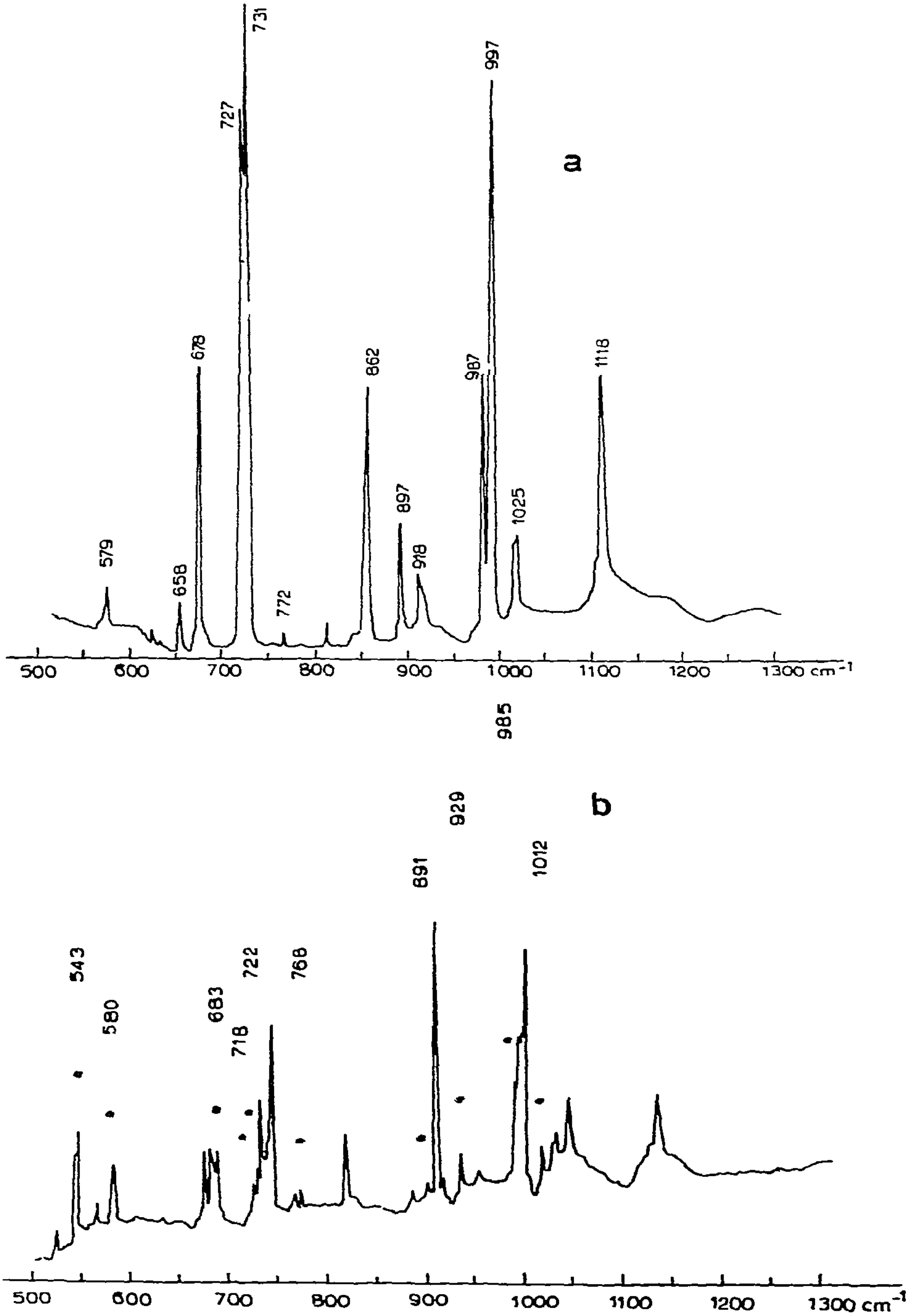


Fig. 5. Infrared spectra of matrix isolated (a) TMSCB-d_6, and (b) its VLPP products at 700°C.

only the A_2 modes being inactive in the IR spectrum. Thus the expected number of bands is reduced to 25. Three modes are assigned to the deformations of the C—Si—C group and two twisting vibrations of CH_3 groups have frequencies lower than 400 cm^{-1}, which are beyond the range of the spectrometer used.

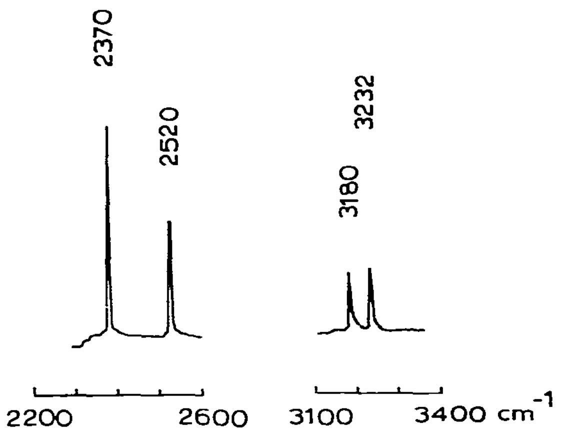


Fig. 6. Bands of C_2D_2, C_2HD, and C_2H_2 in the infrared spectrum (65 K) of DMSCB-d_6 VLPP products at 730°C.

Thus, in the 400—4000 cm^{-1} range one can observe 21 fundamental bands of the following classes of symmetry: $9A_1$, $8B_1$ and $4B_2$.

The following structural parameters were selected: r(Si=C) = 1.69 Å, r(Si—C) = 1.89 Å, r(C—H) = 1.09 Å, r(=C—H) = 1.08 Å. All the angles around double bonds are equal to 120° C, the angles in the CH_3Si group amount to 109.47°. The calculations were carried out in the coordinates of symmetry with the program developed by D.S. Bystrov (Leningrad State University). The force constants of similar molecules were taken as elements of the **F** matrix. The force constants obtained by computing the spectra of $(CH_3)_2SiH_2$ were used for the $(CH_3)_2Si$ group, whereas the force constants of the $=CH_2$ group used were those of from isobutene [21]. The values of f(Si=C) varied between 5×10^6 cm^{-2} and 12×10^6 cm^{-2}. The computed (at f(Si=C) = 9×10^6 cm^{-2}) and experimental absorption bands are given in Table 1. The assignment of experimental bands of DMSE and DMSE-d_6 to the vibrational modes was based on the comparison of isotopic shifts of bands observed in the experimental spectra with the shifts obtained in the calculation and with due regard for the fulfilment of the product rule for the frequencies of deuteroderivatives.

As it follows from the data listed in Table 1, in the spectrum of the pyrolysis products of DMSCB and TMSCB 8 (out of 21) bands can be assigned to the DMSE modes. The spectrum of the pyrolysis products of DMSCB-d_6 and TMSCB-d_6 contains 10 bands, probably produced by the absorption of DMSE-d_6. Out of these 8 were assigned to different vibrational modes. The majority of unobserved bands pertain to the characteristic vibrations of the Si—CH_3 group. Therefore, the corresponding bands in the spectra of DMSE and DMSE-d_6 are overlapped by similar bands of DMSCB and DMSCB-d_6 which are always present in the spectra of pyrolysis products.

It is worth discussing the assignments of 932 and 1001 cm^{-1} bands in the spectrum of DMSE, which correspond to the 929 and 985 cm^{-1} bands in the DMSE-d_6 spectrum. The band 932 (929) cm^{-1} was assigned to the out of plane wagging mode of the $=CH_2$ group. The basis for this was both the poor sensitivity of this vibration to the deuterium label at the CH_3 group and the closeness

TABLE 1

THEORETICAL AND EXPERIMENTAL ABSORPTION BANDS (cm^{-1}) FOR DMSE AND DMSE-d_6

Symmetry class	Vibrations [d]	DMSE		DMSE-d_6		Assignments [b]
		Calculated [a]	Experimental	Calculated [a]	Experimental	
A_1	1	2989	—	2989	—	q, Stretch, $=CH_2$
	2	2984	—	2229	—	q', Stretch, C—H
	3	2882	—	2086	—	in CH_3Si group
	4	1443	—	1442	—	γ, Bend, $=CH_2$
	5	1410	—	1036	—	α $SiCH_3$
	6	1267	1253	1016	1012	α and β CH_3Si
	7	1014	1001	977	985	Q, Stretch, Si=C
	8	867	817	684	718	β CH_3Si
	9	688	644	626	543	q_1, Stretch, Si—C_2
	10	268	—	237	—	τ, Bend, SiC_2
B_1	11	3099	—	3099	—	q, Stretch, $=CH_2$
	12	2983	—	2227	—	q', Stretch, C—H
	13	2881	—	2083	—	in CH_3Si group
	14	1409	—	1033	—	α, CH_3Si
	15	1263	—	963	—	α and β, CH_3Si
	16	1005	—	1006	—	δ, Rock, $=CH_2$
	17	868	824	648	722	β CH_3Si
	18	716	696	710	683	q_1, Stretch, SiC_2
	19	309	—	295	—	φ, Rock, SiC_2
A_2[c]	20	2967	—	2215	—	q', Stretch C—H
	21	1449	—	1062	—	α CH_3Si
	22	897	—	734	—	β CH_3Si
	23	720	—	666	—	χ, Twist $Si=CH_2$
B_2	24	2967	—	2214	—	q', Stretch C—H
	25	1450	—	1061	—	α CH_3Si
	26	912	992	702	768	β CH_3Si
	27	842	932	843	929	ρ, Wagging $=CH_2$
	28	139	—	132	—	ρ, Wagging $=SiC_2$

[a] At $f(Si=C) = 9 \times 10^6$ cm^{-2}. [b] For notations see Fig. 7. [c] Vibrations are inactive in the infrared spectrum. [d] Twisting coordinates of CH_3 group are omitted.

of an analogous band (888 cm^{-1}) in the spectrum of isobutene which is the carbon analogue of DMSE. The band at 1001 cm^{-1} (985 cm^{-1}) was assigned to the Si=C stretching vibration for two reasons. First, weak shift of the frequency of this vibration to lower frequencies when deuterated both in the experimental and computed spectra. Second, dependence of the frequency of this vibration on $f(Si=C)$, which is shown in Fig. 8. It is evident that an increase in $f(Si=C)$ from 5×10^6 to 12×10^6 cm^{-2} results in an increase of frequency $\nu(SiC)$ from 720 to 1160 cm^{-1}, i.e. a two fold growth in $f(Si=C)$ does not increase the frequency of Si=C stretch above 1200 cm^{-1}. For comparison, note that the CC stretch frequency changes from 1016 cm^{-1} (for C_2H_6) to 1622 cm^{-1} (for C_2H_4). The force constant in this case varies from 8.4×10^6 cm^{-2} to 14×10^6 cm^{-2}, i.e. increases by a factor of 1.75. Possibly, the reason for the low value of Si=C stretching is the small inverse mass of silicon (0.0389) compared to carbon (0.0906). It is also emphasized by the lower force constant than for the carbon—carbon bond. Thus, the band of Si—C stretch is hardly expected in the

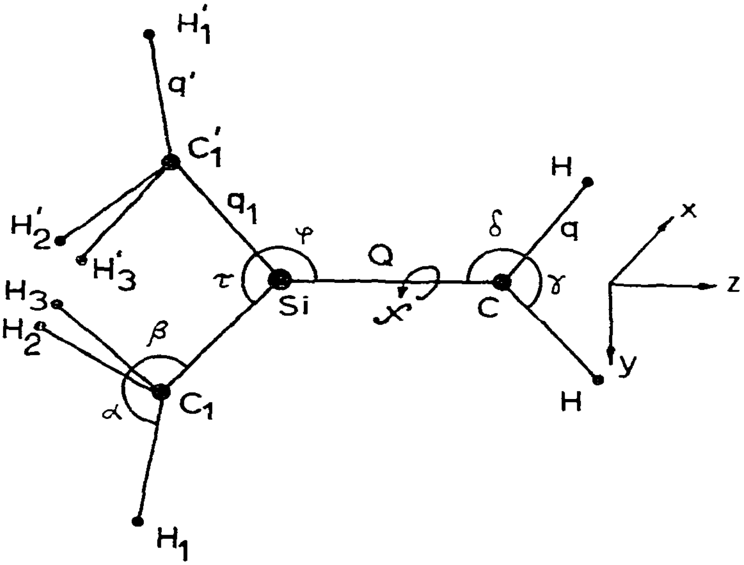


Fig. 7. C_{2v} symmetry model DMSE molecule with notations of vibrational coordinates.

range above 1200 cm^{-1}, and the computed (at $f(Si{=}C) = 9 \times 10^6\ cm^{-2}$) values 1014 and 977 cm^{-1} are very close to the 1001 and 985 cm^{-1} values observed in the spectra of DMSE and DMSE-d_6, respectively.

An eigen vector analysis shows the mixing of Si—C stretch (1152 cm^{-1}) and $=CH_2$ bend (1464 cm^{-1}) vibrations which belong to the same symmetry class A_1. A subject of controversy is the assignment suggested by Schlegel, Wolfe and Mislow [23]. They assigned the 1140 cm^{-1} band to the $=CH_2$ bend and the 1490 to the Si—C stretch. Apparently, this is due to different relationships between the values used for force constants $f(Si{=}C)$ and $f(CH_2)$ bend, which determine the contribution of the coordinates to both normal vibrations. The assignments accepted in this work are preferred for the reason that the CH_2 bend vibration is found at 1420—1450 cm^{-1}, a region normally characteristic

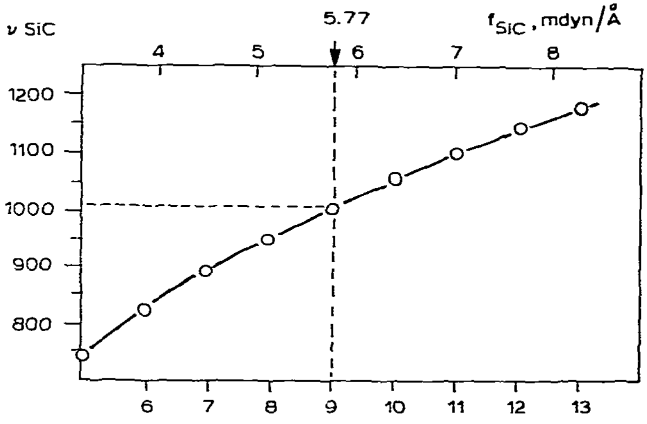


Fig. 8. Plot of frequency of Si=C stretching vibration vs. force constant $f(SiC)$.

for a vibration involving sp^2 carbon. Final improvements in these assignments will be possible after the spectra of $(CH_3)_2Si{=}CD_2$ and $(CD_3)Si{=}CD_2$ have been obtained. This work is in progress.

Note added in proof

Since the submission of the manuscript a number of relevant communications have appeared [31—38]. The band at 800 cm^{-1} assigned [31] to the Si=C stretching vibration in $Cl_2Si{=}CH_2$, is much lower than $\nu(Si{=}C) = 1001\ cm^{-1}$ in the IR spectra of VLPP products of DMSCB and TMSCB [33,35]. The latter assignment is supported [37] by $\nu(Si{=}C)$ at 1003.5 cm^{-1}. An even higher value of $\nu(Si{=}C)$ (1156 cm^{-1}) has been proposed for $H_2Si{=}CH_2$ [36]. Despite the discrepancies in the $\nu(Si{=}C)$ assignments these data together with the electron diffraction determination [38] of $r(Si{=}C) = 1.83$ Å and the thermochemical estimations [35] are indicative of $2p_\pi$—$3p_\pi$ interaction in silaethylenes. However, further spectroscopic studies are required to deduce the nature of the unsaturated silicon—carbon bond the thermally generated intermediates from monosilacyclobutanes.

References

1 L.E. Gusel'nikov, N.S. Nametkin and V.M. Vdovin, Uspekhi Khim., 43 (1974) 1317.
2 L.E. Gusel'nikov, N.S. Nametkjin and V.M. Vdovin, Acc. Chem. Res., 8 (1975) 18.
3 H. Sakurai, Kadaku no ryoiki (J. Japanese Chem.), 29 (1975) 742.
4 P. Jutzi, Angew. Chem., Int. Ed., 14 (1975) 232.
5 W.E. Dasent, Nonexistent Compounds, Marcel Dekker, New York, 1965, p. 61.
6 C.J. Attridge, Organometal. Chem. Rev., "A", 5 (1970) 323.
7 L.E. Gusel'nikov, K.S. Konobeevsky, V.N. Vdovin and N.S. Nametkin, Dokl. Akad. Nauk SSSR, 235 (1977) 1086.
8 T.J. Barton and C.L. McIntosh, J. Chem. Soc., Chem. Commun., (1972) 861.
9 O.L. Chapman, C.-C. Chang, J. Kolc, M.E. Jung, J.A. Lowe, T.J. Barton and M.L. Tumey, J. Amer. Chem. Soc., 98 (1977) 7844.
10 A.K. Maltsev, V.N. Kabashesku and O.M. Nefedov, Dokl. Akad. Nauk SSSR, 233 (1977) 421.
11 M.R. Chedekel, M. Scoglund, R.L. Kreeger and H. Shechter, J. Amer. Chem. Soc., 98 (1976) 7846.
12 A.G. Brook, J.W. Harris, J. Lennon and M.El. Sheikh, J. Amer. Chem. Soc., 101 (1979) 83.
13 N.S. Nametkin, V.M. Vdovin and P.L. Grinberg, Dokl. Akad. Nauk SSSR, 150 (1963) 799.
14 D.R. Weyenberg and L.E. Nelson, J. Org. Chem., 30 (1965) 2618.
15 A.E. Barnes and J.D.R. Howells, J. Chem. Soc. Farad. II, 69 (1973) 532.
16 N.I. Bagdanskis, M.O. Bulanin and Yu.V. Fadeev, Optika i spektroskopia, 29 (1970) 687.
17 A. Cabana, G.B. Savitsky and D.F. Hornig, J. Chem. Phys., 39 (1963) 2942.
18 N.S. Nametkin, R.L. Ushakova, L.E. Gusel'nikov, E.D. Babich and V.M. Vdovin, Izv. Akad. Nauk SSSR, Ser. Khim., (1970) 1676.
19 L.E. Gusel'nikov, N.S. Nametkin and N.N. Dolgopolov, J. Organometal. Chem., 169 (1979) 165.
20 L.M. Sverdlov, M.A. Kovner and E.P. Kraynov, Vibrational Spectra of Polyatomic Molecules (in Russian), Nauka, Moscow, 1970.
21 M.V. Vol'kenstein, L.A. Gribov, M.A. El'yashevich and B.I. Stepanov, Molecular Vibrations (in Russian), Nauka, Moscow, 1972.
22 E.B. Wilson, Jr., J. Chem. Phys., 7 (1939) 1047; 9 (1941) 76.
23 H.B. Schlegel, S. Wolfe and K. Mislow, J. Chem. Soc., Chem. Commun., (1975) 246.
24 M.D. Curtis, J. Organometal. Chem., 60 (1973) 63.
25 R. Damrauer and D.R. Williams, J. Organometal. Chem., 66 (1974) 241.
26 M.J.S. Dewar, D.H. Lo and C.A. Ramsden, J. Amer. Chem. Soc., 97 (1975) 1311.
27 R. Ahlrichs and R. Heinzman, J. Amer. Chem. Soc., 99 (1977) 7452.
28 S. Bantle and R. Ahlrichs, Chem. Phys. Lett., 53 (1978) 148.
29 O.P. Strausz, M.A. Robb, G. Theodorakoupoulos, P.G. Mezey and I.G. Csizmadia, Chem. Phys. Lett., 48 (1977) 162.
30 D.M. Hood and H.F. Schaefer, J. Chem. Phys., 68 (1978) 2985.

31 J. Laane, R.M. Irwin, J.R. Ohlsen, M.M. Strube and M.A. Hartcock, 177th ACS National Meeting, Honolulu, Hawaii, 1979, Abstracts, PHYS 318.
32 A.K. Maltsev, V.N. Khabashesku and O.M. Nefedov, Izv. Akad. Nauk SSSR, Ser. Khim., (1979) 2152.
33 L.E. Gusel'nikov, V.V. Volkova and V.G. Avakyan, All-Union Conference on Low Temperature Chemistry, Moscow, November 1979, Abstracts, p. 57.
34 V.N. Khabashesku, A.K. Matsev and O.M. Nefedov, All-Union Conference on Low Temperature Chemistry, Moscow, November 1979, Abstracts, p. 53.
35 L.E. Gusel'nikov and N.S. Nametkin, Chem. Revs., 79 (1979) 529.
36 N. Auner and J. Grobe, Z. Anorg. Allg. Chem., 459 (1979) 15.
37 A.K. Maltsev, V.N. Khabashesku, E.N. Baskir and O.M. Nefedov, Iszv. Akad. Nauk SSSR, Ser. Khim., (1980) 222.
38 P.G. Mahaffy, R. Gutowsky and L.K. Montgomery, J. Amer. Chem. Soc., 102 (1980) 2854.