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Matrix IR spectroscopic study of the vacuum pyrolysis of octamethylcyclotetrasiloxane, allyloxy- and allyl(allyloxy)dimethylsilanes as well as 2,2,6-trimethyl-2-silapyrane as potential sources of dimethylsilanone *

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Abstract

The mechanism of vacuum pyrolysis of octamethylcyclotetrasiloxane, allyloxy- and allyl(allyloxy)-dimethylsilanes, and 2,2,6-trimethyl-2-silapyrane, potential sources of transient dimethylsilanone, has been studied by matrix isolation IR spectroscopy. Only in the case of allyloxydimethylsilane is there direct evidence of silanone $(CH_3)_2Si{=}O$ formation, by observation of its most intense band at 798 cm^{-1} in the matrix IR spectrum of pyrolysis products. In all other cases the intermediate, $(CH_3)_2Si{=}O$, was found to be thermally unstable, undergoing fragmentation into SiO molecules and CH_3 radicals, thus indicating silanone participation in the reactions studied.

Introduction

Silanones $R_2Si{=}O$ (I) are postulated as intermediates in a great number of thermal and photochemical reactions of organosilicon compounds [1]. These assumptions have usually been based on the composition of final reaction products, chemical trapping experiments, and kinetic data, but only direct physical methods, such as matrix IR spectroscopy [2] should elucidate unambiguously the mechanisms involved in the formation of I.

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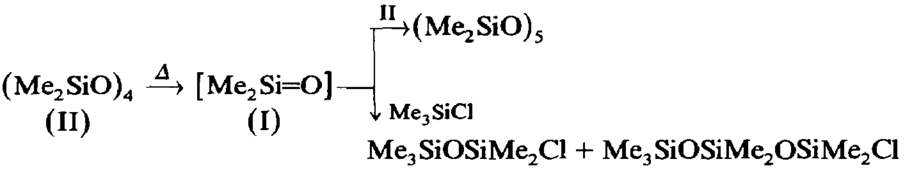
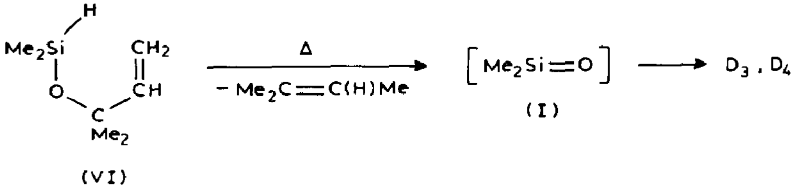
Matrix IR spectroscopy was used to study the intermediates in gas-phase pyrolytic reactions [3] and allowed the first intermediate with Si=C multiple bond to be identified [4,5]. We recently [6] stabilized dimethylsilanone (I, $R = CH_3$) and its deuteromethyl analog (I, $R = CD_3$) and recorded matrix IR spectra (Ar, 12 K) of the intermediates generated by vacuum pyrolysis of 3,3-dimethyl-6-oxa-3-silabicyclo[3.1.0]hexanes and of Diels–Alder adducts of 2,2-dimethyl-2-silapyranes to maleic anyhydride. In order to study the possibility of thermal generation and stabilization of I from another source, an IR spectroscopic study of the vacuum pyrolysis of octamethylcyclotetrasiloxane (II), allyloxydimethylsilane (III), allyl(allyloxy)dimethylsilane (IV) as well as 2,2,6-trimethyl-2-silapyrane (V) was carried out and is described herein. The formation of cyclosiloxanes D_3 and D_5 under thermolysis of II is best described as a monomolecular elimination [7] of the labile intermediates I, which are then able to further insert into the siloxane bonds. Kinetic data [8] on the gas-phase pyrolysis of II and the formation of products of the insertion of I into Si–Cl bond in trimethylchlorosilane under co-pyrolysis of the latter with II also indicate the participation of transient I in the reaction 1.



$$\underset{(II)}{(Me_2SiO)_4} \xrightarrow{\Delta} \underset{(I)}{[Me_2Si{=}O]} \begin{cases} \xrightarrow{II} (Me_2SiO)_5 \\ \xrightarrow{Me_3SiCl} Me_3SiOSiMe_2Cl + Me_3SiOSiMe_2OSiMe_2Cl \end{cases} \qquad (1)$$

It is known [1], that thermal decomposition of allyl-substituted silanes proceeds by retroene reaction with formation of transient species having a Si=C multiple bond, such as silabenzene, silatoluene, dimethylsilaethylene. The kinetic data on the gas-phase pyrolysis of a similar compound, (vinyldimethylcarbinoxy)dimethylsilane (VI), obtained previously [9], and the latest results of Barton [10] on thermolysis of compounds III and VI, also indicate the participation of intermediate I in reaction 2.



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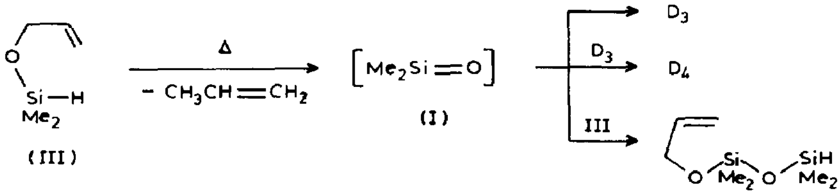
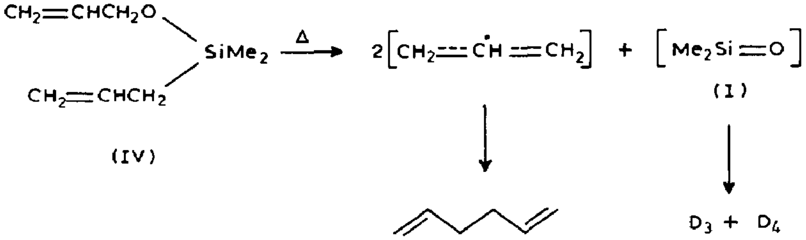


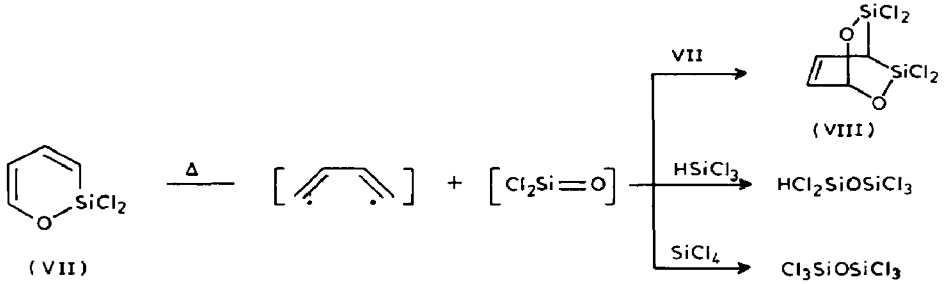
(3)

Allyl(allyloxy)dimethylsilane (IV) was proposed by Barton [11] as being the source of I in the gas phase. The generation of I by pyrolysis of IV has been suggested to be the result of consecutive loss of two allyl radicals. 1,5-Hexadiene and cyclosiloxanes D_3 and D_4 were the final pyrolysis products of IV.



(4)

Here we have studied the vacuum pyrolysis of 2,2,6-trimethyl-2-silapyran (V) and compared the results with data previously published [12] on the thermal decomposition of a similar compound, 2,2-dichloro-2-silapyrane (VII). Data on the chemical trapping of $Cl_2Si{=}O$ intermediates starting with compound VII to give the [2 + 4] cycloaddition product (VIII) and those of the products after insertion into the Si–H bond of trichlorosilane and the Si–Cl bond of tetrachlorosilane are regarded [12] as indirect evidence of thermal generation of silanone from compound VII (eq. 5).



(5)

Experimental

Vacuum pyrolysis of the parent compounds II–V was carried out between 700 and 1100 °C at pressures of 1 to 1×10^{-4} Torr in a flow quartz reactor of internal diameter 5–8 mm and length 50–90 mm. The flow rate of the samples was regulated by grease-free valve made from teflon and glass. The matrix IR spectra of the intermediates were obtained by use of a quartz pyrolyzer coupled to an optical helium cryostat, in which the pyrolysis products were frozen with an excess of argon (1000/1) on the mirror copper plate at 12 K. A closed-cycle refrigerator (Air Products CSW 208R) was used to cool the plate. A layer of sufficient thickness to afford IR spectra of good intensity forms after 0.5–1.5 h.

Spectra were recorded in the range of 400–4000 cm^{-1} by reflection of an IR beam from the mirror plate. This arrangement allows the IR beam to pass twice through the solid matrix layer before entering the monochromator of the LOMO-IKS-24 IR spectrophotometer, via a hand-made optical system. In order to identify the intermediates, controlled warming of the matrix from 12 K to 35–40 K with subsequent recooling to 12 K was carried out.

The final pyrolysis products of II–V were analyzed by GLC and GLC-MS after the condensate from cryostat was refrozen in the trap with solvent at 77 K.

Commercially available siloxane II was purified to 98–99% by distillation. Allyloxysilane III was prepared by a published procedure [13], by reaction of dimethyldichlorosilane with allyl alcohol in the presence of Py. The purity of III was as high as 98% after its rectification and additional purification by preparative GLC. Compound IV was obtained analogously from allyl alcohol and dimethyl(allyl)chlorosilane, which was obtained from the reaction of allylmagnesium chloride with dimethyldichlorosilane. IV was isolated by preparative GLC from the reaction mixture with a purity of 98% by preparative GLC. 2,2,6-Trimethyl-2-silapyrane V was obtained by the reaction of methylmagnesium bromide with 2,2-dichloro-6-methyl-2-silapyrane, synthesized by thermal interaction of trichlorosilane with 2-methylfurane [12]. The final product V was isolated with a purity of 97–98% by rectification and additional purification by preparative GLC.

Results

Thermal decomposition of siloxane II in vacuum (5×10^{-2}–5×10^{-3} Torr) proceeded at significantly higher temperatures than the conditions, used by other workers [8]. The matrix IR spectrum bands of the pyrolysis products of II began to appear at 900 °C, with significant conversion of II being observed at 1000–1050 °C. Matrix IR spectrum of pyrolysis products of II at 1030 °C and 5×10^{-3} Torr is depicted in Fig. 1. The most intense bands in the spectrum are due to the main thermolysis product, cyclosiloxane D_3. Bands of other stable products, methane,

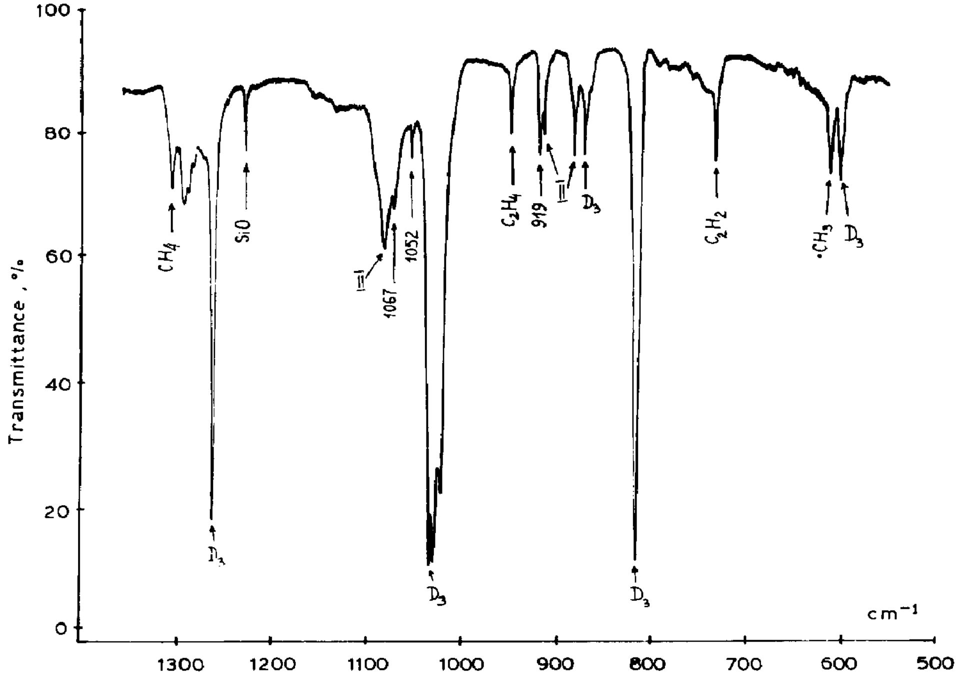


Fig. 1. The matrix IR spectrum (Ar, 12 K) of the vacuum pyrolysis products of octamethylcyclotetrasiloxane (II) at 1030 °C and 5×10^{-3} Torr. The bands of the cyclodimer of I, 1,1,3,3-tetramethyl-1,3-cyclodisiloxane (IX), are marked.

acetylene, ethylene and unstable products of SiO (1225 cm^{-1} [14]), CH_3 radical (617 cm^{-1}) and weak bands of the cyclodimer of silanone I, 1,1,3,3-tetramethyl-1,3-cyclodisiloxane (IX), at 1067, 1052 and 919 cm^{-1} [6] were also present in the spectrum. Our spectrum showed none of the bands that could be attributed to dimethylsilanone I when compared with previously obtained data [6]. On warming the matrix from 12 to 40 K and repeated cooling to 12 K the bands of SiO and methyl radical disappeared at first. Bands of cyclodimer IX disappeared completely but only after longer heating of the matrix.

Vacuum pyrolysis of allyloxydimethylsilane III was carried out at 800–1050 °C and 5×10^{-2}–5×10^{-3} Torr. From the matrix IR spectroscopy data, the thermal decomposition of III in vacuo starts at temperatures above 850 °C. The bands due to propylene, methane, ethylene, acethylene as well as weak bands of SiO, methyl (617 cm^{-1}) and allyl (801.5 cm^{-1} [15]) radicals were observed in the matrix IR spectrum (Fig. 2) of pyrolysis products of III at 900 °C and 5×10^{-3} Torr. In

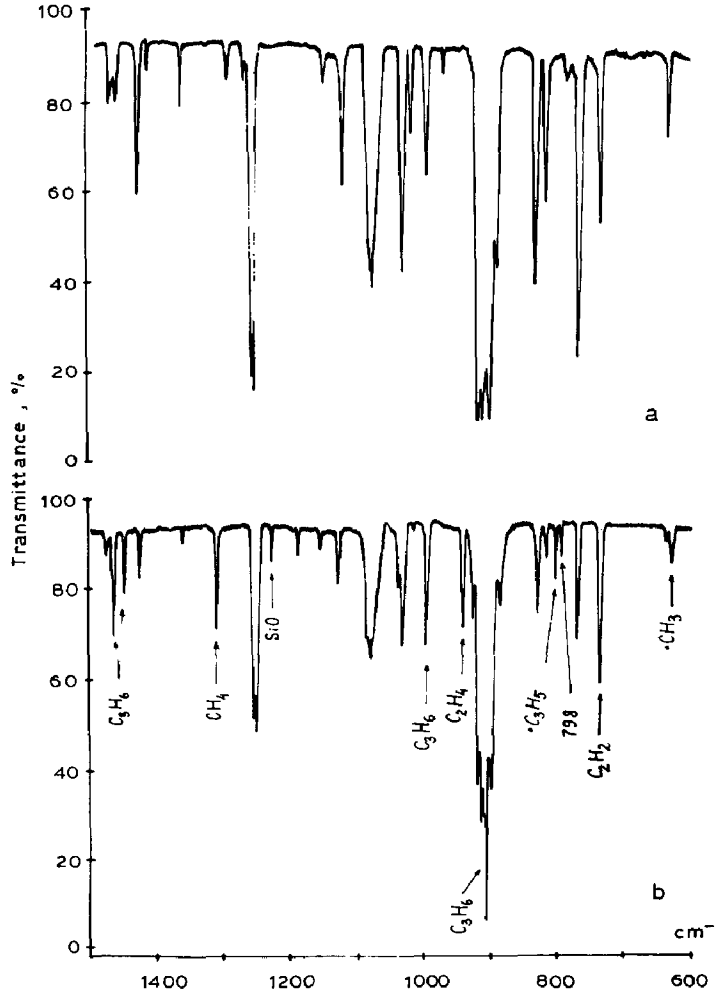


Fig. 2. (a) The matrix IR spectrum (Ar, 12 K) of allyloxydimethylsilane (III). (b) IR spectrum of pyrolysis products of III (900 °C, 5×10^{-3} Torr), frozen in an Ar matrix at 12 K.

addition to the bands mentioned, a single weak band at 798 cm^{-1}, the most intense in the IR spectrum of silanone I according to our data [6], was detected. On warming the matrix from 12 to 40 K all the bands of the less stable products disappeared leaving the bands of the starting compound III and those of the stable molecules in the spectrum.

An increase in the pyrolysis temperature up to 1030–1050 °C led to complete conversion of III. However, the band at 798 cm^{-1}, attributable to silanone I, is not present in these spectra under these conditions; but the intensification of the bands of all the other pyrolysis products was observed.

Marked decomposition of allyl(allyloxy)dimethylsilane IV was observed under pyrolysis in vacuo (1×10^{-2}–5×10^{-3} Torr), at temperatures above 900 °C. The most intense bands were due to the allyl radical at 801.5, 976, 984, 1386 and 1475 cm^{-1} [15], with weaker bands due to CH_3 radical (617 cm^{-1}), SiO (1225 cm^{-1}) and

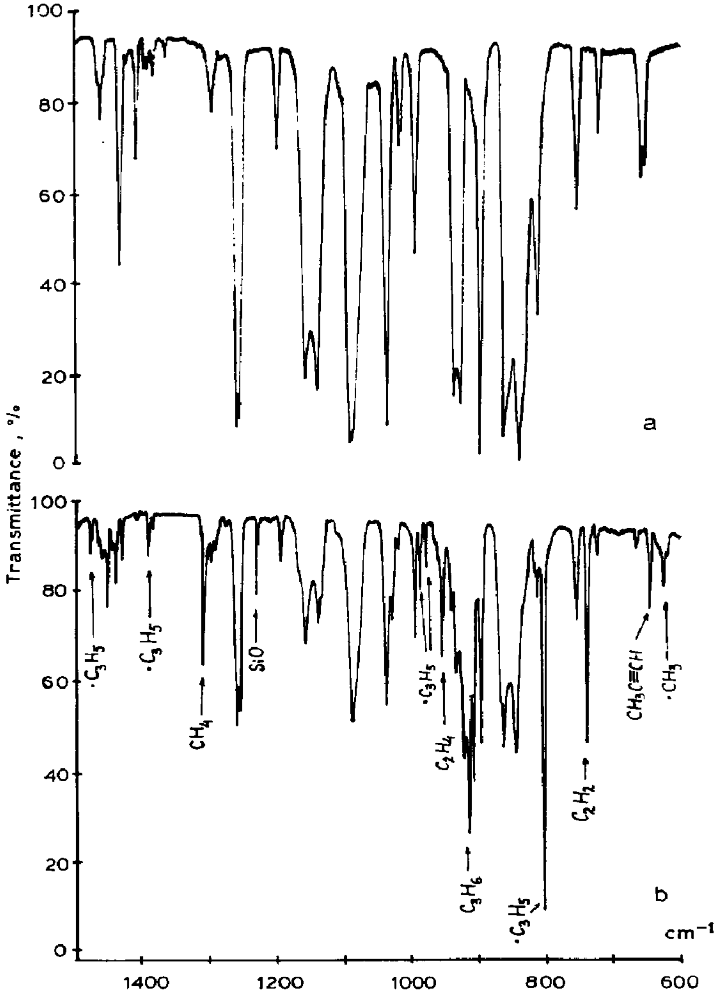


Fig. 3. (a) The matrix IR spectrum (Ar, 12 K) of allyl(alloxy)dimethylsilane (IV). (b) IR spectrum of pyrolysis products of IV (985 °C, 1×10^{-2} Torr), frozen in an Ar matrix at 12 K.

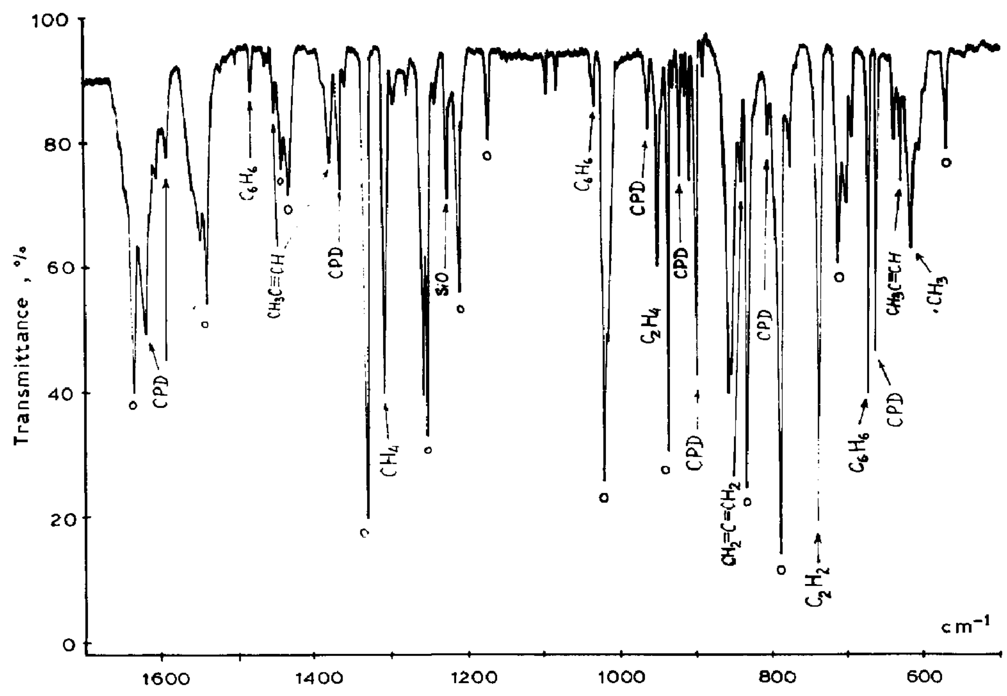


Fig. 4. The matrix IR spectrum (Ar, 12 K) of pyrolysis products of 2,2,6-trimethyl-2-silapyrane (V) at temperature 1050 °C and pressure 1×10^{-2} Torr. The bands of the starting compound V (o) and cyclopentadiene (CPD) are marked.

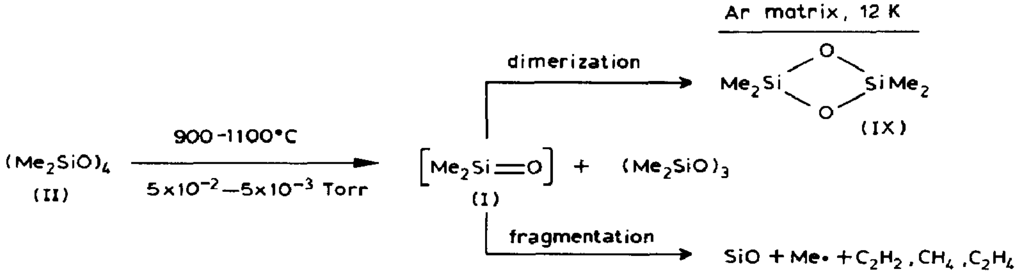
bands due to propylene, acethylene, methane, ethylene, methylacetylene and 1,5-hexadiene also present in the matrix IR spectra, one of which is shown in Fig. 3. On warming the matrix from 12 up to 40 K, the bands of CH_3 and C_3H_5 radicals and those of the SiO molecules disappeared, while the intensity of the 1,5-hexadiene band at 914 cm^{-1} grew. The bands of dimethylsilanone I [6] were not detected in the spectra of the pyrolysis products of IV.

The most thermostable of the compounds II–V under conditions of vacuum pyrolysis was 2,2,6-trimethyl-2-silapyrane (V). The bands of any pyrolysis products of V (at 5×10^{-2}–5×10^{-3} Torr, and 1000 °C) were not observed in the matrix IR spectra. The appearance of new bands in spectra occurred only at higher temperatures (1050–1110 °C). The matrix IR spectrum of the pyrolysis products of V at 1050 °C and 1×10^{-2} Torr is shown in Fig. 4. In addition to the bands of unchanged starting compound, bands were present from cyclopentadiene (662, 806, 896, 916, 959, 1092, 1241, 1293, 1369, 1590, 1622 cm^{-1} [16]), benzene (675, 1037 and 1492 cm^{-1} [17]), acethylene (737 cm^{-1}), methylacethylene (629, 1380 and 1454 cm^{-1}), allene (839 cm^{-1}), methane (1305 cm^{-1}), ethylene (947 cm^{-1}), SiO (1225 cm^{-1}) and CH_3 radical (617 cm^{-1}). On warming the matrix from 12 up to 40 K the bands of SiO and CH_3 radical disappeared completely, while the band intensities of all other compounds, formed during the pyrolysis of V, did not change. The same products were identified in the IR spectrum of the pyrolysis products of V, frozen at 12 K without dilution by argon. GLC-MS analysis of these products, re-cooled into a trap coupled to a cryostat confirmed the presence of cyclopentadiene as the main product of the thermolysis of V under the present conditions.

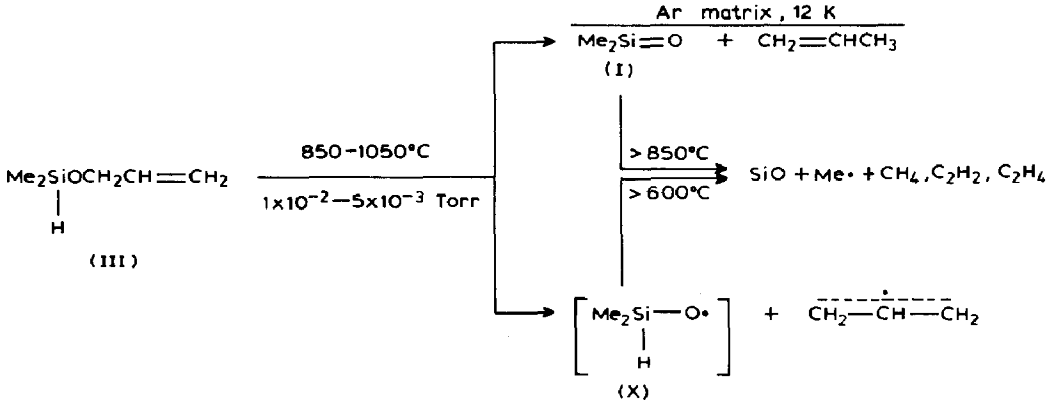
Discussion

In a previous matrix IR spectroscopic study of vacuum pyrolysis of 3,3-dimethyl-6-oxa-3-silabicyclo[3.1.0]hexane and Diels–Alder adducts of 2,2-dimethyl-2-silapyranes to maleic anhydrides [6] we established the upper limits of the thermal (~ 850 °C) and kinetic (~ 5×10^{-4} Torr) stability of dimethylsilanone I in the gas phase. The upper limit of thermal stability was regarded as that temperature, above which the fragmentation of an intermediate begins. Accordingly, the upper limit of kinetic stability means that pressure in the pyrolysis zone, which if increased further results in secondary reactions of I in the gas phase to give cyclodimer IX (D_2) [6,18] and cyclotrimer D_3. The data on the properties of monomeric dimethylsilanone I in the gas phase are consistent with the results on the vacuum pyrolysis of compounds II–V, obtained in the present work.

It should be noted first of all, that because of the high decomposition temperature (~ 850 °C) of these compounds in vacuo, we had to carry out the pyrolyses only at pressures above 5×10^{-3} Torr, to ensure that the number of collisions with heated wall of reactor is sufficient for the visible conversion of compounds II–V. However, these conditions are not optimal for the monomeric silanone I, and this is probably why the bands of cyclodimer IX instead of the bands of silanone I are present in the matrix IR spectrum of the pyrolysis products of cyclosiloxane II (Fig. 1). A high pyrolysis temperature (1030 °C) enhanced the thermal instability of I and it fragmented (in accordance with our data [6]) into SiO, CH_3 radical, methane, ethylene and acethylene. The results on the pyrolysis of II in vacuo are represented in Scheme 1.



Scheme 1.



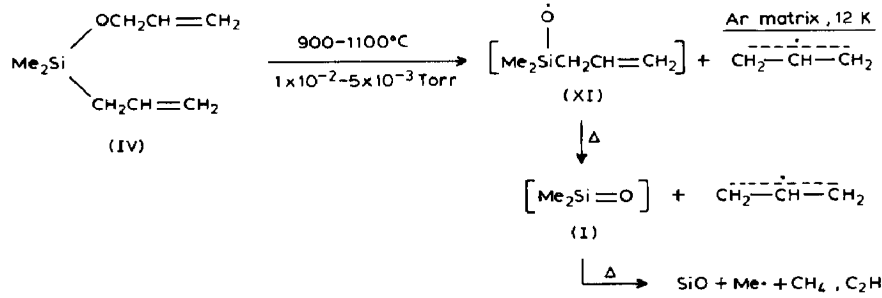
Scheme 2.

The intense bands of propylene in the matrix IR spectrum of the pyrolysis products of allyloxydimethylsilane (Fig. 2) testify to retroene reaction, which should also lead to silanone I in accordance with stoichiometry. Owing to the high temperature of decomposition of III in vacuo, leading to fragmentation of I, we observed only one (the most intense for I) band attributable to silanone I, but interestingly at 940 ° C. At higher temperatures only the products of the decomposition of I were observed. The detection of the most intense band of the allyl radical, at 801.5 cm^{-1}, in the spectrum (Fig. 2) suggests a parallel radical decomposition of III with formation of allyl and dimethylsiloxyl X radicals. On the basis of pyrolysis-MS data [19] the radicals X are thermally unstable above 600 ° C and decompose into the same fragments as silanone I does.

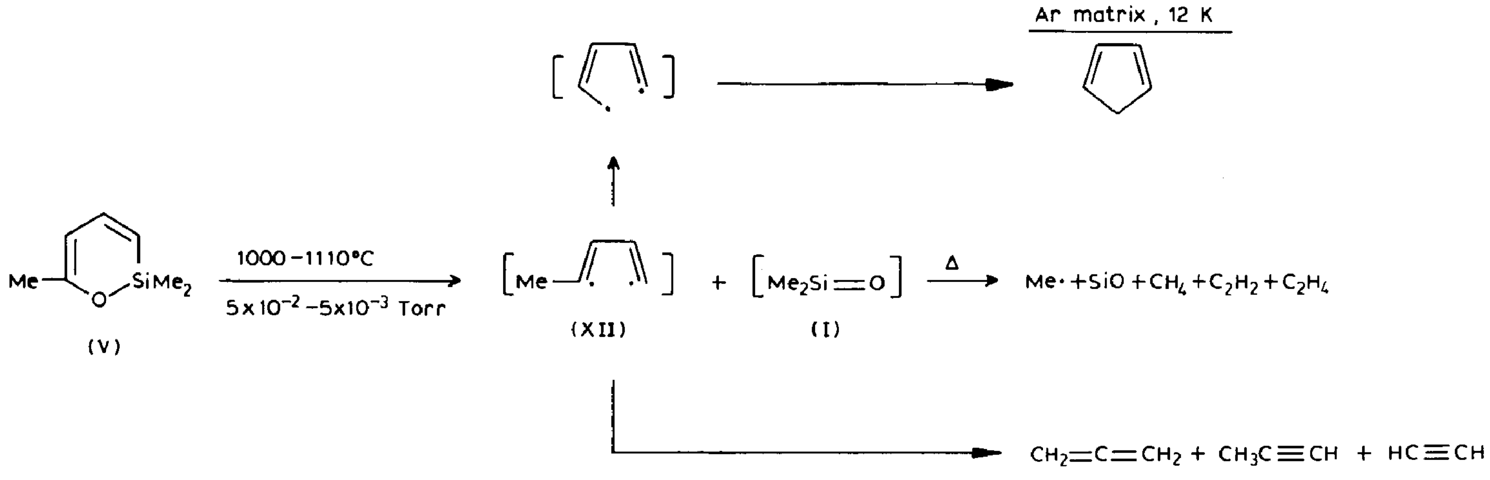
Thus, in contrast to thermolysis of allyloxydimethylsilane in a flow system [10], the decomposition of III in vacuo can be described not only as a molecular mechanism, but also as a radical one, proceeding in parallel (Scheme 2).

Though both thermolyses mechanisms of III depend on the breaking of the same C–O bond, the retroene (molecular) pathway of reaction is more preferable than the simultaneous formation of two free radicals, because the six-membered transition state requires less activation energy (54.6 kcal/mol [10]). This is probably why much more propylene than allyl radical is formed in the reaction.

In contrast, the vacuum pyrolysis of diallyl-substituted silane IV proceeds mainly with formation of allyl radical, with significantly less propylene being formed. Here there is consecutive loss of two allyl radicals from IV. The first step consists in the breaking of the allyl–oxygen bond, which ($\sim$ 52 kcal/mol [20]) is significantly less strong than the allyl–silicon bond ($\sim$ 73 kcal/mol [21]). The breaking of the last bond in the transient allyldimethylsiloxyl radical (XI) is probably more facile than the retroene reaction in which propylene is lost from XI. This assumption is consistent with the kinetic [21] and direct spectroscopic data [22] on the mechanism of the allyltrimethylsilane pyrolysis. At the same time, the high temperature of decomposition, > 900 ° C, of IV in vacuo is the reason why no bands of silanone I, but the bands of its fragmentation products, SiO, CH_3 radical, CH_4, C_2H_2, C_2H_4, are present in the matrix IR spectrum of the pyrolysis products of IV (Fig. 3). The formation of small amounts of products such as propylene, methylacetylene and 1,5-hexadiene is probably due to the secondary recombination and disproportionation reactions of the allyl radical. The appearance of all the products of the pyrolysis of I in vacuo is outlined in Scheme 3.



Scheme 3.


Me
SiMe$_2$
O
(V)
1000–1110°C
5x10^{-2}–5x10^{-3} Torr
Me
(XII)
+
Me$_2$Si=O
(I)
Δ
Me· + SiO + CH$_4$ + C$_2$H$_2$ + C$_2$H$_4$
Ar matrix, 12 K
CH$_2$=C=CH$_2$ + CH$_3$C≡CH + HC≡CH

Scheme 4.

The highest decomposition temperature of the compounds, studied here (~ 1000 °C) that of silapyrane V in vacuo is clearly the reason why there are no IR bands of silanone I in the spectrum. Thus the formation of SiO molecule, CH_3 radical as well as methane and ethylene is a direct result of the fragmentation of I. At the same time, the appearance of cyclopentadiene bands in the spectrum (Fig. 4) is probably because of isomerization and further intramolecular cyclization of the biradical, XII, formed as a transient species under thermolysis of V. In a parallel reaction XII also undergoes fragmentation into methylacetylene, allene, and acetylene (Scheme 3). It is rather difficult to interpret the appearance of the bands attributable to benzene in the spectrum. The formation of benzene is probably the result of bimolecular reactions taking place under the high-temperature conditions used.

Thus matrix IR spectroscopy data show the vacuum pyrolysis of compounds II–V to take place as outlined in the schemes and including the transient formation of dimethylsilanone through both the molecular and radical pathways. It is noteworthy that because of the high temperature of decomposition in vacuo of the compounds studied the direct spectroscopic observation of silanone I (from its most intense band at 798 cm^{-1}) was possible here only in the case of pyrolysis of allyloxydimethylsilane (III). In all other cases, the IR spectrum showed only the bands of the fragmentation products of I, namely SiO molecule and CH_3 radical [6]. Thus there is only indirect evidence of the participation of the transient dimethylsilanone, which is highly unstable under the present conditions.

Acknowledgment

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