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DIRECT DETECTION OF UNSTABLE INTERMEDIATES FROM THE PYROLYSIS

OF ALLYLTRIMETHYLSILANE BY MEANS OF MASS SPECTROMETRY

AND MATRIX IR SPECTROSCOPY

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The spectroscopic detection and study of a new class of compounds possessing the C=Si double bond is associated to a considerable degree with the use of the gas-phase thermal decomposition of silacyclobutanes and allylsilanes [1]. In particular, on the basis of the products of chemical trapping it was proposed [2] that thermal dissociation of allyltrimethylsilane (I) occurs by reaction (1) with the formation of the highly reactive 1,1-dimethyl-1silaethylene (II):

$$\begin{array}{c} \text{AllSiMe}_3 \xrightarrow{\Delta} C_3 H_6 + CH_2 = \text{SiMe}_2 \\ (I) & (II) \end{array} \tag{1}$$

On the other hand, according to kinetic data [3], (I) decomposes with cleavage not of a propylene molecule, but of an allyl radical:

 $\begin{array}{c} \text{AllSiMe}_3 \xrightarrow{\Delta} .C_3 H_5 + .\text{SiMe}_3 \\ (\text{III}) \end{array} \tag{2}$ 

and the formation of (II) is a consequence of a secondary intermolecular disproportionation reaction of the radicals [4]:

 $.SiMe_3 + .SiMe_3 \rightarrow HSiMe_3 + CH_2 = SiMe_2$ (3)

With the aim of elucidating the mechanism of the thermal decomposition of (I) we have undertaken a direct study of the intermediates of this reaction by mass spectrometry and in parallel by matrix IR spectroscopy.

The mass spectrometric method has been previously applied for the detection of both species (II) (as its ion  $C_3H_8Si^+$  with m/z 72) [5, 6] and the radical (III) (as the ion  $C_2H_5^+$ 

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with m/z 41) [7-10], as well as for measurement of their ionization potentials [6, 7]. On the other hand, by utilizing the method of matrix isolation reliable values have been obtained of the vibrational frequencies of the species (II) [11-14] and (III) [15], which permit them to be detected in complex mixtures of reaction products.

### EXPERIMENTAL

For mass spectrometric detection of the primary pyrolysis products we used the equipment described in [16], which is based on the mass spectrometers MKh 7301 and MKh 7303, with a quartz pyrolysis reactor (internal diameter 3 mm and length of heating zone 40 mm) connected directly to the ionization chamber. Pyrolysis of compound (I) was carried out at a pressure of  $10^{-2}$  torr, as well as in a mixture with helium (1:100) at a total pressure of  $\sim 1 \times 10^{-1}$  torr and a contact time of  $10^{-3}$  sec.

For the IR spectroscopic study of the products of vacuum pyrolysis of (I) an apparatus was used for freezing out the intermediate species in an argon matrix at 12°K. The main unit of the apparatus was an optical cryostat with a base of CsI cooled by a closed-cycle cryogenic system. To the cryostat was connected a quartz pyrolyzer similar to that used for the mass spectrometric study. Dilution of the pyrolysis products with argon during formation of the matrix was greater than 1000:1. The spectra were recorded by means of a Hitachi-Perkin-Elmer-225 IR spectrophotometer.

# DISCUSSION OF RESULTS

Mass Spectrometry. In order to analyze the changes in the mass spectra of (I) when the temperature was raised from 20 to 1050°, the relative intensities (with respect to the ion  $[M-15]^+$  with m/z 99) of all the fragment ions were calculated. At reactor temperatures up to 700° no changes in the fragmentation of (I) occurred. Above this temperature an increase was observed of the relative intensity of the ions with m/z 59 (C<sub>2</sub>H<sub>7</sub>Si<sup>+</sup>), 42 (C<sub>3</sub>H<sub>6</sub><sup>+</sup>), 41 (C<sub>3</sub>H<sub>5</sub><sup>+</sup>), 40 (C<sub>3</sub>H<sub>4</sub><sup>+</sup>), 39 (C<sub>3</sub>H<sub>3</sub><sup>+</sup>), 28 (C<sub>2</sub>H<sub>4</sub><sup>+</sup>), 26 (C<sub>2</sub>H<sub>2</sub><sup>+</sup>), 16 (CH<sub>4</sub><sup>+</sup>), and 15 (CH<sub>3</sub><sup>+</sup>), as well as some decrease in the proportion of the [Si(CH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> ion with m/z 73. However, at an electron-beam energy of 70 eV the ion [CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> with m/z 72, corresponding to the molecular ion of silaethylene (II), was practically absent.

The increase in the relative intensity of the  $C_3H_6^+$  ion  $(m/z \ 42)$  due to the formation of propylene could be a result both of reaction (1) and of the secondary reaction of the allyl radical, initially formed by reaction (2). As determined by us, the intensity of the  $C_3H_6^+$  ion grew with increase in the pressure, which facilitates the occurrence of secondary reactions, and indicates to a significant degree the secondary origin of the  $C_3H_6$  molecule. None-theless, the intensity of the  $C_3H_6^+$  ion peak at low pressure indicates the partial formation of propylene by reaction (1). A direct demonstration of the relative intensity of the  $(C_3H_5)^+$  ion  $(m/z \ 41)$ , which can be formed both by dissociative ionization of propylene and the initial compound, and by direction ionization of the allyl radical. The ratio of the intensities of the ions  $I_{42}:I_{41}:I_{40}:I_{39}$  in the mass spectrum of propylene, which we obtained separately under the experimental conditions, was 65:100:30:80. In the pyrolysis of (I) this ratio changed and the intensities of the ions with  $m/z \ 41$ , 40, and 39 were anomalously high with respect to  $I_{42}$ , which demonstrates the additional formation of the  $C_3H_5^+$  ion (-17%) due to ionization of the allyl radical.

The second dissociation product of molecule (I) by reaction (2) — the trimethylsilyl radical — cannot be recorded by the mass spectrometric method, evidently owing to its thermal instability at high temperatures. When the pyrolysis temperature was raised above 700° an increase in the intensities of only the ions with m/z 28, 26, 16, and 15 was observed, indicating the formation of  $C_2H_4$ ,  $C_2H_2$ , and  $CH_4$ , which are the most likely products of the thermal decomposition of Si( $CH_3$ )<sub>3</sub>. This is also indicated by the formation of a solid precipitate of silicon on the reactor walls in the pyrolysis zone.

Analysis of a possible contribution to the intensity of the  $CH_3^+$  ion (m/z 15) as a result of the fragmentation of the molecules (I),  $C_3H_6$ , and  $CH_4$  showed that these processes can explain the observed value of  $I_{15}$  being not more than 20%. The presence of free methyl radicals formed by thermal decomposition of the  $Si(CH_3)_3$  radical must be responsible for the high intensity of the  $CH_3^+$  ion. On the other hand, decomposition of the allyl radical is not the source of the  $CH_3$  radicals, which was indicated in our mass spectrometric study of the pyrolysis of allyl bromide, in which the  $CH_3^+$  ion was practically not observed.



Fig. 1. If spectra (Ar matrix, 12 K): a) products of the pyrolysis of AllSiMe<sub>3</sub> at 950° and a pressure of  $10^{-4}$  torr [(1) AllSiMe<sub>3</sub>, 2) Me<sub>2</sub>Si = CH<sub>2</sub>, 3)  $\overline{CH_2-CH-CH_2}$ ]; b) AllSiMe<sub>3</sub>.

It is interesting that not only is the  $Si(CH_3)_3$  radical unstable but also the  $[Si(CH_3)_3]^+$ ion with m/z 73. Fragmentation of the molecular ion  $(AllSiMe_3)^+$ , obtained by ionization (70 eV) of the molecule (I), which had passed through the pyrolyzer at a temperature above 700° without dissociation, differs from the fragmentation of the same ion at lower temperatures. In the first case a fragment ion with m/z 73 is observed with a 40% reduced intensity, which may be due to its more ready decomposition because of excess vibrational energy [17].

With increase in pressure in the pyrolysis zone not only is the additional formation of propylene observed, but also growth of the ion peak at m/z 59, which is the most intense in the mass spectrum of HSiMe<sub>3</sub> — a product of secondary reactions of the  $\cdot$ SiMe<sub>3</sub> radical.

Matrix IR Spectroscopy. Study of the pyrolysis products of (I) frozen in an argon matrix at 12°K revealed that the matrix IR spectrum (Fig. 1a) compared with the spectrum of the original compound (I) (see Fig. 1b) exhibited a new band at 801.2 cm<sup>-1</sup> as well as weak bands at 509, 983.2, 1389, 1477, 1602, and 3107 cm<sup>-1</sup>. These bands were absent from the spectrum of the pyrolysis products frozen at 12°K without dilution with argon, although the bands of all the stable molecules were retained in the spectrum. Exactly the same set of IR bands obtained for the frozen pyrolysis products of allyl chloride, bromide, or iodide, as well as 1,5-hexadiene disappear when the matrix is heated [15]. This shows that the unstable species isolated in the matrix, characterized by the indicated frequencies, is a common product of these pyrolytic reactions, i.e., the free allyl radical (III).

A full analysis of the matrix IR spectra of the pyrolysis products (Table 1) permits the remaining bands to be assigned to known molecules, the composition of which is found to be in agreement with the mass spectrometric data. They are propylene (908.7, 996.4, 1373, 1438, and 1453 cm<sup>-1</sup>), acetylene (736.5, 3288, 3302 cm<sup>-1</sup>), trimethylsilane (902.5, 2108 cm<sup>-1</sup>), meth-ane (1305 cm<sup>-1</sup>), as well as the CH<sub>3</sub> radical (616.7 cm<sup>-1</sup>). The weak bands at 837 and 1954 cm<sup>-1</sup> are assigned to allene, and those at 630 and 3322 cm<sup>-1</sup> to the isomeric molecule — methyl-acetylene. The spectra do not show the presence of compounds (CH<sub>3</sub>)<sub>3</sub>Si-CH=CH<sub>2</sub> and (CH<sub>3</sub>)<sub>4</sub>Si, which are the main pyrolysis products of (I) at pressures close to atmospheric [18, 19]. Of special interest is the presence in the spectrum of bands at 1003, 825.0, 817.5, and 642.9 cm<sup>-1</sup>, which, as is now reliably established [11-14], characterize the silaethylene molecule

v, cm <sup>-1</sup>	Assignment	v, cm <sup>-1</sup>	Assignment
$\begin{array}{c} 3322.\\ 3302\\ 3288\\ 3275\\ 3239\\ 3107\\ 3089\\ 3034-3013\\ 2965\\ 2940\\ 2925\\ 2887\\ 2108\\ 1954\\ 1651\\ 1653\\ 1602\\ 1477\\ 1453\\ 1438\\ 1426\\ 1421\\ 1435\\ 1438\\ 1426\\ 1421\\ 1415\\ 1394\\ 1388,5\\ 1373\\ 1334\\ 1326\\ 1326\\ 1326\\ 1305\\ 1292\\ 1263\\ 1255\\ 1249\\ 1194\\ \end{array}$	$\begin{array}{c} CH_{3}C \equiv CH\\ C_{2}H_{2}\\ C_{2}H_{2}\\ C_{2}H_{2}\\ C_{3}H_{3}\\ AllSiMe_{3}\\ v(=CH_{2})\\ v(C-H) CH_{3}\\ v(C-H) CH_{4}\\ v(C-H) CH_{4}\\ v(C-H) CH_{4}\\ v(C-H) CH_{4}\\ v(C-H) CH_{4}\\ websliH\\ CH_{2}=C=CH_{2}\\ C_{3}H_{6}\\ C_{3}H_{6}\\ C_{3}H_{6}+C_{2}H_{4}\\ AllSiMe_{3}\\ C_{2}H_{2}\\ CH_{4}\\ AllSiMe_{3}+Me_{3}SiH\\ AllSiMe_{3}\\ \end{array}$	$\left\{\begin{array}{c} 1049\\ 1043\\ 1030\\ 1027\\ 1003\\ 996,4\\ 992,0\\ 983,2\\ 946,9\\ 930,9\\ 930,9\\ 930,9\\ 948,3\\ 908,7\\ 902,5\\ 893,0\\ 856,3\\ 893,0\\ 856,3\\ 852,2\\ 842,0\\ 837,0\\ 825,0\\ 847,5\\ 840\\ 801,2\\ 797,3\\ 765,6\\ 736,5\\ 736,5\\ 736,5\\ 736,5\\ 736,5\\ 736,5\\ 736,6\\ 736,5\\ 736,5\\ 736,6\\ 736,5\\ 736,5\\ 736,2\\ 202,2\\ 616,7\\ 577,4\\ 554\\ \end{array}\right\}$	$\begin{array}{c} ?\\ C_{3}H_{6}\\ AllSiMe_{3}\\ (CH_{3})_{2}Si=CH_{2}\\ C_{3}H_{6}\\ AllSiMe_{3}\\ C_{2}H_{4}\\ AllSiMe_{3}\\ C_{2}H_{4}\\ AllSiMe_{3}\\ C_{2}H_{4}\\ AllSiMe_{3}\\ C_{3}H_{6}\\ Me_{3}SiH\\ AllSiMe_{3}+Me_{3}SiH\\ CH_{2}=C=CH_{2}\\ (CH_{3})_{2}Si=CH_{2}\\ (CH_{3})_{2}Si=CH_{2}\\ ?\\ C_{3}H_{6}\\ AllSiMe_{3}\\ AllSiMe_{3}\\ C_{2}H_{2}\\ AllSiMe_{3}+CH_{3}C=CH\\ CH_{3}\\ CO_{2}\\ (CH_{3})_{2}Si=CH_{2}\\ AllSiMe_{3}+CH_{3}C=CH\\ CH_{3}\\ C_{3}H_{6}\\ AllSiMe_{3}\\ \end{array}$
1101	AIIOIMI63	000	03110

TABLE 1. Vibrational Frequencies of the Pyrolysis Products of AllSiMe<sub>3</sub> in an Argon Matrix at 12°K (950°, 10-4 torr)

(II). The IR bands of (II) are relatively increased in the case where pyrolysis is carried out at a lower pressure, which is an indication of the formation of (II) in the primary reaction (1). However, under these conditions the IR bands of (III) are more intense than the bands of (II) (see Fig. 1a). The data presented, which relate to the pyrolysis of (I) at  $850-950^{\circ}$  and a pressure of  $10^{-3}$  to  $10^{-4}$  torr, indicate that reactions (1) and (2) proceed in parallel.

Raising the pressure in the reaction zone to  $10^{-2}$  torr and above, resulting in an increase in the number of intermolecular collisions, is shown up by an increase in the IR bands of HSiMe<sub>3</sub> and C<sub>3</sub>H<sub>6</sub> and a relative decrease in the bands of silaethylene (II) and the radical (III). Mass spectrometric identification of HSiMe<sub>3</sub> as its fragment with m/z 59 and increase in intensity of the peak as well as of the C<sub>3</sub>H<sup>4</sup> ion peak with increase in pressure agrees with the IR spectroscopic observation of secondary processes under analogous conditions.

Thus, both species (II) and (III) are primary products of the pyrolysis of (I), and compounds  $HSiMe_3$ , and in part  $C_3H_6$ , are formed as a consequence of secondary reactions.

When the pyrolysis temperature was raised to  $1000^{\circ}$ , the intensities of the bands due to (II) in the matrix IR spectra were reduced, which according to the results of [13] indicate the thermal instability of (II) at such high temperatures. The absence from the mass spectra of an ion with m/z 72 corresponding to (II) under pyrolysis conditions in a stream of helium at a pressure of  $10^{-1}$  torr evidently is also explained by a low transient concentration of (II) due to its thermal dissociation. Under the same conditions the allyl radical, however, is a much more stable species and can be clearly recorded both in the mass spectra and in the matrix IR spectra.

We did not detect the second intermediate product of reaction (2) - the radical  $\cdot$ SiMe<sub>3</sub> - either by matrix IR spectroscopy or by mass spectrometry. Evidently, it is thermodynamically

unstable during vacuum pyrolysis and is decomposed with formation of the molecules  $CH_4$ ,  $C_2H_2$ ,  $C_2H_4$ , and  $\cdot CH_3$  radical enclosed in the matrix, as well as of the solid deposit of silicon.

The possibility of stabilization of the  $\cdot$ SiMe<sub>3</sub> radical under the experimental conditions was specially checked by studying the matrix IR spectra of the products of the pyrolysis of the compound Me<sub>3</sub>SiSiMe<sub>3</sub> which occurs, according to the kinetic data in [20], by dissociation into  $\cdot$ SiMe<sub>3</sub> radicals. In this case in our matrix spectra bands of new unstable species were also absent and the main products of the vacuum pyrolysis of Me<sub>3</sub>SiSiMe<sub>3</sub> were C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and CH<sub>4</sub>. The presence of the  $\cdot$ SiMe<sub>3</sub> radical in the reaction system can only be followed from the formation of its stable end product of the secondary reaction HSiMe<sub>3</sub>, the concentration of which is increased when the pressure is increased in the pyrolysis zone.

Comparison of the mass spectrometric and IR spectroscopic results shows the important role of fragmentation of the allyl radical under electron impact for quantitative evaluation. Increase in the intensity of the ion peaks of  $C_3H_4^+$  (m/z 40) and  $C_3H_3^+$  (m/z 39), which was observed in the mass spectra with increase in the pyrolysis temperature, together with increase in I<sub>41</sub> of the molecular ion of the allyl radical  $C_3H_5^+$ , could be due to the pyrolytic formation of allene. However, the IR spectra indicate the absence of a substantial concentration of allene and methylacetylene among the reaction products at temperatures below 900°. Therefore, the ions  $C_3H_4^+$  and  $C_3H_3^+$  should be formed mainly by fragmentation of the  $C_3H_5^+$  ion, and the ratio of their relative intensities is characteristic for the mass spectrometric detection of the allyl radical. From our prior evaluation taking account of the allene contribution, determined experimentally by pyrolysis of allyl bromide, the ratio is  $I_{41}:I_{40}:I_{39} = 25:45:100$ .

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# CONCLUSIONS

1. A parallel detection of the primary unstable products of the vacuum pyrolysis of allyltrimethylsilane has been carried out by means of mass spectrometry and matrix IR spectroscopy, and it has been established that dissociation of this compound occurs both into free allyl and trimethylsilyl radicals and simultaneously into propylene and silaethylene.

2. The radical 'SiMe<sub>3</sub> is unstable under the conditions of vacuum pyrolysis at temperatures above 700° and decomposes with formation of  $C_2H_4$ ,  $C_2H_2$ ,  $CH_4$ , and methyl radicals.

3. The allyl radical is characterized by the ratio of the intensities of the ions generated during its dissociative ionization and the vibrational frequencies in the matrix IR spectra.

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MASS-SPECTROMETRIC INVESTIGATION OF THE THERMOCHEMICAL

CHARACTERISTICS OF PERCHLORYL FLUORIDE AND ITS

DECOMPOSITION PRODUCT - CHLOROSYL FLUORIDE

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The thermochemical characteristics of the perchloryl fluoride molecule  $ClO_3F$  and the chlorosyl fluoride radical ClOF have been studied very little. The heat of formation has been corrected:  $\Delta H_{f~298}^{*}(ClO_3F) = -22.6\pm1.0 \text{ kJ/mole [1]}$ ; the upper limit of the adiabatic ionization potential  $IP(ClO_3F) = 12.975$  eV has been determined by photoelectron spectroscopy [2]. The information on the binding energy of atoms in the  $ClO_3F$  molecule [3] is only approximate, due to the poor precision of the determination of the appearance potentials (AP) of positive and negative ions. Data on the ClOF molecule existing in the free state are not available. When investigating the ionization of the chloryl fluoride molecule  $ClO_2F$ , the electron affinity  $EA(ClOF) \ge 2.00\pm0.19$  eV was determined [4]. The wrong value of  $\Delta H_{f~0}^{*}$ -(ClOF) is given in [4] (see further text for discussion). An approximate value of  $\Delta H_{f~0}^{*} = 298^{-}(ClOF)$  corresponds to -46 kJ/mole [5]. Quantum-chemical calculations gave IP(ClOF) = 12.02 eV [6]. The binding energies of the atoms in the ClOF molecule have not been determined. The present work was undertaken in order to determine new and to correct the existing thermo-chemical characteristics of the  $ClO_3F$  and ClOF molecules.

### EXPERIMENTAL

The work was carried out on a reconstructed MKh-1303 mass spectrometer; the measuring procedure has been described in [7]. Interaction of  $ClO_3 F$  with the construction material of the vacuum system of the mass spectrometer and the substances adsorbed on it leads to the decomposition of  $ClO_3 F$  with the formation of HF, HCl, ClF,  $ClO_2$ , and ClOF. This decomposition can be eliminated practically completely by passivation according to the procedure described in [4] and cooling with liquid N<sub>2</sub> of parts of the ion source and the analyzer chamber of the mass spectrometer.

### DISCUSSION OF RESULTS

The mass spectra, AP, and kinetic energies  $(E_k)$  of the positive and negative ions obtained in the present work and in [3] are presented in Tables 1 and 2. The ionization efficiency curves (IEC) of the negative ions and of the positive ion Cl<sup>+</sup> are shown in Figs. 1-3.

Tables 1 and 2 show a significant discrepancy between the experimental data obtained in this work and in [3]. In distinction from [3], we have also found the ions  $ClOF^+$ ,  $ClOF^-$ , and  $OF^-$  in the spectrum of  $ClO_3F$ . In [3] the relative intensity of practically all fragment ions is higher than in the present work. Decomposition products of  $ClO_3F$  were evidently present in the gas investigated in [3]. This can also explain the poor precision in the determination of the AP of the ions in this work.

 $ClO_3F^+$  Ion. The value of IP(ClO\_3F) obtained is in agreement with the results in [3] and is located in the interval between the first and second adiabatic IP(ClO\_3F) [2]. This is in accordance with the opinion expressed earlier [8]: the AP of the ions determined by

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