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MASS SPECTRA OF 3,3-DIMETHYL-3-SILATHIETANE AND 3,3-DIETHYL-2,4-DIMETHYL-3-SILATHIETANE. FIRST OBSERVATION OF SILATHIONE IONS AND CALCULATION OF THEIR HEATS OF FORMATION

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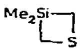
Summary

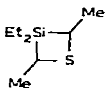
3,3-Dimethyl-3-silathietane (I) and 3,3-diethyl-2,4-dimethyl-3-silathietane (II) have been investigated by electron impact and photoionization mass spectrometry. The loss of ethylene molecules resulting in the formation of silathione ions $[Me_2Si{=}S]^{+\cdot}$ (m/z 90) and $[Et_2Si{=}S]^{+\cdot}$ (m/z 118) is the main fragmentation process of their molecular ions. In addition, cleavage of the four-membered ring "in half" — a common feature of cyclobutane compounds, results in the formation of silaethylene ions $[Me_2Si{=}CH_2]^{+\cdot}$ (m/z 72) and $[Et_2Si{=}CH(Me)]^{+\cdot}$ (m/z 114). The ionization energies for the molecules and the appearance energies for silathione and silaethylene ions have been measured by photoionization mass spectrometry. The heats of formation of the parent compounds and of characteristic ions have also been calculated.

Introduction

Until recently, stable four-membered heterocycles containing silicon and other Group VI elements in the ring were not known. The first compound of this type, 3,3-diethyl-2,4-dimethyl-3-silathietane (II) was reported by Voronkov, Barton, Kirpichenko, Keiko and Pestunovich [1]; subsequently 3,3-dimethyl-3-silathietane (I) [2] was synthesized



(I)



(II)

Of interest was the study of the dissociative ionization of these molecules, particularly of the formation of ions and neutral molecules with double p_π—p_π bonds at the silicon atom [3—6]. The present paper discusses the dissociative ionization of 3-silathietanes I and II, and reports the first observation of silathione ions in electron impact mass spectra. We also report the ionization energies for molecules I and II, the appearance energies for characteristic ions, measured by photoionization mass spectrometry, and their heats of formation.

Experimental

Mass spectra of the compounds studied were obtained on a LKB-2091 mass spectrometer using the heated inlet system (electron current 25 μA, ionization chamber temperature 200°C). The energies of ionizing electrons were 70 and 12 eV. The ionization efficiency curves were obtained on a MC-1302 photoionization mass spectrometer; the vacuum monochromator used had a resolution of 2—3 Å. The samples were admitted into the ion source from a reservoir heated up to 100°C. The curves were obtained for energies varying from threshold to 12 eV.

The methods of preparation of the studied compounds and their properties are discussed in refs. 1 and 2.

Results and discussion

The mass spectra of 3-silathietanes I and II recorded at 12 and 70 eV are given in Table 1 (the intensities are expressed in per cent of the base peak). Table 2 contains the ionization energies of the molecules and the appearance energies of ions for 3-silathietanes. Schemes 1 and 2 show the electron impact decomposition modes of the compounds studied which have been confirmed with the use of metastable ions.

Intense peaks of molecular ions $M_I^{+\cdot}$ and $M_{II}^{+\cdot}$ are observed in mass spectra of I and II. Analogous to the electron impact decomposition of monosilacyclobutanes [3] and thietanes [4] "in half", the fragmentation of 3-silathietanes would be expected to proceed mainly via similar ring cleavage. Thus, the presence of intense peaks due to rearrangement of ions $[M_I - C_2H_4]^{+\cdot}$, $[M_{II} - C_4H_7^\cdot]^+$, and $[M_{II} - C_4H_8]^{+\cdot}$ in the mass spectra of I (Table 1, Scheme 1) and II (Table 1, Scheme 2) is quite unexpected. These peaks have significant intensities in the spectra recorded at 70 eV, and dominate on lowering the energy of ionizing electrons down to 12 eV. The increase in peak intensities of $[M_I - C_2H_4]^{+\cdot}$, $[M_{II} - C_4H_7^\cdot]^+$, and $[M_{II} - C_4H_8]^{+\cdot}$ in low voltage mass spectra indicates that the rearrangement proceeds more readily at low energies of ionizing electrons.

Beside these decompositions, ring cleavage "in half" also takes place which gives rise to ion radicals of dimethylsilaethylene $[Me_2Si{=}CH_2]^+$ (m/z 72) (I) and 1,1-diethyl-2-methyl-1-silaethylene $[Et_2Si{=}CHMe]^{+\cdot}$ (m/z 114) (II) as a result of loss of thioformaldehyde and thioacetaldehyde, respectively.

The competitive expulsion of alkyl substituents at the silicon atom of the molecular ions is insignificant due to ready cleavage of the four-membered ring by the above described mechanisms (Table 1). Nevertheless, as it might be

TABLE 1

MASS SPECTRA (RELATIVE INTENSITIES) OF COMPOUNDS I AND II AT 12 AND 70 eV

m/z	I		II	
	12 eV	70 eV	12 eV	70 eV
41	—	—	—	2.1
42	—	—	—	2.1
43	—	29.6	—	—
44	—	84.8	—	2.3
45	—	84.8	3.4	12.5
46	—	35.2	2.8	7.5
47	—	17.6	—	—
48	—	2.4	—	—
53	—	19.2	—	3.7
54	—	4.8	—	1.5
55	—	17.6	—	10.3
56	—	4.8	—	6.3
57	—	12.0	—	18.8
58	—	5.6	—	62.5
59	—	8.0	—	14.1
60	—	5.6	—	4.7
61	—	13.6	—	12.5
62	—	1.6	—	2.9
63	—	1.6	—	9.4
65	—	1.2	—	—
66	—	1.6	—	—
67	—	1.6	—	—
70	—	13.6	—	—
71	—	12.4	—	12.4
72	26.2	100.0	—	2.7
73	4.6	20.0	—	2.3
74	—	7.2	—	—
75	—	41.6	—	2.6
76	—	4.8	—	—
77	—	4.8	—	4.1
83	—	—	—	3.2
84	—	—	—	1.3
85	—	1.6	—	10.0
86	—	—	4.3	100.0
87	—	2.0	1.0	15.3
88	—	—	—	4.5
89	—	1.6	—	15.6
90	100.0	71.2	6.1	37.5
91	4.7	7.2	2.0	17.8
92	7.5	6.4	—	3.5
93	—	—	—	1.2
103	2.8	4.8	—	1.3
111	—	—	—	2.3
113	—	—	—	1.0
114	—	—	8.7	17.2
115	—	—	5.9	5.6
116	—	—	1.0	1.2
117	—	—	1.7	9.4
118	77.6	32.8	85.2	62.5
119	8.4	3.2	100.0	50.0
120	9.5	3.2	17.0	8.0
121	—	—	8.4	3.6
145	—	—	12.1	8.4
146	—	—	3.9	1.9
147	—	—	1.5	1.1
161	—	—	1.3	1.1
174	—	—	50.4	18.8
175	—	—	7.9	3.0
176	—	—	4.4	1.8

TABLE 2

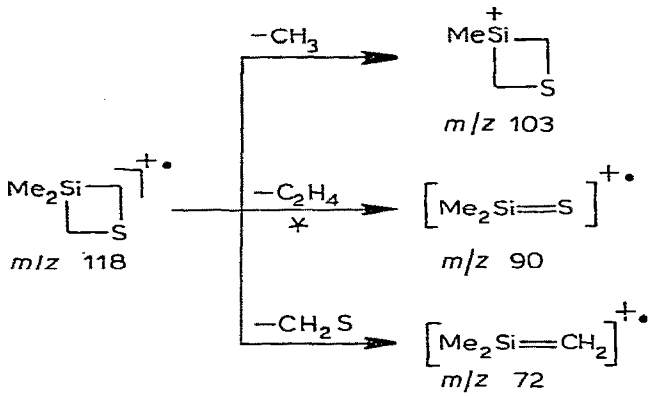
APPEARANCE ENERGIES OF IONS IN PHOTOIONIZATION MASS SPECTRA OF 3-SILATHIETANES

Ion	I		II	
	m/z	Appearance Energy (eV)	*m/z*	Appaerance Energy (eV)
$M^{+\cdot}$	118	8.25 ± 0.03 [a]	174	7.92 ± 0.03 [a]
$[M - 29]^+$		—	145	9.02 ± 0.03
Et_2SiSH		—	119	8.69 ± 0.03
$[Et_2Si{=}S]^{+\cdot}$		—	118	8.81 ± 0.03
$[Et_2Si{=}CHMe]^{+\cdot}$			114	9.91 ± 0.03
$[Me_2Si{=}S]^{+\cdot}$	90	9.23 ± 0.03	—	—
$[Me_2Si{=}CH_2]^{+\cdot}$	72	9.15 ± 0.04	—	—

[a] Adiabatic ionization energy.

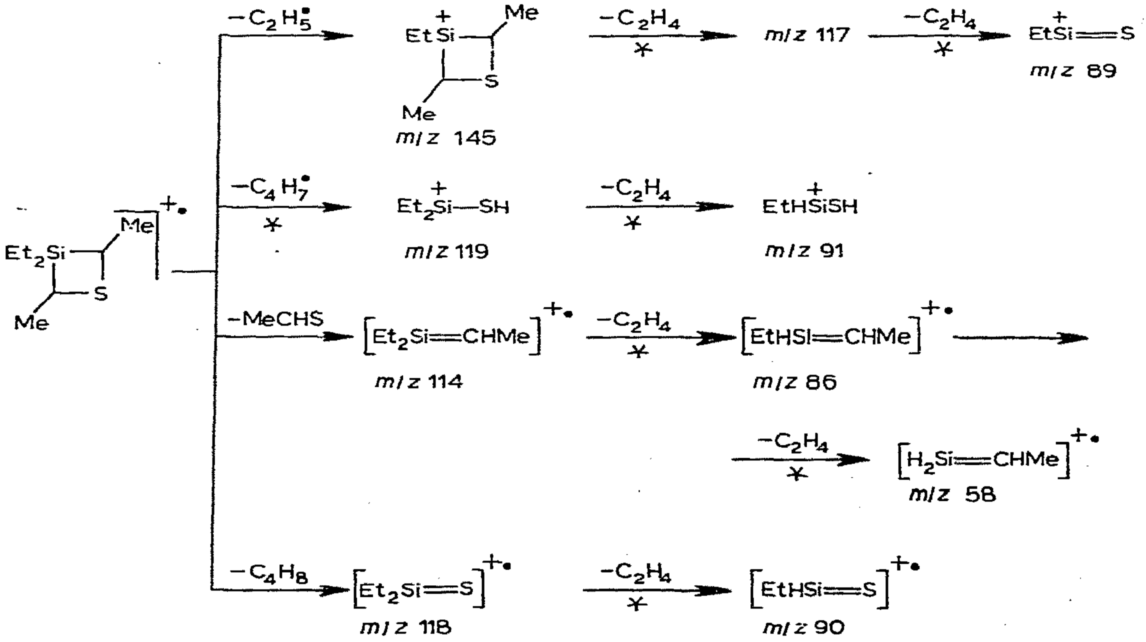
SCHEME 1

3,3-DIMETHYL-3-SILATHIETANE



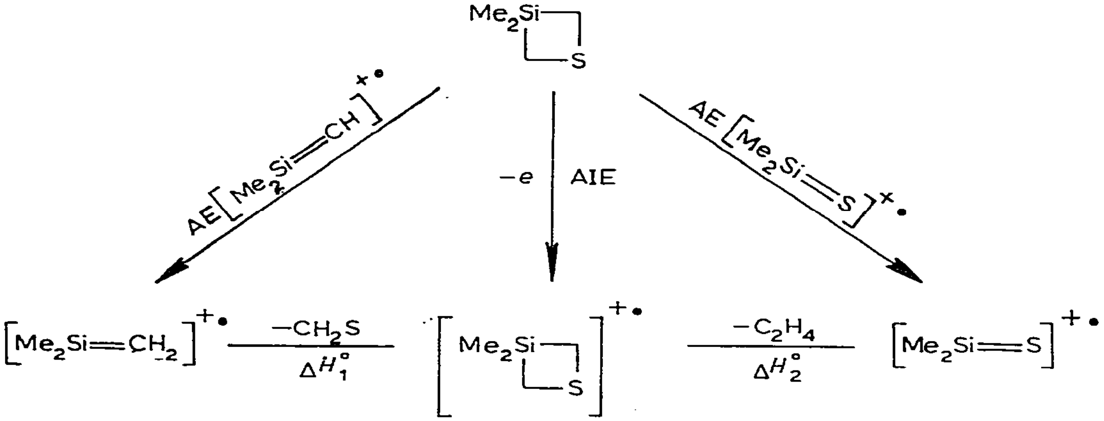
SCHEME 2

3,3-DIETHYL-2,4-DIMETHYL-3-SILATHIETANE



expected, the much heavier $C_2H_5^{\cdot}$ group (compound II, Table 1) is easily lost compared to the $CH_3^{\cdot}$ radical (compound II, Table 1). It should be mentioned that compound II (Scheme 2) decomposes due to the loss of a $C_4H_7^{\cdot}$ radical from the ion $M_{II}^{+\cdot}$. The intensity of the cation $[M_{II} - C_4H_7^{\cdot}]^+$ increases compared to that of the ion $[M_{II} - C_4H_8]^{+\cdot}$ as the ionization energy is decreased to 12 eV. Thus, the presence of an alkyl substituent at position 2 from the sulphur atom in the ring most probably stimulates the rearrangement process, giving rise to the $[M_{II} - C_4H_7^{\cdot}]^+$ ion with probable structure $Et_2\overset{+}{Si}{-}SH$. The ions $[M_{II} - C_4H_7^{\cdot}]^+$, $[M_{II} - C_4H_8]^{+\cdot}$, and $[M_{II} - MeCHS]^{+\cdot}$ further decompose by losing one or two molecules of ethylene. Successive loss of ethylene molecules from the $[M_{II} - C_2H_5]^{+\cdot}$ ion is also observed. The corresponding peaks have significant intensities in the spectra recorded at 70 eV, the peak of the $[M_{II} - 29 - 2\,C_2H_4]^{+\cdot}$ ion being higher than that of the $[M_{II} - 29 - C_2H_4]^{+\cdot}$ ion (Scheme 2).

SCHEME 3



AIE = Adiabatic ionization energy

AE = Appearance energy

The processes constituting the thermodynamic cycle shown in Scheme 3 can be described by eqs. 1 and 2, containing two unknown quantities: $\Delta H_f^0(Me_2Si{=}S)^{+\cdot}$ and $\Delta H_f^0(I)$.

$$AE[Me_2Si{=}CH_2]^{+\cdot} = \Delta H_f^0(Me_2Si{=}CH_2)^{+\cdot} + \Delta H_f^0(CH_2S) - \Delta H_f^0(I) \qquad (1)$$

$$AE[Me_2Si{=}S]^{+\cdot} = \Delta H_f^0(Me_2Si{=}S)^{+\cdot} + \Delta H_f^0(C_2H_4) - \Delta H_f^0(I) \qquad (2)$$

Using our values of the ion appearance energies (Table 2) as well as the heats of formation of thioformadehyde (100.4 kJ mol^{-1}) [7], ethylene (52.3 kJ mol^{-1}) [8], and of the 1,1-dimethyl-1-silaethylene cation-radical (792.0 kJ mol^{-1}) [9], we obtained

$$\Delta H_f^0(I) = \Delta H_f^0(Me_2Si{=}CH_2)^{+\cdot} + \Delta H_f^0(H_2C{=}S) - AE[Me_2Si{=}CH_2]^{+\cdot}$$

$$\Delta H_f^0(I) = 792.0 + 100.4 - 882.8 = 9.6 \text{ kJ mol}^{-1}$$

By substracting eq. 2 from eq. 1 we find $H^0_f(\mathrm{Me_2Si{=}S})^{+\cdot}$:

$$\Delta H^0_f(\mathrm{Me_2Si{=}S})^{+\cdot} = \mathrm{AE}[\mathrm{Me_2Si{=}S}]^{+\cdot} - \Delta H^0_f(\mathrm{C_2H_4}) - \mathrm{AE}[\mathrm{Me_2Si{=}CH_2}]^{+\cdot} + \Delta H^0_f(\mathrm{H_2C{=}S}) + \Delta H^0_f(\mathrm{Me_2Si{=}CH_2})^{+\cdot}$$

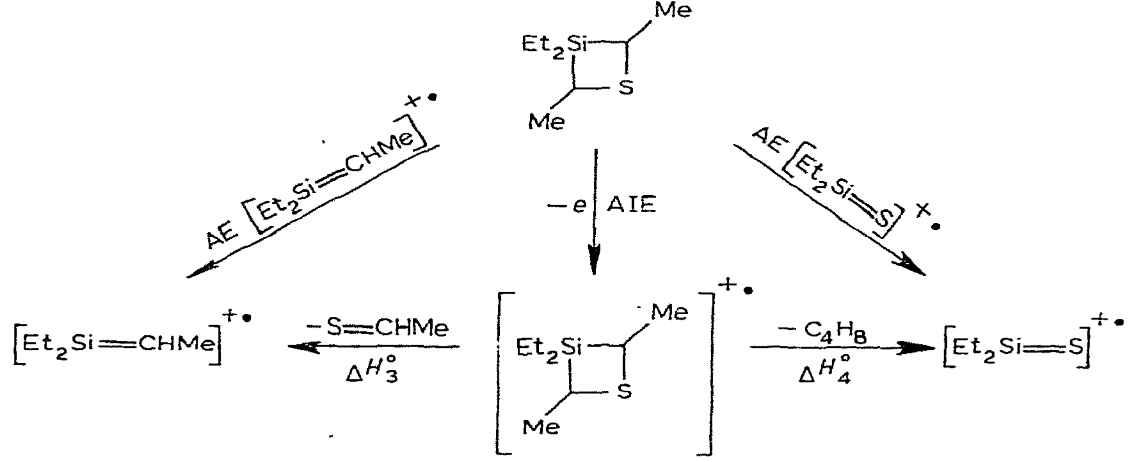
$$\Delta H^0_f(\mathrm{Me_2Si{=}S})^{+\cdot} = 7.7 + 100.4 - 52.3 + 792.0 = 847.8\ \mathrm{kJ\ mol^{-1}}$$

Knowing the values of the ionization energy and the heat of formation of I, the heat of formation of molecular ion I was calculated according to eq. 3.

$$\Delta H^0_f(\mathrm{I})^{+\cdot} = \mathrm{AIE(I)} + \Delta H^0_f(\mathrm{I}) \qquad (3)$$

$$\Delta H^0_f(\mathrm{I})^{+\cdot} = 8.25 \times 23.06 \times 4.184 + 9.6 = 805.6\ \mathrm{kJ\ mol^{-1}}$$

SCHEME 4



The thermodynamic cycle represented in Scheme 4 can be described by eqs. 4 and 5 which contain four unknown quantities: $\Delta H^0_f(\mathrm{II})$, $\Delta H^0_f(\mathrm{Et_2Si{=}S})^{+\cdot}$, $\Delta H^0_f(\mathrm{MeCHS})^{+\cdot}$, and $\Delta H^0_f(\mathrm{Et_2Si{=}CHMe})^{+\cdot}$.

$$\mathrm{AE}[\mathrm{Et_2Si{=}S}]^{+\cdot} = \Delta H^0_f(\mathrm{Et_2Si{=}S})^{+\cdot} + \Delta H^0_f(\mathrm{C_4H_8}) - \Delta H^0_f(\mathrm{II}) \qquad (4)$$

$$\mathrm{AE}[\mathrm{Et_2Si{=}CHMe}]^{+\cdot} = \Delta H^0_f(\mathrm{Et_2Si{=}CHMe})^{+\cdot} + \Delta H^0_f(\mathrm{MeCHS}) - \Delta H^0_f(\mathrm{II}) \qquad (5)$$

In order to determine the heat of formation of II on the basis of ΔH^0_f, we used eqs. 6 and 7 which describe the heats of formation of I and II in terms of *additive contributions of bonds* [10].

$$\Delta H^0_f(\mathrm{I}) = 10\Delta H^0_f(\mathrm{C{-}H}) + 4\Delta H^0_f(\mathrm{Si{-}C}) + 2\Delta H^0_f(\mathrm{C{-}S}) - E_s(\mathrm{I}) \qquad (6)$$

$$\Delta H^0_f(\mathrm{II}) = 18\Delta H^0_f(\mathrm{C{-}H}) + 4\Delta H^0_f(\mathrm{Si{-}C}) + 2\Delta H^0_f(\mathrm{C{-}S}) + 4\Delta H^0_f(\mathrm{C{-}C}) - E_s(\mathrm{II}) \qquad (7)$$

Since $E_s(\mathrm{I}) \approx E_s(\mathrm{II})$, the difference between the heats of formation will be equal to

$$\Delta H^0_f(\mathrm{II}) - \Delta H^0_f(\mathrm{I}) = 8\Delta H^0_f(\mathrm{C{-}H}) + 4\Delta H^0_f(\mathrm{C{-}C})$$

$$\Delta H^0_f(\mathrm{II}) - \Delta H^0_f(\mathrm{I}) = 8(-16.0) + 4(11.4) = -82.5\ \mathrm{kJ\ mol^{-1}}$$

Hence

$$\Delta H_f^0(\mathrm{II}) = 9.6 - 82.5 = -72.9\ \mathrm{kJ\ mol^{-1}} \qquad (11)$$

On the basis of the value of $\Delta H_f^0(H_2CS) = 100.4$ kJ mol^{-1} the heat of formation of thioacetaldehyde was estimated. For this the difference in the heats of formation of $CH_3CH{=}X$ and $CH_2{=}X$ was assumed to be equal at X = O and X = S.

$$\Delta H_f^0(CH_3CHS) = \Delta H_f^0(H_2CS) + \Delta H_f^0(CH_3CHO) - \Delta H_f^0(H_2CO)$$

$$\Delta H_f^0(CH_3CHS) = 100.4 + [-166.1]\ * - [-115.9]\ * = 50.2\ \mathrm{kJ\ mol^{-1}}$$

According to eq. 4

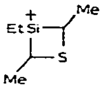
$$\Delta H_f^0(Et_2Si{=}S)^{+\cdot} = \mathrm{AE}[Et_2Si{=}S]^{+\cdot} - \Delta H_f^0(C_4H_8) + \Delta H_f^0(\mathrm{II})$$

Assuming that an equimolar mixture of isomers of butene-2 is formed as a result of photoionization, we made use of the following values in our calculations: $\Delta H_f^0(C_4H_8) = -9.6$ kJ mol^{-1}, $\Delta H_f^0(cis\text{-}C_4H_8) = -7.1$ kJ mol^{-1}, $\Delta H_f^0(trans\text{-}C_4H_8) = -12.1$ kJ mol^{-1}, $\Delta H_f^0(Et_2Si{=}S) = 8.81 \times 23.06 \times 4.184 + 9.6 - 72.9 = 786.7$ kJ mol^{-1}.

From eq. 5:

$$\Delta H_f^0(Et_2Si{=}CHMe)^{+\cdot} = \mathrm{AE}[Et_2Si{=}CHMe]^{+\cdot} - \Delta H_f^0(S{=}CHMe) + \Delta H_f^0(\mathrm{II})$$

$$\Delta H_f^0(Et_2Si{=}CHMe)^{+\cdot} = 9.91 \times 23.06 \times 4.184 - 50.2 - 72.9 = 833.0\ \mathrm{kJ\ mol^{-1}}$$

The processes represented in Scheme 2, which involve the loss of radicals $C_2H_5^{\cdot}$ and $C_4H_7^{\cdot}$ from the molecular ion $M_{\mathrm{II}}^{+\cdot}$, are described by equations similar to eqs. 4 and 5. Knowing that $\Delta H_f^0(C_4H_7^{\cdot}) = 108.8$ kJ mol^{-1} and $\Delta H_f^0(C_2H_5^{\cdot}) = 107.5$ kJ mol^{-1} [12,13], we calculated the heats of formation of cations $Et_2\overset{+\cdot}{Si}SH$ and  .

Knowing the ionization energy and the heat of formation of 3,3-diethyl-2,4-dimethyl-3-silathietane, the heat of formation of the molecular ion can be readily calculated (Table 3).

$$\Delta H_f^0(M_{\mathrm{II}})^{+\cdot} = \mathrm{AIE}(M_{\mathrm{II}})^{+\cdot} + \Delta H_f^0(M_{\mathrm{I}}) = 7.92 \times 23.06 \times 4.184 - 72.9$$

$$= 690.3\ \mathrm{kJ\ mol^{-1}}$$

The decomposition enthalpy of molecular ions I and II (ΔH_1^0, ΔH_2^0 — Scheme 3, and ΔH_3^0, ΔH_4^0 — Scheme 4) were determined as the differences between the appearance energies for particular fragmentation ions and the ionization energies for the corresponding molecules (eq. 7).

$$\Delta H^0 = \mathrm{AE} - \mathrm{AIE} \qquad (7)$$

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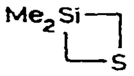
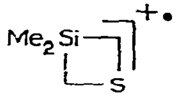
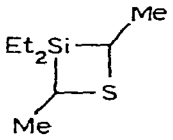
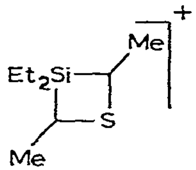
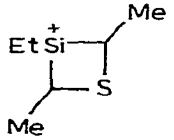
* From ref. 10.

TABLE 3

HEATS OF FORMATION OF 3,3-DIMETHYL-3-SILATHIETANE AND 3,3-DIETHYL-2,4-DIMETHYL-3-SILATHIETANE MOLECULES AND THE HEATS OF FORMATION OF IONS FORMED DURING PHOTOIONIZATION

Molecules, ions	Heats of formation (kJ mol^{-1})
	9.6
	690.3
$[Me_2Si{=}S]^{+\bullet}$	805.6
	−72.9
	690.3
$[Et_2Si{=}CHMe]^{+\bullet}$	833.0
$[Et_2Si{=}S]^{+\bullet}$	786.7
$Et_2\overset{+}{Si}SH$	656.9
	689.9

By substituting the values of the energies listed in Table 2 into eq. 7, we get

$$\Delta H_1^0 = (9.15 - 8.25) \times 23.06 \times 4.184 = 87.0 \text{ kJ mol}^{-1}$$

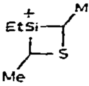
$$\Delta H_2^0 = (9.23 - 8.25) \times 23.06 \times 4.184 = 94.5 \text{ kJ mol}^{-1}$$

$$\Delta H_3^0 = (9.91 - 7.92) \times 23.06 \times 4.184 = 192 \text{ kJ mol}^{-1}$$

$$\Delta H_4^0 = (8.81 - 7.92) \times 23.06 \times 4.184 = 85.8 \text{ kJ mol}^{-1}$$

TABLE 4

ENTHALPIES OF DECOMPOSITION PROCESSES OF 3,3-DIMETHYL-3-SILATHIETANE AND 3,3-DIETHYL-2,4-DIMETHYL-3-SILATHIETANE MOLECULES

Reaction	Enthalpy (kJ mol^{-1})
$M_I^{+\cdot} \rightarrow [Me_2Si{=}CH_2]^{+\cdot} + CH_2S$	86.8
$M_I^{+\cdot} \rightarrow [Me_2Si{=}S]^{+\cdot} + C_2H_4$	94.5
$M_{II}^{+\cdot} \rightarrow [Et_2Si{=}CHMe]^{+\cdot} + CH_3CHS$	192.1
$M_{II}^{+\cdot} \rightarrow [Et_2Si{=}S]^{+\cdot} + C_4H_8$	85.8
$M_{II}^{+\cdot} \rightarrow Et_2Si^{+}SH + C_4H_7^{\cdot}$	74.2
$M_{II}^{+\cdot} \rightarrow$  $+ C_2H_5^{\cdot}$	106.1

In a similar manner the decomposition enthalpies of the molecular ion II, involving loss of radicals $C_2H_5^{\cdot}$ and $C_4H_7^{\cdot}$ (Table 4), were determined.

The results obtained show that for 3-silathietanes the formation of fragment ions by decomposition of the molecular ions "in half" is less characteristic than fragmentation followed by rearrangement of the silathiene ions. This is probably related to the strong 1,3-trans-annular interaction of silicon and sulphur atoms. The method used to obtain silathione ions in the mass spectrometer is of interest from the view point of investigating intermediates with silicon—sulphur double bonds and constitutes a way of obtaining silanone and silaimine ions from structurally similar compounds.

Acknowledgement

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