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A THERMOCHEMICAL STUDY OF DISSOCIATIVE IONIZATION OF 4,4-DIMETHYL-1-THIA-4-SILACYCLOHEXANE AND 2,3,3-TRIMETHYL-1-THIA-3-SILACYCLOPENTANE. DECOMPOSITION PATHWAYS TO PRODUCE A DIMETHYLSILANETHIONE ION-RADICAL $[Me_2Si{=}S]^{+\cdot}$

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Summary

The dissociative ionization of 4,4-dimethyl-1-thia-4-silacyclohexane (I) and 2,3,3-trimethyl-1-thia-3-silacyclopentane (II) has been studied by electron impact (EI) and photoionization (PI) mass spectrometric methods. The molecular ion fragmentation is mainly related to the loss of ethylene and results in a $[Me_2SiSC_2H_4]^{+\cdot}$ (m/z 118) ion-radical (**A**). Further loss of ethylene from **A** produces a dimethylsilanethione $[Me_2Si{=}S]^{+\cdot}$ (m/z 90) ion-radical (**B**). The latter is the most abundant ion in the mass spectra of I and II at 70 eV.

The ionization energies (IE) of I (8.22 ± 0.07 eV) and II (8.06 ± 0.03 eV) and the appearance energies (AE) of ion-radicals **A** and **B** have been determined. Also, the following heats of formation were calculated (kJ/mol): $\Delta H_f^0(\mathrm{I}) = -31.1$; $\Delta H_f^0(\mathrm{II}) = -65.8$; $\Delta H_f^0(M_{\mathrm{I}}^{+\cdot}) = 762.0$; $\Delta H_f^0(M_{\mathrm{II}}^{+\cdot}) = 712.1$; $\Delta H_f^0(\mathbf{A})_{\mathrm{aver}} = 780.2$; $\Delta H_f^0(\mathbf{B})_{\mathrm{aver}} = 847.7$.

Introduction

Highly reactive, double p_π–p_π bonded intermediates $Me_2Si{=}CH_2$, $H_2C{=}S$, and $Me_2Si{=}S$ are formed in the pyrolysis of 3,3-dimethyl-3-silathietane [1]. Its dissociative ionization yields dimethylsilaethylene and dimethylsilanethione ion-radicals [2]. Similar intermediates may appear upon pyrolysis and dissociative ionization of other thiasilacycloalkanes.

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In this paper we shall report on the dissociative ionization of thiasilacycloalkanes I and II, the PI measurements of their ionization energies, and the appearance energies for ions $[Me_2SiSC_2H_4]^{+\cdot}$ (**A**) and $[Me_2Si{=}S]^{+\cdot}$ (**B**). We shall also give the heat of formation calculations for I and II and the characteristic ions in their PI mass spectra.

Experimental

The methods of synthesizing I and II have been discussed in [3].

The electron-impact mass spectra of I and II were recorded on a LKB-2091 mass spectrometer using a heated inlet system (ionization chamber temperature 200°C). The energies of ionizing electrons were 70 and 12 eV, the electron current being 25 μA.

The ionization efficiency curves (IEC) were recorded on a MC-1302 photoionization mass spectrometer in the photon energy range from 7.5 to 12 eV, the resolution of the vacuum monochromator being 2–3 Å at a wavelength of 1215 Å. The samples studied were admitted into the ion source through a flask heated up to 100°C.

Results and discussion

The mass spectra of 4,4-dimethyl-1-thia-4-silacylohexane (I) and 2,3,3-trimethyl-1-thia-3-silacyclopentane (II) are listed in Table 1.

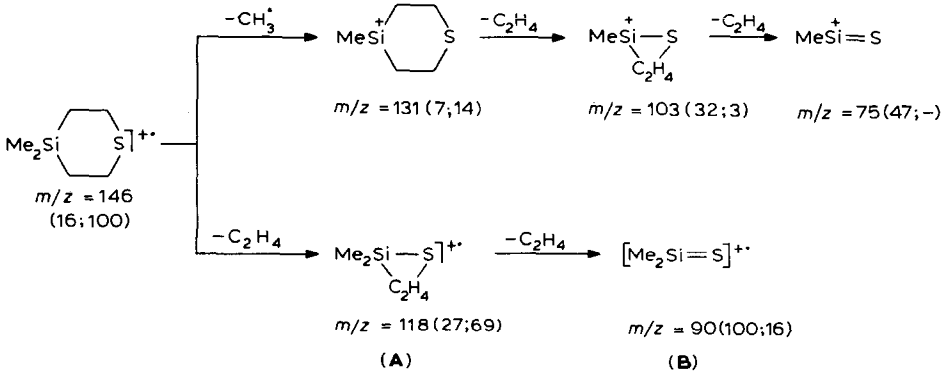
Schemes 1 and 2 show the main decomposition pathways for the molecular ions of I and II, confirmed by metastable ions. The characteristic ion peak intensities at 70 and 12 eV are also given.

Intense peaks of molecular ions are observed in the electron-impact mass spectra

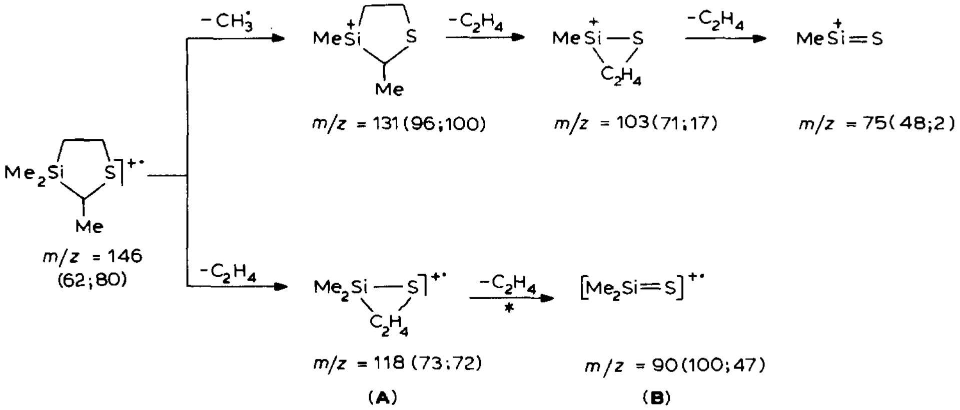
TABLE 1

MASS SPECTRA OF I AND II (relative intensities at 70 and 12 eV)

4,4-Dimethyl-1-thia-4-silacyclohexane (I)	
m/z	148(2; 7), 147(5; 15.5), 146(16; 100), 131(7; 14), 120(2; 7), 119(3; 9), 118(27; 69), 117(2; –), 105(3; –), 104(3; –), 103(32; 3), 92(8; –), 91(12; –), 90(100; 16), 87(2; –), 86(5; –), 85(3; –), 77(7; –), 76(6; –), 75(47; –), 74(2; –), 73(5; –), 72(3; –), 67(2; –), 61(7; –), 60(4; –), 59(18; –), 58(13; –), 57(3; –), 55(6; –); 53(5; –), 46(5; –), 45(16; –), 44(6; –), 43(35; –), 42(7; –), 41(3; –), 39(3; –), 32(6; –), 31(26; –), 30(3; –), 29(14; –), 28(27; –).
2,3,3-Trimethyl-1-thia-3-silacyclopentane (II)	
m/z	148(6; 8), 147(8; 14), 146(62; 80), 133(9; 10), 132(11, 12), 131(96; 100), 120(6; 7), 119(9; 8), 118(73; 72), 117(9; –), 105(6; –), 104(7; –), 103(71; 17), 97(10; 4), 92(10; 5), 91(21; 7), 90 (100; 47), 87(–; 1), 86(–; 2), 85(15; 4), 77(17; 3), 76(14; 2), 75(48; 2), 74(2; –), 73(22; 5), 68.5*(2; 2), 61(8; –), 60(8; –), 59(55; 4), 58(34; 2), 57(3; –), 55(7; –), 53(3; –), 46(5; –), 45(15; (3), 44(5; –), 43(33; –), 42(5; –), 41(4; –), 39(2; –), 32(2; –), 31(19; 3), 30(2; –), 29(10; –), 28(8; –).



SCHEME 1. 4,4-Dimethyl-1-thia-4-silacyclohexane (I).



SCHEME 2. 2,3,3-Trimethyl-1-thia-3-silacyclopentane (II).

of molecules I and II. The molecular ions of compounds I and II decompose mainly with the loss of two molecules of ethylene to form a dimethylsilanethione ion-radical, $m/z = 90$, $[\mathrm{Me_2Si{=}S}]^{+\cdot}$ (**B**). This is the most abundant ion in the mass spectra of I and II at 70 eV. The formation of ion-radical **B** from the molecular ions of I and II apparently occurs via the ion-radical $[\mathrm{Me_2SiSC_2H_4}]^{+\cdot}$ (**A**), $m/z = 118$, with the elimination of an ethylene molecule. The presence of the metastable ion peak at $m/z = 68.6$ in the mass spectrum of compound II confirms the formation of ion-radical **B** directly from ion-radical **A**.

The mass spectra of molecules I and II are very similar, but they display different intensities of the characteristic ions. Therefore, one can suggest that the molecular ion $M_{\mathrm{II}}^{+\cdot}$ isomerizes into the molecular ion $M_{\mathrm{I}}^{+\cdot}$:

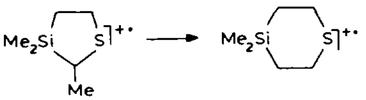


TABLE 2

APPEARANCE ENERGIES OF THE CHARACTERISTIC IONS FOR THE COMPOUNDS I AND II

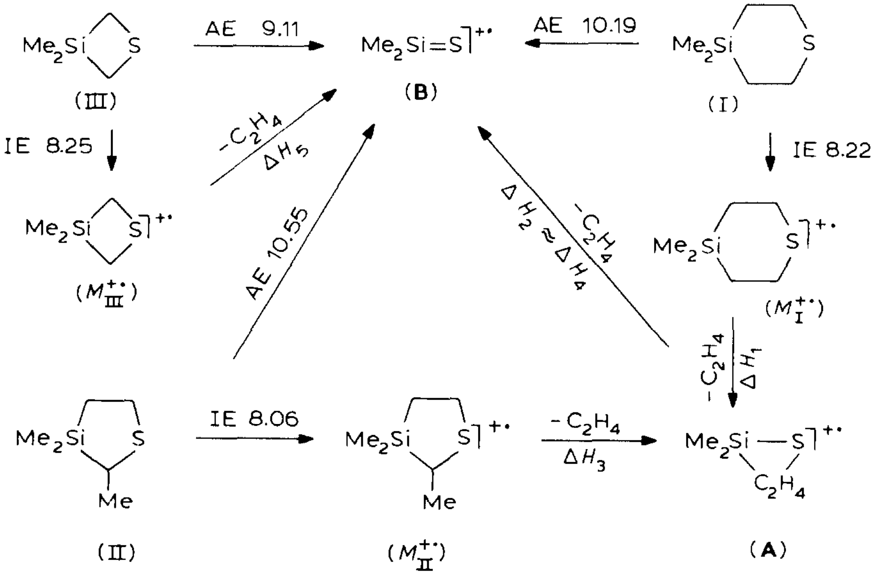
Ions	Compound I		Compound II	
	m/z	AE(eV)	m/z	AE(eV)
$M^{+\cdot}$	146	8.22 ± 0.07	146	8.06 ± 0.03
$[M-15]^{+\cdot}$		–	131	8.76 ± 0.05
$[M-28]^{+\cdot}$	118	8.91 ± 0.03	118	9.35 ± 0.05
$[M-56]^{+\cdot}$	90	10.19 ± 0.04	90	10.55 ± 0.06

The thermochemical calculations support the fact that such an isomerization is possible in principle.

The appearance energies of characteristic ions **A** and **B** and the ionization energies of molecules I and II were determined from the ionization efficiency curves by the photoionization mass spectrometric method. The values obtained are given in Table 2.

Attention is drawn to the fact that within the error of measurement the ionization energy of I (8.22 ± 0.07 eV) is the same as that of 3,3-dimethyl-3-silathietane (8.25 ± 0.03 eV). This is an unexpected coincidence, since in the thiacycloalkane series IE is known to decrease with increasing ring size (see, for example, ref. 4).

The thermodynamic cycles involving fragmentation of I and II and also that of 3,3-dimethyl-3-silathietane (III) are shown in Scheme 3.



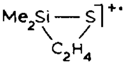
SCHEME 3

According to this scheme, for molecule I AE(**B**) = ΔH_f^0(**B**) + $2\Delta H_f^0(C_2H_4) - \Delta H_f^0(I)$. However, ΔH_f^0(**B**) = 847.8 kJ/mol [2]. Then, $\Delta H_f^0(I) = \Delta H_f^0$(**B**) + $2\Delta H_f^0(C_2H_4)$ − AE(**B**) = 847.7 + 104.4 − 983.2

$\Delta H_f^0(I) = -31.1$kJ/mol

TABLE 3

HEATS OF FORMATIONS OF I, II AND 3,3-DIMETHYL-3-SILATHIETANE AND OF THEIR CHARACTERISTIC IONS

Molecules, ions	Heats of formation (kJ/mol)		
	Compound I	Compound II	3,3-Dimethyl-3-silathietane
M	−31.1	−65.8	9.6
$M^{+\cdot}$	762.0	712.1	805.4
	776.8	783.6	–
$[Me_2Si{=}S]^{+\cdot}$	847.7 (assumed)	847.7 (assumed)	847.7

Knowing the heat of formation of 4,4-dimethyl-1-thia-4-silacyclohexane and its IE, the heat of formation of the molecular ion $M_I^{+\cdot}$ can be calculated as follows:

$$\Delta H_f^0(M_I^{+\cdot}) = IE(I) + \Delta H_f^0(I) = 793.1 - 31.1 \qquad (2)$$

$$\Delta H_f^0(M_I^{+\cdot}) = 762.0 \text{ kJ/mol}$$

The heat of formation of ion-radical **A** derived from I was determined from eq. 3.

$$\Delta H_f^0(\mathbf{A})(M_I^{+\cdot}) = AE(\mathbf{A}) - \Delta H_f^0(C_2H_4) + \Delta H_f^0(I) = 901.6 - 52.2 - 31.1 \qquad (3)$$

$$\Delta H_f^0(\mathbf{A})(M_I^{+\cdot}) = 818.4 \text{ kJ/mol}$$

Analogous calculations were performed for II. According to Scheme 3, the heat of formation of compound II is given by eq. 4.

$$\Delta H_f^0(II) = -AE(\mathbf{B}) + \Delta H_f^0(\mathbf{B}) + 2\Delta H_f^0(C_2H_4) = -1017.9 + 847.7 + 104.4 \qquad (4)$$

$$\Delta H_f^0(II) = -65.8 \text{ kJ/mol}$$

The heat of formation of the molecular ion of compound II as well as that of ion-radical **A** obtained from II were calculated from eqs.5 and 6, respectively.

$$\Delta H_f^0(M_{II}^{+\cdot}) = IE(II) + \Delta H_f^0(II) = 777.9 - 65.8 = 712.1 \text{ kJ/mol} \qquad (5)$$

$$\Delta H_f^0(M_{II}^{+\cdot}) = 712.1 \text{ kJ/mol}$$

$$\Delta H_f^0(M_{II}^{+\cdot}) = AE(\mathbf{A}) - \Delta H_f^0(C_2H_4) + \Delta H_f^0(II) = 901.6 - 52.2 - 65.8 \qquad (6)$$

$$\Delta H_f^0(\mathbf{A}) = 783.6 \text{ kJ/mol}$$

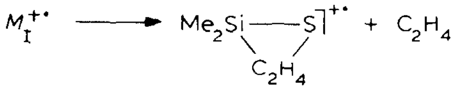
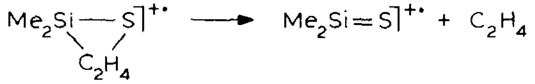
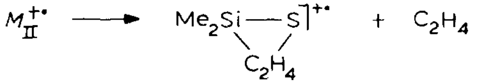
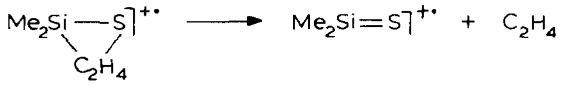
The heats of formation of compounds I and II and 3,3-dimethyl-3-silathiethane and also those of their characteristic ions are given in Table 3.

From this table it follows that compound II is thermodynamically more stable than I, although II is a five-membered ring system and I is an isomeric, unstrained heterocycle.

The values of the heats of formation of ion-radical **A** obtained from molecular ions I and II are almost equal. The average value amounts to 780.2 kJ/mol. This is indicative of the identity of the structures of these ions obtained from different

TABLE 4

DECOMPOSITION ENTHALPIES FOR THE MOLECULAR IONS OF COMPOUNDS I–III

Reaction	Enthalpy (kJ/mol)
 (I)	$\Delta H_1 = 66.6$
 (I)	$\Delta H_2 = 123.5$
 (II)	$\Delta H_3 = 123.7$
 (II)	$\Delta H_4 = 116.3$
$M_{\mathrm{III}}^{+\cdot} \longrightarrow \mathrm{Me_2Si{=}S]^{+\cdot}} + \mathrm{C_2H_4}$	$\Delta H_5 = 83$

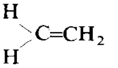
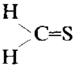
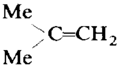
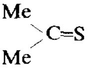
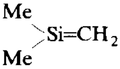
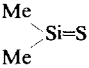
precursors. It is confirmed by the very similar values of the enthalpies of the ion-radical **A** decomposition process, calculated for compounds I and II (Table 4). A higher enthalpy for the loss of ethylene from molecular ion II may be explained by the isomerization of $M_{\mathrm{II}}^{+\cdot}$ into $M_{\mathrm{I}}^{+\cdot}$, the isomerization enthalpy being 57.1 kJ/mol.

In order to estimate the heat of formation of dimethylsilanethione from $\Delta H_f^0(\mathbf{B})$ by eq. 7, one needs to know the ionization energy of $\mathrm{Me_2Si{=}S}$ (IV).

$$\mathrm{IE} = \Delta H_f^0(\mathbf{B}) - \Delta H_f^0(\mathrm{IV}) \tag{7}$$

TABLE 5

IONIZATION ENERGIES FOR DIMETHYLSILAETHYLENE, DIMETHYLSILANETHIONE AND THEIR CARBON ANALOGUES

Compound	IE(eV)	Compound	IE(eV)
 $\mathrm{H_2C{=}CH_2}$	10.51 [6]	 $\mathrm{H_2C{=}S}$	9.34 [9]
 $\mathrm{Me_2C{=}CH_2}$	9.21 [7]	 $\mathrm{Me_2C{=}S}$	8.60 [9]
 $\mathrm{Me_2Si{=}CH_2}$	7.71 [8]	 $\mathrm{Me_2Si{=}S}$	9.15 [5]

The experimental value of IE (IV) measured by photoelectron spectroscopy amounts to 9.15 eV [5]. The known ionization energies for dimethylsilaethylene, dimethylsilanethione and their carbon analogues are shown in Table 5.

Indeed, the ionization energies gradually decrease from top to bottom and from left to right. According to this, the expected value of IE (IV) should not, apparently, exceed 8 eV. Our theoretical estimation of the orbital energies of dimethylsilanethione and dimethylsilaethylene, estimated by non-empirical and semi-empirical quantum calculations, reveals that the first ionization potentials of these molecules should be close. By high-temperature photoelectron spectroscopic data, an improved value is obtained for the adiabatic IE ($Me_2Si{=}CH_2$), amounting to 7.71 eV. Substituting IE ($Me_2Si{=}S$) = 9.15 eV in eq. 7 gives $\Delta H_f^0 = -35.0$ kJ/mol, while IE ($Me_2Si{=}S$) = 8 eV yields $\Delta H_f^0 = +75.9$ kJ/mol. Since the heat of formation of 1,1-dimethyl-1-silaethylene ($Me_2Si{=}CH_2$) is 64.8 kJ/mol [10], the latter value of ΔH_f^0(IV) seems to be more realistic than the former one.

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