

## Thermochemistry of organosilicon compounds

### III \*. (Organylthioalkyl)trialkoxysilanes and 1-(organylthioalkyl)silatranes

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#### Abstract

The enthalpies of combustion and evaporation of the (organylthioalkyl)trialkoxysilanes  $\text{RS}(\text{CH}_2)_n\text{Si}(\text{OR}')_3$  ( $n = 1-3$ ), and the enthalpies of combustion and sublimation of the 1-(organylthioalkyl)silatranes  $\text{RS}(\text{CH}_2)_n\text{Si}(\text{OCH}_2\text{CH}_2)_m\text{N}[\text{OCH}(\text{CH}_3)\text{CH}_2]_{3-m}$  ( $n = 1-3$ ;  $m = 1-3$ ) have been determined. The values obtained serve as a basis for calculating the enthalpies of formation and atomization. The energy of interaction between the sulfur and the silicon atoms in the compounds studied has been calculated on the basis of the Franklin–Benson parameters.

From the thermochemical data, it was clear that there was very little interaction between the sulfur and silicon atoms in the  $\text{S}(\text{CH}_2)_n\text{Si}$  fragment with  $n = 3$ , whereas with  $n = 1$  and 2 it is  $24.0 \pm 9$  and  $6.0 \pm 1.5$   $\text{kJ mole}^{-1}$ , respectively.

The enthalpy of formation of the silatranyl group  $\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}$  ( $-780 \pm 7.0$   $\text{kJ mole}^{-1}$ ) has also been determined.

#### Introduction

To throw light on the stereoelectronic structure of the molecules of (organylthioalkyl)trialkoxysilanes  $\text{RS}(\text{CH}_2)_n\text{Si}(\text{OR}')_3$  ( $n = 1-3$ ) [1,2] and 1-

\* For part II see ref. 22.

(organylthioalkyl)silatrane  $\text{RS}(\text{CH}_2)_n\overline{\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}}$  ( $n = 1-3$ ) [3] there is need for information on the intramolecular interaction between the sulfur and silicon atoms.

The charge-transfer complexes of the (alkylthiomethyl)trialkoxysilanes and the 1-(alkylthiomethyl)silatrane with tetracyanoethylene (TCE), the UV spectra of the (alkylthioalkyl)trialkoxysilanes ( $n = 1-3$ ) and the photoelectron spectra of the (alkylthiomethyl)trimethoxysilanes ( $n = 1$ ) [4-6] have been studied previously. The nature of the charge-transfer complex in (alkylthiomethyl)trialkoxysilanes  $\text{RSCH}_2\text{Si}(\text{OR}')_3$  ( $\text{R}' = \text{CH}_3, \text{C}_2\text{H}_5$ ) and that of the corresponding 1-(alkylthiomethyl)silatrane  $\text{RSCH}_2\overline{\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}}$  with TCE reveals that the donor properties with respect to TCE are displayed not by the pure  $p$ -atomic orbitals of sulfur, but by a mixed orbital comprising, in addition, the respective orbitals of the trialkoxysilylmethyl and silatranylmethyl groups. This is consistent with the UV spectra of  $\text{RS}(\text{CH}_2)_n\text{Si}(\text{OR}')_3$ , and indicates a change in the localization of the unshared electron pairs of the sulfur atom on going from compounds with  $n = 1$  to those with  $n = 2$ . Furthermore, on going to  $n = 3$  the UV spectra practically do not change. Quantum-chemical calculations of the electron density confirm that the Wieberg indexes and the energy indexes of the Si...S bond have much greater values when  $n = 1$ , as compared to compounds with  $n = 2$  and 3. The photoelectron spectra of the (alkylthiomethyl)trimethoxysilanes  $\text{RSCH}_2\text{Si}(\text{OCH}_3)_3$  indicate that the two upper molecular orbitals of their molecules are very similar in terms of energy, but differ greatly in terms of their nature. The first orbital is made up mainly of the  $p$ -orbitals of the sulfur atom and is perpendicular to the C-S-C plane. The other orbital, which comprises the  $s$ - and  $p$ -orbitals of the sulfur atom with a similar contribution from the Si-C and S-C bonds, is destabilized by the interaction of the  $n$ -electrons in the oxygen and sulfur atoms.

In order to extend our study we determined the enthalpies of combustion and evaporation of the 15 liquid (organylthioalkyl)trialkoxysilanes  $\text{RS}(\text{CH}_2)_n\text{Si}(\text{OR}')_3$  (I-XV, Table 1), and the enthalpies of combustion and sublimation of 17 crystalline 1-(organylthioalkyl)silatrane  $\text{RS}(\text{CH}_2)_n\overline{\text{Si}(\text{OCH}_2\text{CH}_2)_m[\text{OCH}(\text{CH}_3)\text{CH}_2]_{3-m}\text{N}}$  (XVI-XXXII, Table 2). The values obtained served as a basis to calculate the enthalpies of formation and atomization of these molecules, thus enabling the interaction energy between the sulfur and silicon atoms to be assessed in accordance with the number of methylene groups ( $n$ ) separating them. Up to now only the enthalpies of formation of either organosulfur or organosilicon compounds had been known. Thus, one of the objectives of the present study was to find a method for determining the heats of combustion of sulfur-containing organosilicon compounds, in which the sulfur and silicon atoms are involved in the  $\text{S}(\text{CH}_2)_n\text{Si}$  group.

## Results

The observed enthalpies of combustion and evaporation of the (organylthioalkyl)trialkoxysilanes I-XV, and the enthalpies of combustion and sublimation of the 1-(organylthioalkyl)silatrane (XVI-XXXII) are listed in Tables 1 and 2, respectively. The error in their determination is expressed as a confidence interval with 95% probability.

In calculating the enthalpies of formation and atomization, use was made of the

**Table 1**  
 Enthalpies of combustion, formation, evaporation and atomization for the (organylthioalkyl)trialkoxysilanes,  $\text{RS}(\text{CH}_2)_n\text{Si}(\text{OR}')_3$ , in the liquid and gaseous states at 298.15 K ( $\text{kJ mol}^{-1}$ )

Compound Nos.	R	R'	n	$-\Delta H_{\text{f}}^{\circ}(\text{l})$	$-\Delta H_{\text{f}}^{\circ}(\text{l})$	$-\Delta H_{\text{f}}^{\circ}(\text{l})$	$\Delta H_{\text{v}}$	$-\Delta H_{\text{f}}^{\circ}(\text{g})(\text{found})$	$\Delta H_{\text{f}}^{\circ}(\text{g})(\text{found})$
I	$\text{CH}_3$	$\text{CH}_3$	1	$4520.4 \pm 6.5$	$989.5 \pm 7.0$	$40.2 \pm 0.6$	$949.3 \pm 7.3$	$9059.1 \pm 7.8$	
II	$\text{CH}_3$	$\text{CH}_3$	2	$5197.5 \pm 6.6$	$991.8 \pm 7.1$	$45.2 \pm 0.7$	$946.6 \pm 7.4$	$10209.1 \pm 8.0$	
III	$\text{CH}_3$	$\text{CH}_3$	3	$5868.1 \pm 6.6$	$1000.5 \pm 7.1$	$43.5 \pm 0.6$	$957.0 \pm 7.4$	$11372.2 \pm 8.0$	
IV	$\text{C}_2\text{H}_5$	$\text{CH}_3$	1	$5180.2 \pm 6.7$	$1009.1 \pm 7.3$	$41.4 \pm 0.6$	$967.7 \pm 7.6$	$10230.2 \pm 8.2$	
V	$\text{C}_2\text{H}_5$	$\text{CH}_3$	2	$5859.0 \pm 6.5$	$1009.6 \pm 7.0$	$41.4 \pm 0.7$	$968.2 \pm 7.3$	$11383.3 \pm 7.9$	
VI	$\text{C}_2\text{H}_5$	$\text{CH}_3$	3	$6526.3 \pm 6.7$	$1021.7 \pm 7.3$	$41.8 \pm 0.6$	$979.9 \pm 7.6$	$12547.8 \pm 8.2$	
VII	$\text{C}_2\text{H}_5$	$\text{C}_2\text{H}_5$	1	$7117.2 \pm 6.7$	$1110.1 \pm 7.3$	$42.3 \pm 0.6$	$1067.8 \pm 7.3$	$13778.3 \pm 7.9$	
VIII	$\text{C}_2\text{H}_5$	$\text{C}_2\text{H}_5$	2	$7790.8 \pm 6.7$	$1115.9 \pm 7.2$	$46.9 \pm 0.7$	$1069.0 \pm 7.5$	$14942.2 \pm 8.1$	
IX	$\text{C}_4\text{H}_9$	$\text{CH}_3$	1	$6499.9 \pm 6.6$	$1048.1 \pm 7.1$	$41.6 \pm 0.6$	$1006.5 \pm 7.1$	$12574.3 \pm 7.7$	
X	$\text{C}_4\text{H}_9$	$\text{C}_2\text{H}_5$	3	$9778.6 \pm 6.9$	$1166.1 \pm 7.4$	$47.1 \pm 0.6$	$1119.0 \pm 7.4$	$18450.2 \pm 8.0$	
XI	$(\text{CH}_3)_2\text{CHCH}_2$	$\text{CH}_3$	1	$6497.2 \pm 7.1$	$1050.8 \pm 7.5$	$38.7 \pm 0.6$	$1012.1 \pm 7.8$	$12579.9 \pm 8.4$	
XII	$(\text{CH}_3)_3\text{C}$	$\text{CH}_3$	1	$6480.4 \pm 6.8$	$1067.6 \pm 7.3$	$50.6 \pm 0.7$	$1017.0 \pm 7.6$	$12584.7 \pm 8.2$	
XIII	$\text{C}_6\text{H}_5$	$\text{CH}_3$	1	$6923.3 \pm 6.6$	$840.0 \pm 7.1$	$56.4 \pm 0.7$	$783.6 \pm 7.4$	$12912.8 \pm 8.0$	
XIV	$\text{C}_6\text{H}_5\text{CH}_2$	$\text{CH}_3$	1	$7574.5 \pm 6.8$	$868.2 \pm 7.3$	$56.1 \pm 0.7$	$812.1 \pm 7.6$	$14094.4 \pm 8.2$	
XV	$\text{CH}_2=\text{CHCH}_2$	$\text{CH}_3$	1	$5706.0 \pm 6.6$	$876.8 \pm 7.1$	$38.6 \pm 0.5$	$838.2 \pm 7.4$	$10817.4 \pm 8.0$	

Table 2  
 Enthalpies of combustion, formation, sublimation and atomization for the 1-(organythioalkyl)silatranes  $\text{RS}(\text{CH}_2)_n\text{Si}(\text{OCH}_2\text{CH}_2)_m[\text{OCH}(\text{CH}_3)\text{CH}_2]_3-n\text{N}$  in the crystalline and gaseous states at 298.15 K ( $\text{kJ mol}^{-1}$ )

Compound Nos.	R	n	m	$-\Delta H_{\text{f}}^{\circ}(\text{solid})$	$-\Delta H_{\text{f}}^{\circ}(\text{solid})$	$\Delta H_{\text{s}}$	$-\Delta H_{\text{f}}^{\circ}(\text{g(found)})$	$\Delta H_{\text{f}}^{\circ}(\text{g(found)})$
XVI	$\text{CH}_3$	1	3	$6188.7 \pm 8.6$	$930.5 \pm 8.8$	$90.0 \pm 0.4$	$840.5 \pm 9.0$	$12227.0 \pm 9.6$
XVII	$\text{CH}_3$	2	3	$6865.4 \pm 7.5$	$933.2 \pm 7.9$	$92.8 \pm 0.3$	$840.4 \pm 8.1$	$13379.6 \pm 8.7$
XVIII	$\text{C}_2\text{H}_5$	1	3	$6852.2 \pm 8.2$	$946.4 \pm 8.4$	$96.0 \pm 0.4$	$850.4 \pm 8.6$	$13389.6 \pm 9.2$
XIX	$\text{C}_2\text{H}_5$	2	3	$7516.2 \pm 7.2$	$961.7 \pm 7.6$	$98.2 \pm 0.4$	$863.1 \pm 7.8$	$14555.4 \pm 8.4$
XX	$\text{C}_2\text{H}_5$	3	3	$8190.8 \pm 5.7$	$966.5 \pm 8.2$	$96.4 \pm 0.5$	$870.1 \pm 8.5$	$15714.7 \pm 9.1$
XXI	$\text{C}_3\text{H}_7$	1	3	$7497.9 \pm 4.5$	$980.0 \pm 7.7$	$97.8 \pm 0.4$	$882.2 \pm 7.9$	$14574.1 \pm 8.5$
XXII	$\text{C}_3\text{H}_7$	2	3	$8178.5 \pm 4.8$	$984.8 \pm 7.8$	$99.9 \pm 0.4$	$884.9 \pm 8.0$	$15729.5 \pm 8.6$
XXIII	$\text{C}_3\text{H}_7$	3	3	$8841.3 \pm 8.0$	$995.3 \pm 8.9$	$104.8 \pm 0.6$	$890.5 \pm 9.2$	$16887.8 \pm 9.8$
XXIV	$\text{C}_4\text{H}_9$	1	3	$8159.2 \pm 7.6$	$998.1 \pm 8.6$	$98.6 \pm 0.4$	$889.5 \pm 8.8$	$15744.1 \pm 9.4$
XXV	$\text{C}_4\text{H}_9$	3	3	$9495.5 \pm 6.3$	$1020.4 \pm 8.6$	$107.6 \pm 0.6$	$912.8 \pm 8.9$	$18062.7 \pm 9.5$
XXVI	$(\text{CH}_3)_2\text{CHCH}_2$	1	3	$8150.6 \pm 6.3$	$1006.7 \pm 8.5$	$101.4 \pm 0.5$	$905.3 \pm 8.8$	$15749.9 \pm 9.4$
XXVII	$(\text{CH}_3)_2\text{C}$	1	3	$8132.0 \pm 6.2$	$1025.3 \pm 8.2$	$106.8 \pm 0.6$	$918.5 \pm 8.5$	$15763.1 \pm 9.1$
XXVIII	$\text{C}_6\text{H}_5$	1	3	$8581.9 \pm 9.0$	$790.7 \pm 9.6$	$114.6 \pm 0.6$	$676.1 \pm 9.9$	$16082.0 \pm 10.5$
XXIX	$\text{C}_6\text{H}_5\text{CH}_2$	1	3	$9224.4 \pm 8.6$	$827.6 \pm 9.2$	$118.4 \pm 0.6$	$709.2 \pm 9.5$	$17267.8 \pm 10.1$
XXX	$\text{C}_6\text{H}_5\text{CH}_2$	1	2	$9878.9 \pm 7.8$	$852.4 \pm 8.6$	$125.9 \pm 0.7$	$726.5 \pm 9.0$	$18437.8 \pm 9.6$
XXXI	$\text{C}_6\text{H}_5\text{CH}_2$	1	1	$10534.3 \pm 8.0$	$876.4 \pm 9.0$	$143.5 \pm 0.8$	$732.9 \pm 9.4$	$19596.9 \pm 10.0$
XXXII	$\text{CH}_2\text{CHCH}_2$	1	3	$7342.5 \pm 7.8$	$849.6 \pm 9.0$	$93.3 \pm 0.6$	$756.3 \pm 9.3$	$14012.2 \pm 9.9$

following key values of  $\Delta H_f^\circ$ , kJ mole<sup>-1</sup> at 298.15 K:

$$-285.830 \pm 0.042(\text{H}_2\text{O, liq.});$$

$$-393.514 \pm 0.13(\text{CO}_2, \text{g})[7];$$

$$-939.39 \pm 0.52(\text{SiO}_2, \text{am.hydr.})[8]$$

$$-888.01 \pm 0.29(\text{H}_2\text{SO}_4 \cdot 115\text{H}_2\text{O, liq.})[9];$$

$$716.67 \pm 0.44(\text{c, g}); 217.997 \pm 0.006(\text{H, g});$$

$$276.98 \pm 0.25(\text{S, g}); 450.00 \pm 8(\text{Si, g})[7].$$

To calculate the energy of interaction between the silicon and sulfur atoms in our compounds, as well as the enthalpy of formation of the silatranyl group  $\overline{\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}}$  we calculated the enthalpies of atomization and formation of these substances, disregarding the above energy. To calculate the enthalpies of formation and atomization in the gaseous state we made use of the Franklin–Benson additive scheme, taking into account the mutual effect of the atoms separated by not more than one other atom [10,11].

To this end, the molecular skeleton of the compound was divided into fragments [12]. For instance, in the case of the  $\text{CH}_3\text{SCH}_2\text{Si}(\text{OCH}_3)_3$  the following fragments were taken into account (Table 3).

$$\text{X}_5 = \text{C}(\text{S})(\text{H})_3 \quad \text{X}_{21} = \text{S}(\text{C})_2$$

$$\text{X}_{25} = \text{C}(\text{Si})(\text{S})(\text{H})_2 \quad \text{X}_{18} = \text{Si}(\text{O})_3(\text{C})$$

$$\text{X}_{17} = \text{O}(\text{Si})(\text{C}) \quad \text{X}_2 = \text{C}(\text{O})(\text{H})_3$$

Similarly, for  $\text{CH}_3\text{SCH}_2\overline{\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}}$ :

$$\text{X}_5 = \text{C}(\text{S})(\text{H})_3 \quad \text{X}_{21} = \text{S}(\text{C})_2$$

$$\text{X}_{25} = \text{C}(\text{Si})(\text{S})(\text{H})_2 \quad \text{X}_{18} = \text{Si}(\text{O})_3\text{C}$$

$$\text{X}_{17} = \text{O}(\text{Si})(\text{C}) \quad \text{X}_{22} = \text{C}(\text{O})(\text{C})(\text{H}_2)$$

$$\text{X}_9 = \text{C}(\text{C})(\text{N})(\text{H})_2 \quad \text{X}_{12} = \text{N}(\text{C})_3$$

If  $E_i$  is the energy of a fragment and  $K_i$  is the number of fragments, then

$$\Delta H_a^\circ, \text{ calc.} = \sum_{i=1}^n K_i E_i \quad (1)$$

Thus for a general formula  $\text{C}_a\text{H}_b\text{O}_3\text{SSi}$ :

$$\Delta H_{\text{fC}_a\text{H}_b\text{O}_3\text{SSi, g}}^\circ, \text{ calc.} = \sum_{i=1}^n K_i H_i \quad (2)$$

where

$$H_i = -E_i + a \Delta H_{\text{fC, g}}^\circ + b \Delta H_{\text{fH, g}}^\circ + 3 \Delta H_{\text{fO, g}}^\circ + \Delta H_{\text{fS, g}}^\circ + \Delta H_{\text{fSi, g}}^\circ \quad (3)$$

To calculate the energy of the fragments we used the observed enthalpies of formation of hydrocarbons, alcohols, ethers, amines, aminoalcohols, sulphides, as well as the data for tetraalkoxy-, tetraalkyl-, organylalkoxy-silanes, which had been published previously [13–17]. In addition, we used the least squares method and a system of linear equations to estimate the energy values of the fragments in the Franklin–Benson scheme (Table 3).

Table 3

Energies of fragments in the Franklin–Benson scheme for evaluating  $\Delta H_f^\circ$  and  $\Delta H_a^\circ$  at 298.15 K ( $\text{kJ mol}^{-1}$ )<sup>a</sup>

Nos.	Fragment	Values	
		$\Delta H_f^\circ$	$\Delta H_a^\circ$
X <sub>1</sub>	C(C)(H) <sub>3</sub>	-44.27	1414.9
X <sub>2</sub>	C(O)(H) <sub>3</sub>	-44.27	1414.9
X <sub>3</sub>	C(Si)(H) <sub>3</sub>	-44.27	1414.9
X <sub>4</sub>	C(N)(H) <sub>3</sub>	-44.27	1414.9
X <sub>5</sub>	C(S)(H) <sub>3</sub>	-44.27	1414.9
X <sub>6</sub>	C(C) <sub>2</sub> (H) <sub>2</sub>	-19.3	1172.0
X <sub>7</sub>	C(C <sub>3</sub> )(H)	-7.95	942.62
X <sub>8</sub>	C(C) <sub>4</sub>	2.09	714.82
X <sub>9</sub>	C(N)(C)(H) <sub>2</sub>	-23.5	1176.16
X <sub>10</sub>	C(N)(C) <sub>2</sub> (H)	-21.76	956.43
X <sub>11</sub>	C(N)(C) <sub>3</sub>	-13.39	730.06
X <sub>12</sub>	N(C) <sub>3</sub>	106.3	366.38
X <sub>13</sub>	C(C)(S)(H) <sub>2</sub>	-22.64	1175.33
X <sub>14</sub>	C(C) <sub>2</sub> (S)(H)	-11.04	945.71
X <sub>15</sub>	C(C) <sub>3</sub> (S)	3.4	713.27
X <sub>16</sub>	C(C)(Si)(H) <sub>2</sub>	-16.6	1169.39
X <sub>17</sub>	O(Si)(C)	-237.33	486.5
X <sub>18</sub>	Si(O) <sub>3</sub> (C)	-56.96	506.96
X <sub>19</sub>	Si(C) <sub>4</sub>	-53.2	503.2
X <sub>20</sub>	Si(O) <sub>4</sub>	-611.38	1061.38
X <sub>21</sub>	S(C) <sub>2</sub>	45.16	231.87
X <sub>22</sub>	C(O)(C)(H) <sub>2</sub>	-33.12	1185.78
X <sub>23</sub>	C(O)(C) <sub>2</sub> (H)	-15.6	950.27
X <sub>24</sub>	C(O)(C) <sub>3</sub>	-27.6	744.27
X <sub>25</sub>	C(Si)(S)(H) <sub>2</sub>	-15.7	1168.49
X <sub>26</sub>	C <sub>B</sub> -(C <sub>B</sub> ) <sub>2</sub> (H)	13.81	920.86
X <sub>27</sub>	C <sub>B</sub> -(C <sub>B</sub> ) <sub>2</sub> (C)	23.51	693.16
X <sub>28</sub>	C <sub>B</sub> -(C <sub>B</sub> ) <sub>2</sub> (S)	27.81	688.86
X <sub>29</sub>	S-(C <sub>B</sub> )(C)	60.16	216.87
X <sub>30</sub>	C-(S)(C <sub>B</sub> )(H) <sub>2</sub>	13.19	1165.85
X <sub>31</sub>	C <sub>α</sub> -(C <sub>α</sub> )(H) <sub>2</sub>	26.19	1126.47
X <sub>32</sub>	C <sub>α</sub> -(C <sub>α</sub> )(C)(H)	35.94	898.73
X <sub>33</sub>	C-(C <sub>α</sub> )(S)(H) <sub>2</sub>	-9.74	1162.40
X <sub>34</sub>	C <sub>B</sub> -(C <sub>B</sub> ) <sub>2</sub> (Si)	14.6	702.07
X <sub>35</sub>	Si-(C <sub>B</sub> )(O) <sub>3</sub>	-488.4	938.4
X <sub>36</sub>	Si-(C <sub>α</sub> )(O) <sub>3</sub>	515.6	965.6
X <sub>37</sub>	C-(Si)(C <sub>α</sub> )(H)	8.16	926.51
X <sub>38</sub>	C <sub>B</sub> -(CO)(C <sub>B</sub> ) <sub>2</sub>	3.3	713.37
X <sub>39</sub>	CO-(C <sub>B</sub> )(O)	-135.98	1101.82
X <sub>40</sub>	O-(CO)(C)	-185.35	434.52
X <sub>41</sub>	C-(Si)(O)(H) <sub>2</sub>	-16.6	1169.39
X <sub>42</sub>	Si-(C) <sub>2</sub> (O) <sub>2</sub>	-336.86	786.86
X <sub>43</sub>	Si-(C) <sub>3</sub> (O)	-189.14	639.14
X <sub>44</sub>	CN-(C)	9.49	1179.86
X <sub>45</sub>	C-(CN)(C)(H) <sub>2</sub>	94.2	1058.46
X <sub>46</sub>	N-(C)(H) <sub>2</sub>	20.08	888.59
X <sub>47</sub>	Si-(C <sub>B</sub> ) <sub>3</sub> (O)	-255.5	685.5
X <sub>48</sub>	Si-(C) <sub>3</sub> (C <sub>α</sub> )	-90.54	540.54

<sup>a</sup> Skeletal C–C bonds assumed to be similar. C<sub>α</sub> is the double bond carbon atom; C<sub>B</sub> is benzene ring carbon atom.

Table 4

Enthalpies of atomization and the energy of the Si...S interaction in the (organylthioalkyl)trialkoxysilanes,  $RS(CH_2)_nSi(OR')_3$ , ( $\text{kJ mol}^{-1}$ )

R	R'	n	$\Delta H_{a(g)298.15}^\circ(\text{found})$	$\Delta H_{a(g)298.15}^\circ(\text{calc.})$	$E_{Si...S}$
CH <sub>3</sub>	CH <sub>3</sub>	1	9059.1	9026.4	32.7
CH <sub>3</sub>	CH <sub>3</sub>	2	10209.1	10202.5	6.6
CH <sub>3</sub>	CH <sub>3</sub>	3	11372.2	11374.7	-2.5
C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	1	10230.2	10201.7	28.5
C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	2	11383.3	11377.9	5.4
C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	3	12547.8	12550.0	-2.2
C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	1	13788.3	13759.1	29.2
C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	2	14942.2	14935.3	6.9
C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub>	1	12574.3	12545.8	28.5
C <sub>4</sub> H <sub>9</sub>	C <sub>2</sub> H <sub>5</sub>	3	18450.2	18451.3	-1.1
(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub>	CH <sub>3</sub>	1	12579.9	12559.3	20.6
(CH <sub>3</sub> ) <sub>3</sub> C	CH <sub>3</sub>	1	12584.7	12569.3	15.2
C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	1	12912.8	12889.7	23.1
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	CH <sub>3</sub>	1	14094.4	14074.8	19.6
CH <sub>2</sub> =CHCH <sub>2</sub>	CH <sub>3</sub>	1	10817.4	10799.1	18.3

The fragment energy values obtained by use of equations 1 and 2 permitted the calculation of the enthalpies of atomization and formation in the gaseous state of the (organylthioalkyl)trialkoxysilanes, but disregarding the energy of interaction between the silicon and sulfur atoms ( $E_{Si...S}$ ), and for the 1-(organylthioalkyl)silatrane, but disregarding the strain energy of the silatrane skeleton ( $E_{cycl.}$ ), the bond energy between the silicon and nitrogen ( $E_{Si \leftarrow N}$ ) and the energy of interaction between the silicon and sulfur atoms ( $E_{Si...S}$ ).

The energy of interaction between the silicon and sulfur atoms in (organylthioalkyl)trialkoxysilanes was calculated by eq. 4 [18]:

$$E_{Si...S} = \Delta H_{a(g)298.15}^\circ(\text{found}) - \Delta H_{a(g)298.15}^\circ(\text{calc.}) \quad (4)$$

where  $\Delta H_{a(g)298.15}^\circ(\text{found})$  and  $\Delta H_{a(g)298.15}^\circ(\text{calc.})$  are the experimentally obtained enthalpy of atomization, and that calculated by use of the additive scheme as the sum of fragment energies, respectively (Table 4).

The cycle strain energy is the difference between the observed  $\Delta H_f^\circ$  value and that calculated by use of the additivity rule. In this case we used the values of the group contributions, obtained for non-tensioned compounds [18]:

$$E_{cycl.} = \Delta H_{f(g)298.15}^\circ \text{ found} - \Delta H_{f(g)298.15}^\circ \text{ calc.} \quad (5)$$

But

$$\Delta H_{a(g)298.15}^\circ \text{ found} = \Delta H_{f(g, \text{atoms})298.15}^\circ - \Delta H_{f(g)298.15}^\circ \text{ found} \quad (6)$$

$$\Delta H_{a(g)298.15}^\circ \text{ calc.} = \sum \Delta H_{f(g, \text{atoms})298.15}^\circ - \Delta H_{f(g)298.15}^\circ \text{ calc.} \quad (7)$$

$$\Delta H_{a(g)298.15}^\circ \text{ calc.} = \sum E_i - E_{cycl.} + E_{Si \leftarrow N} + E_{Si...S} \quad (8)$$

From equations 5, 6, 7, 8 we obtain:

$$E_{cycl.} - E_{Si \leftarrow N} - E_{Si...S} = E_i - \Delta H_{a(g)298.15}^\circ \text{ found} \quad (9)$$

The calculated data are listed in Table 5.

Table 5

Enthalpies of atomization and the intramolecular energy of the inter  $E_{\text{cycl.}} - E_{\text{Si} \leftarrow \text{N}} - E_{\text{Si} \dots \text{S}}$  interaction in the (organylthioalkyl)silatranes,  $\text{RS}(\text{CH}_2)_n\text{Si}(\text{OCH}_2\text{CH}_2)_m[\text{OCH}(\text{CH}_3)\text{CH}_2]_{3-m}\text{N}$  ( $\text{kJ mol}^{-1}$ )

R	<i>n</i>	<i>m</i>	$\Delta H_{a(g)298.15}^{\circ}$ (found)	$\Delta H_{a(g)298.15}^{\circ}$ (calc.)	$E_{\text{cycl.}} - E_{\text{Si} \leftarrow \text{N}} - E_{\text{Si} \dots \text{S}}$
CH <sub>3</sub>	1	3	12227.0	12223.9	6.9
CH <sub>3</sub>	2	3	13379.6	13410.1	30.5
C <sub>2</sub> H <sub>5</sub>	1	3	13389.6	13409.2	19.6
C <sub>2</sub> H <sub>5</sub>	2	3	14555.4	14585.5	30.1
C <sub>2</sub> H <sub>5</sub>	3	3	15714.7	15757.5	42.8
C <sub>3</sub> H <sub>7</sub>	1	3	14574.1	14581.3	7.2
C <sub>3</sub> H <sub>7</sub>	2	3	15729.5	15757.5	28.0
C <sub>3</sub> H <sub>7</sub>	3	3	16887.8	16929.5	41.7
C <sub>4</sub> H <sub>9</sub>	1	3	15744.1	15753.3	9.2
C <sub>4</sub> H <sub>9</sub>	3	3	18062.7	18101.5	38.8
(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub>	1	3	15749.9	15766.8	16.9
(CH <sub>3</sub> ) <sub>3</sub> C	1	3	15763.1	15777.0	13.9
C <sub>6</sub> H <sub>5</sub>	1	3	16082.0	16097.2	15.2
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	1	3	17267.8	17282.3	14.5
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	1	2	18437.8	18461.7	23.9
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	1	1	19596.9	19641.1	44.2
CH <sub>2</sub> =CHCH <sub>2</sub>	1	3	14012.2	14006.6	-5.6

For identifying the energy of interaction  $E_{\text{Si} \leftarrow \text{N}}$  in 1-(organylthioalkyl)silatranes in calculating  $\Delta H_f^{\circ}$ , calc. and  $\Delta H_a$ , calc. we have taken into account the fragments  $\text{X}_{18} = \text{Si}(\text{O})_3(\text{C})$  and  $\text{X}_{12} = \text{N}(\text{C})_3$  instead of  $\text{Si}(\text{O})_3(\text{N})$  and  $\text{N}(\text{C})_3(\text{Si})$ .

## Discussion

The data in Table 4 indicate that in the series  $\text{RS}(\text{CH}_2)_n\text{Si}(\text{OR}')_3$  for  $n = 3$  the calculated and experimental enthalpies of atomization are practically the same. This points to the fact that in the  $\text{S}(\text{CH}_2)_3\text{Si}$  group the interaction of the silicon and sulfur atoms is practically absent (either through space or by an inductive mechanism).

For compounds of the same series with  $n = 2$  the experimental values of the enthalpies of atomization on average are  $6.3 \pm 1.6 \text{ kJ mole}^{-1}$  higher than the calculated ones. This difference is apparently due to the vicinal interaction between the silicon and sulfur atoms, and can be cancelled out by the corresponding parameters in the calculation scheme.

Accordingly, in the Franklin-Benson scheme for the fragment  $\text{SCH}_2\text{CH}_2\text{Si} = 1/2[\text{S}-(\text{C})_2] + \text{C}-(\text{C})(\text{S})(\text{H})_2 + \text{C}-(\text{Si})(\text{C})(\text{H})_2 + 1/4[\text{Si}-(\text{C})(\text{C})_3]$  in place of the calculated value of  $\Delta H_{a,298.15}^{\circ} = 2587.4$  ( $\Delta H_{f,298.15}^{\circ} = -30.7$ )  $\text{kJ mole}^{-1}$  the value,  $\Delta H_{a,298.15}^{\circ} = 2593.7$  ( $\Delta H_{f,298.15}^{\circ} = -37.0$ )  $\text{kJ mole}^{-1}$ , should be used i.e. with a correction of  $6.3 \pm 1.6 \text{ kJ mole}^{-1}$ . Thus, the energy of interaction between the silicon and sulfur atoms in molecules of the series  $\text{RSCH}_2\text{CH}_2\text{Si}(\text{OR}')_3$  is about  $6 - 7 \text{ kJ mole}^{-1}$ .

Finally, for the compound  $\text{RSCH}_2\text{Si}(\text{OR}')_3$  ( $n = 1$ ) the observed enthalpy of atomization is  $15 - 33 \text{ kJ mole}^{-1}$  ( $24 \pm 9 \text{ kJ mole}^{-1}$ ) higher than the calculated values. This discrepancy of  $24 \pm 9 \text{ kJ mole}^{-1}$  is apparently a measure of the energy

Table 6

Enthalpies of atomization and the intramolecular energy of interaction with regard to  $E_{\text{Si}\cdots\text{S}}$  for the 1-(organylthioalkyl)silatrane,  $\text{RS}(\text{CH}_2)_n\text{Si}(\text{OCH}_2\text{CH}_2)_m[\text{OCH}(\text{CH}_3)\text{CH}_2]_{3-m}\text{N}$  ( $\text{kJ mol}^{-1}$ )

R	<i>n</i>	<i>m</i>	$\Delta H_{a(\text{g})298.15}^{\circ}$ (found)	$\Delta H_{a(\text{g})298.15}^{\circ}$ (calc.)	$E_{\text{cycl.}} - E_{\text{Si}\leftarrow\text{N}}$
CH <sub>3</sub>	1	3	12227.0	12257.9	30.9
CH <sub>3</sub>	2	3	13379.6	13416.4	36.8
C <sub>2</sub> H <sub>5</sub>	1	3	13389.6	13433.2	43.6
C <sub>2</sub> H <sub>5</sub>	2	3	14555.4	14591.8	36.4
C <sub>2</sub> H <sub>5</sub>	3	3	15714.7	15757.5	42.8
C <sub>3</sub> H <sub>7</sub>	1	3	14574.1	14605.3	31.9
C <sub>3</sub> H <sub>7</sub>	2	3	15729.5	15763.8	34.3
C <sub>3</sub> H <sub>7</sub>	3	3	16887.8	16929.5	41.7
C <sub>4</sub> H <sub>9</sub>	1	3	15744.1	15777.3	33.2
C <sub>4</sub> H <sub>9</sub>	3	3	18062.7	18101.5	38.8
(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub>	1	3	15749.9	15790.8	40.9
(CH <sub>3</sub> ) <sub>3</sub> C	1	3	15763.1	15801.0	37.9
C <sub>6</sub> H <sub>5</sub>	1	3	16082.0	16121.2	39.2
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	1	3	17267.8	17306.3	38.5
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	1	2	18437.8	18485.7	47.9
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	1	1	19596.9	19665.1	68.2
CH <sub>2</sub> =CHCH <sub>2</sub>	1	3	14012.2	14030.6	18.4

of geminal interaction between the silicon and sulfur atoms in the SCH<sub>2</sub>Si fragment in RSCH<sub>2</sub>Si(OR')<sub>3</sub>.

The data suggest that the optimal energy of the SCH<sub>2</sub>Si fragment, on the basis of the Benson scheme is 1437.8 kJ mole<sup>-1</sup>.

In the series  $\text{RS}(\text{CH}_2)_n\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}$  with  $n = 3$  the observed enthalpies of atomization are found to be 39–43 kJ mole<sup>-1</sup> less than the calculated values.

The interaction between the silicon and sulfur atoms is negligible in this case, so that such a discrepancy can obviously be attributed to a negative contribution of the silatranyl group to the calculated enthalpy of atomization of the molecule  $\text{RS}(\text{CH}_2)_3\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}$ , which consists of the strain energy of the silatrane skeleton ( $E_{\text{cycl.}}$ ) and the energy of the Si ← N bond ( $E_{\text{Si}\leftarrow\text{N}}$ ). Thus, in the case of  $n = 3$ , the formation of the silatranyl group  $\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}$  results in a surplus of energy ( $41 \pm 2$  kJ mole<sup>-1</sup>).

The calculated enthalpy of atomization of the 1-(2-organylthioethyl)silatrane ( $n = 2$ ), when due account is taken of the above correction for the vicinal interaction between the silicon and sulfur atoms ( $6.3 \pm 1.6$  kJ mole<sup>-1</sup>) (Table 6), exceeds the observed values by 34.3 – 36.8 kJ mole<sup>-1</sup>.

The difference between the calculated and experimental values of enthalpy of atomization of the 1-(organylthiomethyl)silatrane ( $n = 1$ ), lies within 31 – 44 kJ mole<sup>-1</sup> (Table 6) once the geminal interaction between the silicon and sulfur atoms (26.0 kJ mole<sup>-1</sup>) has been taken into account.

Thus, on the basis of the thermochemical calculations by the Benson scheme and taking into account the vicinal or geminal interaction between the silicon and sulfur atoms, a surplus in the enthalpy of atomization in the formation of the silatrane skeleton amounts to 37 kJ mole<sup>-1</sup>, a value which is supported by much experimental data, and by numerous thermochemical and quantum-chemical calculations [19–21]. It is nonetheless important to consider that the corrections for the vicinal

Table 7

Differences between the enthalpies of atomization of the 1-(organylthioalkyl)silatrane,  $\overline{\text{RSi}(\text{OCH}_2\text{CH}_2)_3\text{N}}$ , and the (organylthioalkyl)trialkoxysilane,  $\text{RSi}(\text{OR}')_3$ , in the gaseous state at 298.15 K ( $\text{kJ mol}^{-1}$ )

R	R'	$\Delta H_{\text{a}}^{\circ}(\text{silatr.}) - \Delta H_{\text{a}}^{\circ}(\text{silane})$
$\text{CH}_3\text{CH}_2$	$\text{OCH}_3$	3167.9
$\text{CH}_3(\text{CH}_2)_2$	$\text{OCH}_3$	3170.5
$\text{C}_2\text{H}_5\text{CH}_2$	$\text{OCH}_3$	3159.4
$\text{C}_2\text{H}_5(\text{CH}_2)_2$	$\text{OCH}_3$	3172.1
$\text{C}_2\text{H}_5(\text{CH}_2)_3$	$\text{OCH}_3$	3166.9
$\text{C}_4\text{H}_9\text{CH}_2$	$\text{OCH}_3$	3169.8
$(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2$	$\text{OCH}_3$	3170.0
$(\text{CH}_3)_3\text{CCH}_2$	$\text{OCH}_3$	3178.4
$\text{C}_6\text{H}_5\text{CH}_2$	$\text{OCH}_3$	3169.2
$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2$	$\text{OCH}_3$	3173.4
$\text{C}_2\text{H}_5\text{CH}_2$	$\text{OC}_2\text{H}_5$	-398.7
$\text{C}_2\text{H}_5(\text{CH}_2)_2$	$\text{OC}_2\text{H}_5$	-386.8
$\text{C}_4\text{H}_9(\text{CH}_2)_3$	$\text{OC}_2\text{H}_5$	-387.5

and the geminal interactions between the silicon and sulfur atoms in the Benson scheme in the case of the 1-(organylthioalkyl)silatrane with  $n = 1, 2$  differ slightly from those cited above, because their silicon atom is pentacoordinate.

Successive introductions of methyl groups into the 3- and 7-positions of the silatrane skeleton (XXIX–XXXI) will reduce the enthalpy of formation by 48 – 68  $\text{kJ mole}^{-1}$  (Table 6). This is obviously due to the contribution of Prelog stress, which is in agreement with the thermochemical data for the other 1-(organyl)silatrane [22].

A difference in the enthalpies of formation of the groups  $\overline{\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}}$  and  $\text{Si}(\text{OCH}_3)_3$  can be estimated from the difference between the energies of atomization (the enthalpies of formation) of the molecules  $\overline{\text{RS}(\text{CH}_2)_n\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{N}}$  and  $\text{RS}(\text{CH}_2)_n\text{Si}(\text{OCH}_3)_3$  with equal R and  $n$  values. This difference lies between 3159.0 + 3178.0  $\text{kJ mole}^{-1}$  and on average amounts to  $3170.8 \pm 3.0 \text{ kJ mole}^{-1}$  (Table 7). The difference between the enthalpies of atomization of  $\overline{\text{RSi}(\text{OCH}_2\text{CH}_2)_3\text{N}}$  and of  $\text{RSi}(\text{OC}_2\text{H}_5)_3$  lies between 387 – 398  $\text{kJ mole}^{-1}$ . The energy of formation of the  $\text{Si}(\text{OCH}_3)_3$  group, as estimated by the Benson scheme, is  $-888 \pm 7 \text{ kJ mole}^{-1}$ , and the energy of formation of the silatranyl group is  $-780 \pm 7.0 \text{ kJ mole}^{-1}$ . The enthalpy of formation of the whole silatranyl group, as compared to the  $\text{Si}(\text{OC}_2\text{H}_5)_3$  group, is about  $209.0 \pm 3.5 \text{ kJ mole}^{-1}$  less and is equal to  $-778 \pm 7.0 \text{ kJ mole}^{-1}$ .

Thus, the energy of formation of the silatranyl group can be put at  $-780 \pm 7.0 \text{ kJ mole}^{-1}$ , which corresponds to the data published previously ( $-782 \pm 10.0 \text{ kJ mole}^{-1}$ ) [22].

## Experimental

The (organylthioalkyl)trialkoxysilanes (I–XV, Table 1) were purified by distillation in vacuo. Their purity determined on the TVET-100 chromatograph, was 99.6%.

The 1-(organylthioalkyl)silatranes (XVI–XXXII, Table 2) were purified by multiple sublimations in vacuo. Their purity, as determined from their melting points was in excess of 99.4%.

The enthalpies of formation of sulfur-containing organosilicon compounds were determined from their enthalpies of combustion. Both the investigated and auxiliary substances were burned in a large precision-made calorimeter, equipped with an isothermal jacket, and rotating around two mutually perpendicular axes [17].

To achieve complete oxidation of sulfur, 10 cm<sup>3</sup> of distilled water was introduced into the 346-cm<sup>3</sup> bomb. The bomb was not "washed" as usual, but was immediately filled with oxygen to 3.04 MPa pressure. The temperature of the liquid thermostat was adjusted to an error of  $2 \times 10^{-3}$  K. Temperature variation in the calorimetric system was monitored by a copper resistance thermometer ( $R = 8054$  Ohm). Ignition of the specimens was carried out by use of a cotton thread ( $\Delta U_c^\circ/M = -16736 \pm 7$  J g<sup>-1</sup>) which in turn was lit by a discharge from an electrolytic capacitor. Ignition energy was constant in all experiments ( $q$  of spiral 4.05 J). The initial temperature of the main period in all experiments was 298.15 K. Ninety seconds after igniting the specimen the bomb was set in rotation which was continued throughout the main and terminal periods.

The energy equivalent of the calorimetric system, as determined with reference to standard benzoic acid  $K^{-1}$ , is  $151.16 \pm 0.02$  J Ohm<sup>-1</sup> (mean of 18 measurements). The energy of combustion of benzoic acid, was assumed to be  $-26433.15$  J g<sup>-1</sup>, after the Jessup factor had been taken into account.

To ensure complete burning, the substances under investigation were burned with finely dispersed carbon (particle size  $10^{-7}$ – $10^{-9}$  m,  $\Delta U_c^\circ/M = -33388 \pm 7$  J g<sup>-1</sup>).

The nitrogen oxides that formed from the air nitrogen remaining in the bomb, and the surface of the iridium crucible and plate served as catalysts which completely oxidized the sulfur. To test our technique for determining the enthalpies of combustion of crystalline 1-(organylthioalkyl)silatranes, we burned a mixture of 1,1,2,2-tetramethyl-3,3,4,4-tetraphenylcyclotetrasiloxane (99.8% purity from the melting point curves) with sulfur (99.7% purity) containing finely dispersed carbon. The enthalpy of formation of this siloxane has reliably been determined by the method of Good [23]. Prior to mixing, the first two components were thoroughly ground. The mixture prepared thus contained 0.15 g of carbon, about 0.2 g of siloxane and about 0.027 g of sulfur. The siloxane and the sulfur were mixed using a needle, with the benzoic acid standard in an iridium crucible which was then mounted in the platinum circular electrode of the bomb. To prevent the reaction powder being blown from the crucible, the oxygen isolated from the combustible impurities was introduced into the bomb at a rate of 0.05 mPa min<sup>-1</sup>.

The proposed technique for burning liquid (organylthioalkyl)trialkoxysilanes was checked by use of a composition of hexamethyldisiloxane (about 0.20 g) with sulfur (about 0.023 g) in the presence of 0.25 g of finely dispersed carbon. The enthalpy of formation of hexamethyldisiloxane was determined by Good and coworkers [24].

Hexamethyldisiloxane was placed separately in a terylene container ( $\Delta U_c^\circ/M = -23056$  J g<sup>-1</sup>). Sulfur was thoroughly mixed with carbon in an iridium crucible. The container was suspended from a platinum stand 4 cm from the crucible. An iridium plate ( $d = 35$  mm,  $\delta = 0.3$  mm) was placed between the crucible and the container, 5–10 mm from the latter.

The enthalpy of formation, calculated on the basis of the combustion energy of

1,1,2,2-tetramethyl-3,3,4,4-tetraphenylcyclotetrasiloxane and hexamethyldisiloxane (an average from 6 determinations), is in good agreement with published data:

Reference	$-\Delta H_{f,298.15}^{\circ}$ (kJ mole <sup>-1</sup> )	
	1,1,2,2-tetramethyl-3,3,4,4-tetraphenylcyclotetrasiloxane (solid)	hexamethyldisiloxane (liquid)
23	1824.2 ± 9.2	—
24	—	814.6 ± 6.0
Our data	1827.0 ± 7.0	815.8 ± 4.0

All the compounds under investigation were burned in the same way.

The heats of sublimation of the 1-(organylthioalkyl)silatranes were determined by the Knudsen method, that of measuring the rate of effluence of vapour through a small aperture from a space containing saturated vapour [25].

The heats of evaporation of the (organylthioalkyl)trialkoxysilanes were determined calorimetrically (calorimeter DAK-1-1A) [25].

#### *Analysis of combustion products*

The presence of nitrogen, silicon and sulfur in our compounds accounts for the formation of the combustion products viz. nitric and sulfuric acid, silica, as well as, presumably, HNO<sub>2</sub>, nitrogen dioxide, silicon carbide and silicon nitride.

The nitric and sulfuric acids formed during combustion of the compounds under study were jointly detected. To this end, we developed a technique in which the total acidity could be determined, followed by the determination of sulfuric acid in the same sample. Hence the nitric acid content could be determined. An aliquot of the solution was titrated with a 0.1 *N* alkaline solution in the presence of methyl red (*V*<sub>NaOH</sub>). Then, to the same mixture was added water, an acetate buffer mixture (pH 4.5–4.7), acetone, and the indicator carboxyarsenase ( $\omega$  0.3%), and the mixture was titrated with 0.1 *N* barium chloride solution until the violet colour turned to blue (*V*<sub>BaCl<sub>2</sub></sub>) [26]. Calculations were then carried out using the formulae:

$$n_{\text{H}_2\text{SO}_4} = V_{\text{BaCl}_2} \cdot C_{M \text{BaCl}_2} \cdot K/100, \text{ mol.}$$

$$n_{\text{NHO}_3} = V_{\text{NaOH}} \cdot C_{M \text{NaOH}} \cdot K/100 - 2n_{\text{H}_2\text{SO}_4} \text{ mol,}$$

where *K* is a correction coefficient reducing the concentration of sodium hydroxide and barium chloride exactly to 0.1 *N*; *C*<sub>M BaCl<sub>2</sub></sub>, *C*<sub>M NaOH</sub> are the molar concentrations of barium chloride and the sodium hydroxide solutions, kmole m<sup>-3</sup>. The nitrite ion (detectable by the Griess reaction) was not identified among the combustion products [27]. The nitrogen dioxide content did not exceed 10<sup>-6</sup>–10<sup>-7</sup> mole, so, a correction for the enthalpy of its formation was not introduced.

The structure of the silica formed was studied by electronography and X-ray crystallography. It was found that only amorphous silica was formed in the course of combustion, while the formation of silicon carbide and nitride was not observed.

The degree of combustion of the substances studied (above 99.7%) was determined on the basis of CO<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub> contents. The mass of burnt substances was calculated with respect to the quantity of the carbon dioxide formed (Rossini method).

In calculating the standard enthalpy of combustion we also used a correction for the difference between the thermal capacities of those substances used in the bomb in experiments with benzoic acid and those in experiments with the substances under study. A correction for the variation in the number of moles of gas and the Washburn correction were also used [28].

## References

- 1 M.G. Voronkov, M.S. Sorokin, V.M. Dyakov and M.V. Sigalov, *Zh. Obshch. Khim.*, 45 (1975) 1807.
- 2 M.G. Voronkov and M.S. Sorokin, *Zh. Obshch. Khim.*, 54 (1984) 2020.
- 3 M.G. Voronkov, M.S. Sorokin and V.M. Dyakov, *Zh. Obshch. Khim.*, 49 (1979) 605.
- 4 M.G. Voronkov, M.S. Sorokin, V.E. Traven, M.I. German and B.I. Stepanov, *Dokl. Akad. Nauk SSSR*, 243 (1978) 926.
- 5 A.I. Yermakov, N.A. Makrushin, M.S. Sorokin, E.A. Kirichenko and M.G. Voronkov, *Zh. Obshch. Khim.*, 27 (1986) 68.
- 6 A.I. Yermakov, N.A. Makrushin, M.S. Sorokin, V.I. Kleimenov, E.A. Kirichenko and M.G. Voronkov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 5 (1986) 1105.
- 7 CODATA Recommended key values for thermodynamics, 1977, *J. Chem. Thermodyn.*, 10 (1978) 903.
- 8 V.A. Klyuchnikov, Thesis Cand. of Chemistry, Kalinin, 1979.
- 9 M. Manson and S. Sunner, *Acta Chem. Scand.*, 17 (1963) 723.
- 10 J.L. Franklin, *J. Chem. Phys.*, 21 (1953) 2029.
- 11 S.W. Benson and J.H. Buss, *J. Chem. Phys.*, 29 (1958) 546.
- 12 S.W. Benson, *Chem. Rev.*, 69 (1969) 279.
- 13 I.D. Cox and G.A. Pilcher, *Thermochemistry of Organic and Organometallic Compounds*, Academic Press, London-New York, 1970, p. 643.
- 14 V.I. Telnoi and I.B. Rabinovich, *Usp. Khim.*, 49 (1980) 1137.
- 15 D. Stall, E. Westrum and G. Zinke, *Chemical Thermodynamics of Organic Compounds*, Moscow: Mir Publishers (Russian translation), 1971, p. 807.
- 16 Yu.M. Zhorov, *Thermodynamics of Chemical Processes, Manual.*, Moscow: Khimiya Publishers, 1985, p. 458.
- 17 V.A. Klyuchnikov, T.F. Danilova, M.G. Voronkov and V.M. Dyakov, *Dokl. Akad. Nauk SSSR*, 281 (1985) 1141.
- 18 V.M. Tatevsky, *Structure of molecules*, Moscow, Khimiya Publishers, 1977, p. 511.
- 19 M.G. Voronkov and V.M. Dyakov, *Silatranes*, Novosibirsk: Nauka Publishers, 1978, p. 208.
- 20 M.G. Voronkov, V.M. Dyakov and S.V. Kirpichenko, *Silatranes (Review)*, *J. Organomet. Chem.*, 233 (1982) 1.
- 21 M.G. Voronkov, V.A. Klyuchnikov, T.F. Danilova, V.I. Pepekin, A.N. Korchagina, Yu.I. Khudobin and V.P. Baryshok, *J. Organomet. Chem.*, 345 (1988) 27.
- 22 M.G. Voronkov, V.P. Baryshok, V.A. Klyuchnikov, A.N. Korchagina and V.I. Pepekin, *J. Organomet. Chem.*, 359 (1989) 169.
- 23 R.M. Aizatullova and V.G. Genchel, 6th All-Union Conf. Calorimetry. *Abstr. Papers*, Tbilisi, 1973, p. 133.
- 24 W.D. Good, J.L. Lacina, B.L. De Prater and J.P. McCullough, *J. Phys. Chem.*, 68 (1964) 579.
- 25 Yu.A. Lebedev and E.A. Miroshnichenko, *Thermochemistry of Vapour Formation of Organic Substances*, Moscow, Nauka Publishers, 1981, p. 214.
- 26 S.B. Savvin, T.G. Akimova and V.P. Dedkova, *Organic Reagents for Determining Ba<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup>*, Moscow, Nauka Publishers, 1971, p. 192.
- 27 G. Sharlaut, *Methods of analytical chemistry*, Moscow, Khimiya Publishers, 1969, p. 1206.
- 28 S. Sunner and M. Mansson (Eds.), *Experimental Chemical Thermodynamics, Vol. 1, Combustion Calorimetry*, Oxford, Pergamon Press, 1979, p. 428.