

Thermochemistry of organosilicon compounds

I. Triorganyl-, tetraorganyl-, organylorganoxy- and tetraorganoxy-silanes

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Abstract

A technique for the controlled combustion of liquid and solid organosilicon compounds has been developed. Seventy-two tetracoordinate silicon compounds: triorganyl-, tetraorganyl-, organylorganoxy- and tetraorganoxysilanes have been investigated thermochemically. Their combustion and sublimation, or evaporation, enthalpies have been determined. Formation enthalpies of the compounds concerned in the condensed and gaseous states, and their atomization enthalpies in the gas phase have been calculated. The magnitudes of the fragments for an additive scheme of calculation of atomization enthalpies and bond energies in organosilicon compounds of the above type have been determined.

Introduction

The information available on the enthalpies of combustion, ΔH^0 , and of formation (ΔH_f^0) of organosilicon compounds is rather scarce [1–5]. Furthermore, the published data often show significant discrepancies largely due to the fact that the combustion of organic silicon compounds meets with significant difficulties.

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These manifest themselves at the very beginning of the process, so that the arising silicon dioxide either envelops or sorbs the substance being burned, thus preventing access by oxygen and combustion ceases. The methods that have been described up to now are either laborious [6,7] or fail to ensure complete burning [8–11]. Thus to embark on thermochemical investigations of organosilicon compounds we were first compelled to develop a reliable technique for the determination of their combustion enthalpies. This made it possible to obtain accurate thermochemical constants for the simplest silane derivatives, viz. triorganyl-, tetraorganyl-, organylorganoxy- and tetraorganoxy-silanes.

Results and discussion

Experimental values for combustion and evaporation enthalpies, and those for atomization and formation which were calculated for the investigated organosilicon compounds in condensed and gaseous state, are listed in Tables 1 and 2.

In calculating the formation and atomization enthalpies use was made of the following key values (kJ mol^{-1}):

$$\Delta H_f^0(298.15 \text{ H}_2\text{O}(\text{liquid})) = -285.83 \pm 0.04 [2]$$

$$\Delta H_f^0(298.15 \text{ CO}_2(\text{gas})) = -393.514 \pm 0.046 [2]$$

$$\Delta H_f^0(298.15 \text{ SiO}_2(\text{high-dispers. hydr. amorphous})) = -939.39 \pm 0.52 [6]$$

$$\Delta H_f^0(298.15 \text{ C}(\text{gas})) = 716.670 \pm 0.44 [12]$$

$$\Delta H_f^0(298.15 \text{ Si}(\text{gas})) = 450.00 \pm 0.88 [12]$$

$$\Delta H_f^0(298.15 \text{ H}(\text{gas})) = 217.997 \pm 0.06 [12]$$

$$\Delta H_f^0(298.15 \text{ O}(\text{gas})) = 249.170 \pm 0.10 [12]$$

Calculation of the atomization enthalpies and bond energies by use of an additive scheme

To calculate the atomization enthalpies of gaseous triorganyl-, tetraorganyl-, organylorganoxy- and tetraorganoxysilanes, use was made of an additive scheme taking into account the reciprocal effect of atoms both directly bonded and separated by one or two other atoms. If E_i is the energy of the fragment, K_i is the number of fragments, I_{ij} is the energy of interaction between nonbonded atoms through one and two atoms in the fragments $\text{C}_i\text{--C}_j$ ($i, j = 1, 2, 3, 4; i \leq j$), and n_{ij} is the number of the latter, then

$$\Delta H_{a(\text{C}_n\text{H}_{2n+1}\text{O}_k\text{Si}_m)}^0 = \sum K_i E_i + \sum n_{ij} \cdot I_{ij} \quad (i = 1; i \leq j) \quad (1)$$

K_i are interrelated with n_{ij} by:

$$K_1 = 2n_{11} = n_{12} + n_{13} + n_{14};$$

$$2K_2 = n_{12} + 2n_{22} + n_{23} + n_{24};$$

$$3K_3 = n_{13} + n_{23} + 2n_{33} + n_{34};$$

$$4K_4 = n_{14} + 2n_{24} + n_{34} + 2n_{44}.$$

Or, in general:

$$iK_i = n_{ij} + \sum_{j=1}^4 n_{ij} \quad (i = 1, 2, 3, 4) \quad (2)$$

So that expression (1) can be reduced to:

$$\Delta H_{a(C_nH_{2n+1}O_kSi_m)}^0 = \sum n_{ij} \cdot E_{ij} \quad (i \leq j) \quad (3)$$

This represents the Tatevsky scheme, where E_{ij} is the energy of fragments, taking into account a reciprocal effect of directly bonded atoms or of those separated by one or two atoms; n_{ij} is the number of these fragments. Taken into account are the energies of the following fragments: $E_{C_i-C_j}$; E_{C_i-Si} ; E_{C_i-O} ; E_{O-Si} , etc.

Ref. 13 gives:

$$E_{C_i-Si} = \epsilon_{C_i-Si} + \frac{4-i}{i} \epsilon_{C_i-H} \quad (4)$$

where ϵ_{C_i-Si} is the bond energy of C_i-Si and ϵ_{C_i-H} is the bond energy of C_i-H , adopted by taking into account the closest environment.

On the basis of the values of the atomization enthalpies obtained for gaseous triorganyl-, tetraorganyl-, organylorganoxy- and tetraorganoxysilanes (Tables 1 and 2) we used the least-squares method to determine the fragments of the scheme (Table 3). In calculating the fragment energies, apart from organosilicon compounds, we also made use of the enthalpy of formation of alkanes [13].

The bond energies ϵ_{C_i-H} , ϵ_{C_i-Si} , ϵ_{C_i-O} etc. cannot be found from eq. (4) first assuming that there, is an empirical dependence of bond energy E on length r [14].

$$E_{C_i-Si} = A \cdot r_{C_i-Si}^2 + B \cdot r_{C_i-Si} + C + a \cdot r_{C_i-H} + b \quad (5)$$

The energies of the identified fragments in the compounds investigated can be represented as a system of equations:

$$E_{C_1-C_2} = A_1 \cdot r_{C_1-C_2}^2 + B_1 \cdot r_{C_1-C_2} + C_1 + a(3r_{C_1-H} + r_{C_2-H}) + 4b$$

$$E_{C_1-C_3} = A_1 \cdot r_{C_1-C_3}^2 + B_1 \cdot r_{C_1-C_3} + C_1 + a(3r_{C_1-H} + \frac{1}{3}r_{C_3-H}) + \frac{10}{3}b$$

$$E_{C_1-C_4} = A_1 \cdot r_{C_1-C_4}^2 + B_1 \cdot r_{C_1-C_4} + C_1 + a(3r_{C_1-H}) + 3b$$

$$E_{C_2-C_2} = A_1 \cdot r_{C_2-C_2}^2 + B_1 \cdot r_{C_2-C_2} + C_1 + a(2r_{C_2-C_2}) + 2b$$

$$E_{C_2-C_3} = A_1 \cdot r_{C_2-C_3}^2 + B_1 \cdot r_{C_2-C_3} + C_1 + a(r_{C_2-H} + \frac{1}{3}r_{C_3-H}) + \frac{4}{3}b$$

$$E_{C_1-Si} = A_2 \cdot r_{C_1-Si}^2 + B_2 \cdot r_{C_1-Si} + C_2 + a(3r_{C_1-H}) + 3b$$

$$E_{C_2-Si} = A_2 \cdot r_{C_2-Si}^2 + B_2 \cdot r_{C_2-Si} + C_2 + a(r_{C_2-H}) + b$$

$$E_{C_3-Si} = A_2 \cdot r_{C_3-Si}^2 + B_2 \cdot r_{C_3-Si} + C_2 + a(\frac{1}{3}r_{C_3-H}) + \frac{1}{3}b$$

$$E_{C_1-O} = A_3 \cdot r_{C_1-O}^2 + B_3 \cdot r_{C_1-O} + C_3 + a(3r_{C_1-H}) + 3b$$

$$E_{C_2-O} = A_3 \cdot r_{C_2-O}^2 + B_3 \cdot r_{C_2-O} + C_3 + a(r_{C_2-H}) + b$$

$$E_{C_3-O} = A_3 \cdot r_{C_3-O}^2 + B_3 \cdot r_{C_3-O} + C_3 + a(\frac{1}{3}r_{C_3-H}) + \frac{1}{3}b$$

(Continued on p. 33)

Table 1
Thermochemical constants for triorganyloxy- and tetraorganoxy-silanes (kJ mol^{-1})

Compound	$-\Delta H_{\text{C},298.15}^0$	$-\Delta H_{\text{f},298.15}^0(\text{liquid})$	ΔH^0 evap.	$-\Delta H_{\text{f},298.1}^0(\text{gas})$	$\Delta H_{\text{a},298.15}^0(\text{gas})$	Calc.
	Found	Found	Found	Found	Found	
$(\text{C}_2\text{H}_5)_3\text{SiH}$	5333.0 ± 3.6	254.0 ± 4.0	37.4 ± 0.6	217.5 ± 5.0	8455.0 ± 6.0	8455.0 ± 6.0
$(\text{C}_3\text{H}_7)_3\text{SiH}$	7306.0 ± 4.3	319.0 ± 5.0	39.1 ± 0.7	280.0 ± 6.0	11976.0 ± 7.0	11976.0 ± 7.0
$(\text{C}_4\text{H}_9)_3\text{SiH}$	9279.0 ± 5.4	384.0 ± 6.0	42.9 ± 0.7	341.0 ± 7.0	15495.0 ± 8.0	15496.0 ± 8.0
$(\text{C}_5\text{H}_{11})_3\text{SiH}$	11251.0 ± 5.5	450.0 ± 6.0	48.1 ± 0.8	402.0 ± 7.0	19014.0 ± 8.0	19016.0 ± 8.0
$(\text{C}_6\text{H}_{13})_3\text{SiH}$	13222.0 ± 5.6	517.0 ± 6.0	51.0 ± 0.7	466.0 ± 7.0	22536.0 ± 8.0	22536.0 ± 8.0
$(\text{C}_7\text{H}_{15})_3\text{SiH}$	15191.0 ± 5.9	586.0 ± 6.0	57.4 ± 0.8	529.0 ± 7.0	26056.0 ± 8.0	26057.0 ± 8.0
$(\text{C}_8\text{H}_{17})_3\text{SiH}$	17164.0 ± 6.0	651.0 ± 6.0	59.8 ± 0.8	591.0 ± 7.0	29577.0 ± 9.0	29577.0 ± 9.0
$(\text{C}_9\text{H}_{19})_3\text{SiH}$	19140.0 ± 6.4	713.0 ± 7.0	61.8 ± 0.8	651.0 ± 8.0	33095.0 ± 9.0	33097.0 ± 9.0
$(\text{C}_{10}\text{H}_{21})_3\text{SiH}$	21130.0 ± 6.4	778.0 ± 7.0	65.3 ± 0.8	713.0 ± 8.0	36615.0 ± 9.0	36617.0 ± 9.0
$(i\text{-C}_4\text{H}_9)_3\text{SiH}$	9268.0 ± 5.4	395.0 ± 6.0	40.0 ± 0.7	355.0 ± 7.0	15509.0 ± 8.0	15505.0 ± 8.0
$(i\text{-C}_5\text{H}_{11})_3\text{SiH}$	11244.0 ± 5.4	457.0 ± 6.0	43.8 ± 0.7	413.0 ± 7.0	19025.0 ± 8.0	19025.0 ± 8.0
$(\text{CH}_3)(\text{C}_2\text{H}_5)_2\text{SiH}$	4673.0 ± 3.6	235.0 ± 4.0	34.6 ± 0.7	200.0 ± 5.0	7285.0 ± 6.0	7285.0 ± 6.0
$(\text{CH}_3)(\text{C}_3\text{H}_7)_2\text{SiH}$	5990.0 ± 4.4	276.0 ± 5.0	35.9 ± 0.7	240.0 ± 6.0	9631.0 ± 7.0	9632.0 ± 7.0
$\text{CH}_3(\text{C}_2\text{H}_5)_2\text{SiH}$	7306.0 ± 4.5	319.0 ± 5.0	36.2 ± 0.7	283.0 ± 6.0	11979.0 ± 7.0	11979.0 ± 7.0
$\text{CH}_3(\text{C}_3\text{H}_7)_2\text{SiH}$	8619.0 ± 4.4	365.0 ± 5.0	40.3 ± 0.7	325.0 ± 6.0	14326.0 ± 7.0	14326.0 ± 7.0
$\text{CH}_3(\text{C}_6\text{H}_{13})_2\text{SiH}$	9934.0 ± 5.3	409.0 ± 6.0	42.6 ± 0.7	366.0 ± 7.0	16672.0 ± 8.0	16672.0 ± 8.0
$\text{CH}_3[\text{CH}_3(\text{CH}_2)_9]_2\text{SiH}$	15189.0 ± 6.5	588.0 ± 7.0	57.4 ± 0.8	531.0 ± 8.0	26059.0 ± 9.0	26060.0 ± 9.0
$\text{CH}_3(i\text{-C}_3\text{H}_7)_2\text{SiH}$	5979.0 ± 4.5	287.0 ± 5.0	32.4 ± 0.8	255.0 ± 6.0	9646.0 ± 7.0	9641.0 ± 7.0
$\text{CH}_3[(\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2)]_2\text{SiH}$	7291.0 ± 4.4	334.0 ± 5.0	38.1 ± 0.7	296.0 ± 6.0	11992.0 ± 7.0	11985.0 ± 7.0

$(C_6H_5)_2(CH_3)SiH$	8104.0 ± 4.5	- 48.0 ± 5.0	64.6 ± 0.8	- 113.0 ± 6.0	12706.0 ± 7.0	12707.0 ± 7.0
$(C_3H_7)_2(C_2H_5)SiH$	6649.0 ± 4.4	297.0 ± 5.0	37.9 ± 0.6	259.0 ± 6.0	10802.0 ± 7.0	10802.0 ± 7.0
$(C_4H_9)_2(C_2H_5)SiH$	7963.0 ± 4.5	341.0 ± 5.0	39.9 ± 0.7	301.0 ± 6.0	13150.0 ± 7.0	13149.0 ± 7.0
$(C_5H_{11})_2(C_2H_5)SiH$	9282.0 ± 4.6	381.0 ± 5.0	41.2 ± 0.7	340.0 ± 6.0	15494.0 ± 7.0	15495.0 ± 7.0
$(C_6H_{13})_2(C_2H_5)SiH$	10596.0 ± 4.7	426.0 ± 5.0	44.8 ± 0.7	381.0 ± 6.0	17840.0 ± 7.0	17842.0 ± 7.0
$(C_8H_{17})_2(C_2H_5)SiH$	13224.0 ± 5.6	515.0 ± 6.0	47.3 ± 0.7	468.0 ± 7.0	22538.0 ± 8.0	22535.0 ± 8.0
$(C_{10}H_{21})_2(C_2H_5)SiH$	15853.0 ± 5.6	604.0 ± 6.0	58.7 ± 0.8	545.0 ± 7.0	27226.0 ± 8.0	27229.0 ± 8.0
$(i-C_3H_7)_2(C_2H_5)SiH$	6638.0 ± 4.3	308.0 ± 5.0	38.1 ± 0.7	270.0 ± 6.0	10813.0 ± 7.0	10811.0 ± 7.0
$(i-C_4H_9)_2(C_2H_5)SiH$	7949.0 ± 4.6	355.0 ± 5.0	39.8 ± 0.7	315.0 ± 6.0	13164.0 ± 7.0	13155.0 ± 7.0
$(i-C_5H_{11})_2(C_2H_5)SiH$	9262.0 ± 4.7	401.0 ± 5.0	42.6 ± 0.7	358.0 ± 6.0	15512.0 ± 7.0	15502.0 ± 7.0
$(C_6H_5)_2(C_2H_5)SiH$	8763.0 ± 5.0	- 28.0 ± 5.3	66.1 ± 0.8	- 94.0 ± 5.0	13877.0 ± 7.0	13877.0 ± 7.0
$(CH_3)_4Si$	3973.0 ± 2.7	255.0 ± 3.0	26.0 ± 0.6	229.0 ± 3.0	6162.0 ± 4.0	6160.0 ± 4.0
$(C_2H_5)_4Si$	6610.0 ± 3.1	336.0 ± 4.0	39.0 ± 0.7	297.0 ± 5.0	10840.0 ± 6.0	10840.0 ± 6.0
$(C_3H_7)_4Si$	9243.0 ± 3.6	420.0 ± 4.0	42.2 ± 0.7	378.0 ± 5.0	15532.0 ± 6.0	15534.0 ± 6.0
$(CH_2=CH)_4Si$	5678.0 ± 3.7	125.0 ± 4.0	42.7 ± 0.7	82.0 ± 5.0	8882.0 ± 6.0	8883.0 ± 6.0
$CH_3(C_2H_5)_3Si$	5946.0 ± 3.6	321.0 ± 4.0	40.5 ± 0.6	281.0 ± 5.0	9671.0 ± 6.0	9670.0 ± 6.0
$CH_3(C_3H_7)_3Si$	7918.0 ± 3.6	386.0 ± 4.0	42.6 ± 0.6	343.0 ± 5.0	13192.0 ± 6.0	13190.0 ± 6.0
$(CH_3)_2Si(C_2H_5)_2$	5285.0 ± 3.5	302.0 ± 4.0	38.9 ± 0.6	263.0 ± 5.0	8501.0 ± 6.0	8500.0 ± 6.0
$(CH_3)_2Si(C_3H_7)_2$	6600.0 ± 3.7	346.0 ± 4.0	40.2 ± 0.6	306.0 ± 5.0	10849.0 ± 6.0	10847.0 ± 6.0
$(CH_3)_3Si(C_2H_5)$	4398.0 ± 3.5	224.0 ± 4.0	33.1 ± 0.6	191.0 ± 5.0	6840.0 ± 6.0	6841.0 ± 6.0
$(C_2H_5)_2Si(C_3H_7)_2$	7922.0 ± 3.6	382.0 ± 4.0	41.5 ± 0.7	341.0 ± 5.0	13189.0 ± 6.0	13187.0 ± 6.0
$(C_2H_5)_3Si(C_2H_5)$	7266.0 ± 4.5	359.0 ± 5.0	40.0 ± 0.7	319.0 ± 6.0	12015.0 ± 7.0	12013.0 ± 7.0
$C_2H_5Si(C_3H_7)_3$	8583.0 ± 4.5	401.0 ± 5.0	41.0 ± 0.7	360.0 ± 6.0	14361.0 ± 7.0	14360.0 ± 7.0
$(C_1H_7)_2Si(C_4H_9)_2$	10555.0 ± 5.5	467.0 ± 6.0	44.0 ± 0.8	423.0 ± 7.0	17882.0 ± 8.0	17880.0 ± 8.0
$(C_3H_7)_2Si(C_4H_9)_3$	11211.0 ± 5.5	490.0 ± 6.0	45.0 ± 0.8	444.0 ± 7.0	19056.0 ± 8.0	19053.0 ± 8.0

Table 2

Thermochemical constants of organylorganoxo- and tetraorganoxysilanes (kJ mol^{-1})

Compound	$-\Delta H_{\text{C}_{298.15}}^{\circ}$	$-\Delta H_{\text{f}_{298.15}^{\circ}(\text{liquid})}$	$\Delta H_{\text{f}^{\circ}, \text{evap.}}$	$-\Delta H_{\text{f}_{298.15}^{\circ}(\text{gas})}$	$\Delta H_{\text{f}^{\circ}, 298.15(\text{gas})}$	Calc.
	Found					
$(\text{CH}_3)_3\text{SiOC}_2\text{H}_5$	4371.0 ± 3.5	537.0 ± 4.0	38.4 ± 0.6	499.0 ± 5.0	7832.0 ± 6.0	7834.0 ± 6.0
$(\text{CH}_3)_3\text{SiOC}_3\text{H}_7$	5032.0 ± 3.6	555.0 ± 4.0	34.3 ± 0.6	521.0 ± 5.0	9008.0 ± 6.0	9007.0 ± 6.0
$(\text{CH}_3)_3\text{SiOCH}(\text{CH}_3)_2$	5031.0 ± 3.5	556.0 ± 4.0	31.8 ± 0.6	524.0 ± 5.0	9011.0 ± 6.0	9013.0 ± 6.0
$(\text{CH}_3)_3\text{SiOC}_6\text{H}_5$	6041.0 ± 4.3	441.0 ± 5.0	56.9 ± 0.8	384.0 ± 6.0	10585.0 ± 7.0	10585.0 ± 7.0
$(\text{CH}_3)_3\text{Si}(2\text{-CH}_3\text{OC}_6\text{H}_4)$	6684.0 ± 4.7	477.0 ± 5.0	59.4 ± 0.8	418.0 ± 6.0	11771.0 ± 7.0	11768.0 ± 7.0
$(\text{CH}_3)_3\text{Si}(3\text{-CH}_3\text{OC}_6\text{H}_4)$	6683.0 ± 4.6	478.0 ± 5.0	56.1 ± 0.8	422.0 ± 6.0	11776.0 ± 7.0	11768.0 ± 7.0
$(\text{CH}_3)_3\text{Si}(4\text{-CH}_3\text{OC}_6\text{H}_4)$	6686.0 ± 4.0	475.0 ± 5.0	56.9 ± 0.8	418.0 ± 6.0	11772.0 ± 7.0	11768.0 ± 7.0
$(\text{C}_6\text{H}_5)_3\text{SiOC}_2\text{H}_5$ (Solid)	11446.0 ± 4.3	222.0 ± 5.0	142.7 ± 1.0	79.0 ± 6.0	19472.0 ± 7.0	19477.0 ± 7.0
$(\text{CH}_3)_2\text{Si}(\text{OC}_2\text{H}_5)_2$	4769.0 ± 3.6	818.0 ± 4.0	43.1 ± 0.7	775.0 ± 5.0	9511.0 ± 6.0	9508.0 ± 6.0
$(\text{CH}_3)_2\text{Si}(\text{OC}_6\text{H}_5)_2$	8529.0 ± 5.4	606.0 ± 6.0	64.4 ± 0.9	542.0 ± 7.0	15011.0 ± 8.0	15011.0 ± 8.0
$(\text{CH}_3)_2\text{Si}(2\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2$	9425.0 ± 5.0	669.0 ± 6.0	63.6 ± 0.8	605.0 ± 7.0	17380.0 ± 8.0	17376.0 ± 8.0
$(\text{CH}_3)_2\text{Si}(3\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2$	9424.0 ± 4.6	670.0 ± 5.0	61.5 ± 0.8	609.0 ± 6.0	17384.0 ± 7.0	17376.0 ± 7.0
$(\text{CH}_3)_2\text{Si}(4\text{-CH}_3\text{C}_6\text{H}_4\text{O})_2$	9424.0 ± 4.4	670.0 ± 5.0	65.3 ± 0.9	605.0 ± 6.0	17380.0 ± 7.0	17376.0 ± 7.0
$(\text{C}_3\text{H}_7)_2\text{Si}(\text{C}_2\text{H}_5\text{O})_2$	7406.0 ± 3.6	898.0 ± 4.0	46.5 ± 0.7	852.0 ± 5.0	14199.0 ± 6.0	14197.0 ± 6.0
$\text{CH}_3\text{Si}(\text{OCH}_3)_3$	3250.0 ± 3.5	978.0 ± 4.0	34.3 ± 0.6	944.0 ± 5.0	7624.0 ± 6.0	7624.0 ± 6.0
$\text{CH}_3\text{Si}(\text{OC}_2\text{H}_5)_3$	5176.0 ± 3.7	1090.0 ± 4.0	45.1 ± 0.7	1045.0 ± 5.0	11183.0 ± 6.0	11182.0 ± 6.0
$\text{CH}_2\text{Si}(\text{OC}_6\text{H}_5)_3$	10220.0 ± 5.6	769.0 ± 6.0	71.5 ± 0.9	698.0 ± 7.0	19436.0 ± 8.0	19436.0 ± 8.0
$\text{CH}_3\text{Si}(\text{OC}_6\text{H}_5)_2$	12159.0 ± 5.3	868.0 ± 6.0	68.2 ± 0.9	800.0 ± 7.0	22996.0 ± 8.0	22984.0 ± 8.0
$\text{CH}_3\text{Si}(2\text{-CH}_3\text{C}_6\text{H}_4\text{O})_3$	12150.0 ± 5.4	877.0 ± 6.0	66.9 ± 0.8	810.0 ± 7.0	23006.0 ± 8.0	22984.0 ± 8.0
$\text{CH}_3\text{Si}(3\text{-CH}_3\text{C}_6\text{H}_4\text{O})_3$	12166.0 ± 6.0	861.0 ± 7.0	70.3 ± 0.9	791.0 ± 8.0	22986.0 ± 9.0	22984.0 ± 9.0
$\text{CH}_3\text{Si}(4\text{-CH}_3\text{C}_6\text{H}_4\text{O})_3$	7583.0 ± 3.7	1115.0 ± 4.0	52.3 ± 0.9	1063.0 ± 5.0	15376.0 ± 6.0	15383.0 ± 6.0
$\text{C}_2\text{H}_5\text{Si}(\text{C}_3\text{H}_7\text{O})_3$	5605.0 ± 3.8	1055.0 ± 5.0	50.2 ± 0.8	1005.0 ± 6.0	11860.0 ± 7.0	11863.0 ± 7.0
$\text{C}_2\text{H}_5\text{Si}(\text{C}_6\text{H}_5\text{O})_3$	7558.0 ± 4.0	962.0 ± 5.0	58.3 ± 0.9	904.0 ± 6.0	15061.0 ± 7.0	15063.0 ± 7.0
$\text{C}_6\text{H}_5\text{Si}(\text{C}_2\text{H}_5\text{O})_3$	8257.0 ± 4.1	1336.0 ± 5.0	71.3 ± 0.9	1265.0 ± 6.0	17790.0 ± 7.0	17791.0 ± 7.0
$(\text{C}_6\text{H}_5)_3\text{COOC}_2\text{H}_5\text{Si}(\text{OC}_2\text{H}_5)_3$	3007.0 ± 3.7	1221.0 ± 4.0	41.4 ± 0.7	1180.0 ± 5.0	8112.0 ± 6.0	8112.0 ± 6.0
$(\text{C}_6\text{H}_5)_4\text{Si}$	5583.0 ± 4.0	1363.0 ± 5.0	48.5 ± 0.8	1315.0 ± 6.0	12855.0 ± 7.0	12856.0 ± 7.0
$(\text{C}_3\text{H}_7\text{O})_4\text{Si}$	8216.0 ± 4.1	1447.0 ± 5.0	49.8 ± 0.8	1397.0 ± 6.0	17548.0 ± 7.0	17550.0 ± 7.0
$(\text{C}_4\text{H}_9\text{O})_4\text{Si}$	10847.0 ± 6.0	1534.0 ± 7.0	52.0 ± 1.0	1482.0 ± 8.0	22243.0 ± 9.0	22243.0 ± 9.0
$(\text{C}_6\text{H}_5\text{O})_4\text{Si}$ (Solid)	12270.0 ± 5.6	872.0 ± 1.2	124.7 ± 1.2	847.0 ± 7.0	23855.0 ± 8.0	23861.0 ± 8.0
$(2\text{-CH}_3\text{C}_6\text{H}_4\text{O})_4\text{Si}$	14894.0 ± 5.6	1065.0 ± 6.0	76.2 ± 1.0	989.0 ± 7.0	28606.0 ± 8.0	28591.0 ± 8.0
$(3\text{-CH}_3\text{C}_6\text{H}_4\text{O})_4\text{Si}$	14883.0 ± 6.0	1076.0 ± 7.0	73.6 ± 0.9	1002.0 ± 8.0	28620.0 ± 8.0	28592.0 ± 9.0
$(4\text{-CH}_3\text{C}_6\text{H}_4\text{O})_4\text{Si}$	14886.0 ± 6.4	1073.0 ± 7.0	97.1 ± 1.0	976.0 ± 8.0	28593.0 ± 9.0	28592.0 ± 9.0

Table 3

Atomization enthalpies and molecular bond energies of fragments of organosilicon compounds ^a

Fragment	Atomization enthalpy of fragment (kJ mol ⁻¹)	Bond	Bond energy (kJ mol ⁻¹)	Mean bond length (Å)	Reference
$E_{C_1-C_2}$	2003.59	$\epsilon_{C_1-C_2}$	353.10	1.5345	14
$E_{C_2-C_2}$	1173.40	$\epsilon_{C_2-C_2}$	350.98	1.539	14
$E_{C_1-C_3}$	1727.41	ϵ_{C_1-H}	412.92	1.102	14
$E_{C_1-C_4}$	1590.80	ϵ_{C_2-H}	411.71	1.108	14
$E_{C_2-C_3}$	898.78	ϵ_{C_3-H}	409.68	1.118	14
E_{C_1-Si}	1540.00	$\epsilon_{C_2-C_3}$	350.51	1.540	14
E_{C_2-Si}	706.43	ϵ_{O-C_1}	334.93	1.430	15
E_{C_3-Si}	432.00	ϵ_{O-C_2}	344.39	1.425	17
$E_{C_\alpha-Si}$	550.1	ϵ_{O-C_3}	347.01	1.420	17
$E_{CC_\alpha-C_\alpha}$	1670.58	$\epsilon_{C_1-C_3}$	352.86	1.535	17
E_{O-Si}	454.38	ϵ_{O-Si}	454.38	1.670	17
E_{O-C_1}	1773.70	ϵ_{C_2-Si}	301.82	1.870	16
E_{O-C_2}	756.10	ϵ_{C_1-Si}	298.57	1.88	17
E_{O-C_3}	483.57	$\epsilon_{C_\alpha-C_\alpha}$	351.87	1.537	14
E_{Si-H}	325.10	$\epsilon_{C_\alpha-Si}$	296.14	1.885	17
$E_{C_{ap}-Si}$	320.60	ϵ_{Si-H}	325.10		
$E_{C_{ap}-C_{ap}}$	920.86				
$E_{C_{ap}-C_{ap,3}}$	708.51				
$E_{O-C_{ap,3}}$	410.50				
$E_{C_{ap,3}-CO}$	797.22				
$E_{C_{ap,3}-C_{ap,3}}$	496.11				
E_{CO-O}	788.68				

^a $C_1, C_2, C_3; C_\alpha, C_{\alpha_2}$: CH_3- , $-CH_2-$, $-CH-$, $=CH$, $=CH_2$ groups, respectively; C_{ap} . CH group in the benzene ring, $C_{ap,3}$ a substituted carbon atom in the benzene ring.

The unknown values $A_1, B_1, C_1; A_2, B_2, C_2; A_3, B_3, C_3; a$ and b used for calculating the bond energies in kcal (1 cal = 4.184 J) were calculated by the least-squares method and are as follows:

$$\begin{array}{lll}
 A_1 = 226.275 & B_1 = -807.724 & C_1 = 791.036 \\
 A_2 = 6260 & B_2 = -23630.5 & C_2 = 22370.437 \\
 A_3 = 613.333 & B_3 = -1869.933 & C_3 = 1501.517 \\
 a = -48.381 & & b = 152.007
 \end{array}$$

For some of the investigated organosilicon compounds the combustion and formation enthalpies have been already determined ([18–26], Table 4). From Table 4 it can be seen that the published enthalpies of formation for compounds II, III, IV, V, XII, XIII and XIV differ significantly from those obtained by us. This is due to an incomplete combustion of these substances, a fact which was admitted at time of publication [22,27–29]. In calculating enthalpies of formation for $(CH_2=CH)_4Si$ values of $\Delta H_f^0(298.15 \text{ SiO}_2)$: from -870.7 to $-869.9 \text{ kJ mol}^{-1}$ [19–25]. In a number of cases it was not even indicated what modification of silica was formed after combustion in the bomb calorimeter [25].

We used the value of $\Delta H_f^0(298.15 \text{ SiO}_2 \text{ (hydr. amorph.)}) = -939.4 \text{ kJ mol}^{-1}$ previously determined experimentally [6], by taking into account the hydration enthalpy. In this study it was tested by reaction calorimetry.

Table 4
Formation enthalpies of tetraalkylsilanes (kJ mol^{-1})

Compounds	$-\Delta H_f^0(298.15)$		Reference
	liquid	gas	
$(\text{CH}_3)_4\text{Si}$ (I)		236.0	18
		227.6	19
		231.4	20
	255.2 ± 4.2	230.1 ± 4.1	21, 22
$(\text{C}_2\text{H}_5)_4\text{Si}$ (II)	276.1 ± 16.7	134.3 ± 17.0	21
	277.8 ± 18.8	238.1 ± 19.0	23
	205		24
	276.1 ± 16.7	234.3 ± 17.0	22, 25
$(\text{CH}_3)_2\text{Si}(\text{C}_3\text{H}_7)_2$ (III)	234.3 ± 33.5		22
$(\text{CH}_3)_3\text{SiC}_2\text{H}_5$ (IV)	-16.7 ± 4.1		26
$(\text{CH}_3\text{O})_4\text{Si}$ (V)	1267.7 ± 12.0	1225.9 ± 12.6	24
$(\text{C}_2\text{H}_5\text{O})_4\text{Si}$ (VI)	1380.7 ± 20.0	1330.5 ± 21	30
$(\text{CH}_3\text{O})_3\text{SiCH}_3$ (VII)	974.9 ± 8.1	941.4 ± 8.1	31
$\text{C}_3\text{H}_7\text{OSi}(\text{CH}_3)_3$ (VIII)	564.0 ± 4.1	531.4 ± 4.3	32
$(\text{CH}_3)_3\text{SiOC}_3\text{H}_7$ (IX)	556.5 ± 4.1	518.0 ± 4.1	33
$(\text{CH}_3)_3\text{SiOC}_2\text{H}_5$ (X)	527.2 ± 4.1	489.0 ± 4.1	28
$\text{C}_2\text{H}_3\text{Si}(\text{OC}_2\text{H}_5)_3$ (XI)	1042.2 ± 4.1	1016.7 ± 4.1	33
$(\text{C}_3\text{H}_7)_2\text{Si}(\text{OC}_2\text{H}_5)_2$ (XII)	937.2 ± 8.2		29
$(\text{CH}_3)_2\text{Si}(\text{OC}_2\text{H}_5)_2$ (XIII)	861.9 ± 4.1	820.0 ± 4.1	34
$(\text{C}_6\text{H}_5)_3\text{SiOC}_2\text{H}_5$ (XIV)	644.3 ± 16.0		35

The formation enthalpies of tri-n-alkyl, tetra-n-alkyl-, tetra-n-alkoxy-, n-alkyl-n-alkoxylanes are a linear function of the total number of carbon atoms (n_C) in the molecule. Moreover, for the homologous series [36,37] containing similar types of bonds it is strictly linear. This dependence is reflected in:

$$-\Delta H_f^0(298.15(\text{gas})) = B + \sum Z_i + K \cdot n_C$$

where B is a constant for a given class of compounds; $\sum Z_i$ is a correction of the bonds Si-CH₃, Si-OCH₃, etc; K is the variation in enthalpy of formation as the n-alkyl chain progressively lengthens by one CH₂ group (homologous difference).

In the case of tetraalkylsilanes this equation takes the form:

$$-\Delta H_f^0(298.15(\text{gas})) = 132 + 3.6Z_{\text{Si-CH}_3} + 20.62 \cdot n_C$$

and for the case of trialkylsilanes:

$$-\Delta H_f^0(298.15(\text{gas})) = 93.5 + 3.6Z_{\text{Si-CH}_3} + 20.62 \cdot n_C$$

where $Z_{\text{Si-CH}_3}$ is the number of methyl groups bound with a silicon atom, whilst 3.6 is the difference between enthalpies of formation of the bonds Si-C₁ and Si-C₂. For tetraalkoxysilanes the equation becomes:

$$-\Delta H_f^0(298.15(\text{gas})) = 1150 - 13.1Z_{\text{Si-OCH}_3} + 20.62 \cdot n_C$$

where $Z_{\text{Si-OCH}_3}$ is the number of methoxyl groups bound with the silicon atom, whilst 13.1 is a difference between enthalpies of formation of the bonds Si-OC₁ and Si-OC₂. For n-alkyl-n-alkoxylanes

$$\begin{aligned} &[\text{CH}_3(\text{CH}_2)_m\text{O}]_x\text{Si}[(\text{CH}_2)_n\text{CH}_3]_{4-x} \quad \Delta H_f^0(298.15(\text{gas})) = \\ &132 + 254.5x + 3.6Z_{\text{SiCH}_3} - 13.1Z_{\text{SiOCH}_3} + 20.62 \cdot n_C \end{aligned}$$

This formula is also valid for calculating the $\Delta H_f^0(298.15(\text{gas}))$ for tetra-n-alkylsilanes ($X = 0$) and tetra-n-alkoxysilanes ($X = 4$). The $-\Delta H_f^0(298.15(\text{gas}))$ values for the above substances, calculated by use of this equation, are listed in Table 5. The latter indicates that the calculated and observed ΔH_f values for the investigated

Table 5

Experimental and computed formation enthalpies of tri-, alkyl-, tetra-alkyl, tetra-alkoxy-, -alkyl and -alkoxysilanes (kJ mol^{-1})

Compound	$-\Delta H_{f,298}^0$		B	Discrepancy
	Found	Calc		
$(\text{C}_2\text{H}_5)_3\text{SiH}$	217.0 ± 5.0	217.0	93.5	0
$(\text{C}_3\text{H}_7)_3\text{SiH}$	280.0 ± 6.0	279.0	93.5	1.0
$(\text{C}_4\text{H}_9)_3\text{SiH}$	341.0 ± 7.0	341.0	93.5	0
$(\text{C}_5\text{H}_{11})_3\text{SiH}$	402.0 ± 7.0	403.0	93.5	-1.0
$(\text{C}_6\text{H}_{13})_3\text{SiH}$	466.0 ± 7.0	465.0	93.5	1.0
$(\text{C}_7\text{H}_{15})_3\text{SiH}$	529.0 ± 7.0	527.0	93.5	2.0
$(\text{C}_8\text{H}_{17})_3\text{SiH}$	591.0 ± 7.0	588.0	93.5	3.0
$(\text{C}_9\text{H}_{19})_3\text{SiH}$	651.0 ± 8.0	650.0	93.5	1.0
$(\text{C}_{10}\text{H}_{21})_3\text{SiH}$	713.0 ± 8.0	712.0	93.5	1.0
$(\text{C}_2\text{H}_5)_2\text{CH}_3\text{SiH}$	200.0 ± 5.0	200.0	97	0
$(\text{C}_3\text{H}_7)_2\text{CH}_3\text{SiH}$	240.0 ± 6.0	241.0	97	-1.0
$(\text{C}_4\text{H}_9)_2\text{CH}_3\text{SiH}$	283.0 ± 6.0	283.0	97	0
$(\text{C}_5\text{H}_{11})_2\text{CH}_3\text{SiH}$	325.0 ± 6.0	324.0	97	1.0
$(\text{C}_6\text{H}_{13})_2\text{CH}_3\text{SiH}$	366.0 ± 7.0	365.0	97	1.0
$(\text{C}_3\text{H}_7)_2(\text{C}_2\text{H}_5)\text{SiH}$	259.0 ± 6.0	258.0	93.5	1.0
$(\text{C}_4\text{H}_9)_2(\text{C}_2\text{H}_5)\text{SiH}$	201.0 ± 6.0	300.0	93.5	1.0
$(\text{C}_5\text{H}_{11})_2(\text{C}_2\text{H}_5)\text{SiH}$	340.0 ± 6.0	341.0	93.5	-1.0
$(\text{C}_6\text{H}_{13})_2(\text{C}_2\text{H}_5)\text{SiH}$	381.0 ± 6.0	382.0	93.5	-1.0
$(\text{C}_8\text{H}_{17})_2(\text{C}_2\text{H}_5)\text{SiH}$	468.0 ± 7.0	465.0	93.5	3.0
$(\text{C}_{10}\text{H}_{21})_2\text{C}_2\text{H}_5\text{SiH}$	545.0 ± 7.0	547.0	93.5	-2.0
$(\text{CH}_3)_4\text{Si}$	229.0 ± 3.0	229.0	146	0
$(\text{C}_2\text{H}_5)_4\text{Si}$	297.0 ± 5.0	297.0	132.0	0
$(\text{C}_3\text{H}_7)_4\text{Si}$	378.0 ± 5.0	379.0	132.0	1.0
$(\text{CH}_3)\text{Si}(\text{C}_2\text{H}_5)_3$	281.0 ± 5.0	280.0	135.6	1.0
$(\text{CH}_3)\text{Si}(\text{C}_3\text{H}_7)_3$	343.0 ± 5.0	342.0	135.6	1.0
$(\text{CH}_3)_2\text{Si}(\text{C}_2\text{H}_5)_2$	263.0 ± 5.0	263.0	139.0	0
$(\text{CH}_3)_2\text{Si}(\text{C}_3\text{H}_7)_2$	306.0 ± 5.0	304.0	132.0	2.0
$\text{C}_2\text{H}_5\text{Si}(\text{C}_3\text{H}_7)_3$	360.0 ± 6.0	359.0	132.0	1.0
$(\text{C}_2\text{H}_5)_2\text{Si}(\text{C}_3\text{H}_7)_2$	341.0 ± 5.0	338.0	132.0	3.0
$(\text{C}_2\text{H}_5)_3\text{SiC}_3\text{H}_7$	319.0 ± 6.0	318.0	132.0	1.0
$\text{C}_3\text{H}_7\text{Si}(\text{C}_4\text{H}_9)_3$	444.0 ± 7.0	441.0	132.0	3.0
$(\text{C}_3\text{H}_7)_2\text{Si}(\text{C}_4\text{H}_9)_2$	423.0 ± 6.0	421.0	132.0	2.0
$(\text{CH}_3\text{O})_4\text{Si}$	1180.0 ± 5.0	1180.0	1097.0	0
$(\text{C}_2\text{H}_5\text{O})_4\text{Si}$	1315.0 ± 6.0	1315.0	1097.0	0
$(\text{C}_3\text{H}_7\text{O})_4\text{Si}$	1397.0 ± 6.0	1397.0	1150.0	0
$(\text{C}_4\text{H}_9\text{O})_4\text{Si}$	1482.0 ± 8.0	1480.0	1150.0	2.0
$(\text{CH}_3)_3\text{SiOC}_2\text{H}_5$	499.0 ± 5.0	500.0	397.0	-1.0
$(\text{CH}_3)_2\text{Si}(\text{OC}_2\text{H}_5)_2$	775.0 ± 5.0	778.0	648.0	-3.0
$\text{CH}_3\text{Si}(\text{OCH}_3)_3$	944.0 ± 5.0	942.0	860.0	2.0
$\text{CH}_3\text{Si}(\text{OC}_2\text{H}_5)_3$	1045.0 ± 5.0	1043.0	899.0	2.0
$(\text{CH}_3)_3\text{SiOC}_3\text{H}_7$	521.0 ± 5.0	521.0	397.0	0
$(\text{C}_3\text{H}_7)_2\text{Si}(\text{OC}_2\text{H}_5)_2$	852.0 ± 5.0	847.0	641.0	5.0

organosilicon compounds are within experimental error (maximum discrepancy being $\pm 3 \text{ kJ mol}^{-1}$).

Experimental

Combustion of the substances under investigation was made in a precision calorimeter equipped with an isothermal jacket 6, rotating around two mutually perpendicular axes, and in an automatic combustion calorimeter AKS-3. The calorific value of the calorimetric system, as determined by reference to standard benzoic acid, was found to be $151.6 \pm 0.02 \text{ J ohm}^{-1}$ (an average from 18 determinations). Its heat of combustion, Jessup factor was found to be $26433.26 \text{ J g}^{-1}$.

Liquid organosilicon compounds were purified by rectification in a suitable column (high-boiling ligands in vacuo) and solid compounds, by repeated recrystallization prior to burning. Their purities, on the basis of GLC (chromatograph T8VET-100) and melting curves [38], was over 99.4%. Tetraorganysilanes were additionally purified by preparative chromatography, their purity exceeded 99.98%.

It was found that for complete combustion of the substances temperatures above 1800°C are required. To attain such temperatures, use was made of ultradispersed carbon (particle size 0.1–0.001 micron) whose combustion temperature, determined by an optical pyrometer EOL-66, was above 2000°C . Variation of the internal energy of combustion of ultradispersed carbon in a bomb calorimeter was found to be $\Delta U_{\text{R}}^0(298.15) = -33388.3 \pm 7.0 \text{ kJ kg}^{-1}$ (average of eight determinations).

Liquid organosilicon compounds were burned as follows: A tablet made of ultradispersed carbon was placed in a flat iridium crucible ($m = 8.7 \text{ g}$, $d = 20 \text{ mm}$, $h = 7.5 \text{ mm}$). A sample of 0.12–0.15 g was then placed in a terylene container which was suspended 4 cm above the carbon tablet. Between tablet and terylene container with the substance at 5–10 mm distance from the latter was put an iridium plate ($d = 35 \text{ mm}$, $\delta = 0.8 \text{ mm}$). As much as 2 cm^3 of distilled water was introduced into the bomb. The tablet was ignited by a cotton thread ($-\Delta U_{\text{R}}^0(298.15) = 16736 \text{ J g}^{-1}$) attached at one end to a platinum spiral ($d = 0.1 \text{ mm}$, $l = 7 \text{ cm}$) heated by electric current, the other end was pressed into the carbon tablet.

The energy of combustion of terylene was found to be $\Delta U_{\text{R}}^0(298.15) = -23056 \text{ J g}^{-1}$ (an average of seven determinations).

The substance in the terylene was ignited by the carbon tablet, ignition was explosive and the iridium plate prevented burning liquid from falling onto the bottom of the bomb, thus ensuring that combustion sample had taken place.

As a check on the reliability of the burning procedure we determined the energy of combustion of hexamethyldisiloxane which was purified by rectification and preparative chromatography. Its purity was 99.98%. The obtained value of enthalpy of formation, as given in Table 2 is consistent with that published previously, $816.3 \text{ kJ mol}^{-1}$ [7].

The extent of burning checked from the mass of silica formed was 99.7–99.9%. Spectroscopy (spectrophotometer UR-20) showed that the content of unburnt substance in the combustion products was less than 0.3%, silicon carbide was not identified in this case. X-ray crystallography of the highly-dispersed silica formed indicated that there were no crystalline modifications. Our combustion technique is recommended for burning many types of organosilicon compounds. Enthalpies of

evaporation of the substances under investigation were determined calorimetrically (precision calorimeter DAK-1-1A) by use of a procedure previously described [39–41].

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