

Thermochemistry of organosilicon compounds VII¹. Permethylcyclosilazanes and 1,1,3,3-tetramethyldisilazane

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Abstract

The enthalpy of formation (ΔH_f^0), enthalpy of evaporation (ΔH_v^0) and enthalpy of atomization (ΔH_a) of permethylcyclosilazanes (Me_2SiNH)_n ($n = 3, 4$) and 1,1,3,3-tetramethyldisilazane (Me_2SiH)₂NH have been determined. The enthalpies of formation of these compounds were compared with those calculated by the Benson–Buss–Franklin and Tatevskii additive schemes. In higher permethylcyclosilazanes the energy of the endocyclic Si–N bond is $306 \pm 2 \text{ kJ mol}^{-1}$ (73 kcal mol^{-1}), that is $12 \pm 2 \text{ kJ mol}^{-1}$ (3 kcal mol^{-1}) lower than the energy of the acyclic Si–N bond. The strain energy of the cyclotrisilazane ring is estimated to be 10.5 kJ mol^{-1} ($2.5 \text{ kcal mol}^{-1}$), whereas the energy of the ring Si–N bond is 295 kJ mol^{-1} ($70.5 \text{ kcal mol}^{-1}$).

The thermochemical data for permethylcyclosilazanes were compared with the corresponding values for permethylcyclosiloxanes calculated from the results of previously reported studies.

Keywords: Silicon; Thermochemistry; Bond energy; Enthalpy of formation; Permethylcyclosilazanes; Permethylcyclosiloxanes

1. Introduction

The thermochemical investigation of nitrogen-containing organosilicon compounds [1–6] has not covered peralkyloligocyclosilazanes (R_2SiNH)_n. However, in the literature [5] there is a reference to unpublished data of Dupree, Sinke and Stull on the enthalpies of formation of octamethylcyclotetrasilazane ($270.1 \pm 2.5 \text{ kcal mol}^{-1}$) and the energy of the Si–N bond in its molecule ($82.1 \pm 0.3 \text{ kcal mol}^{-1}$); these data, however, cannot be regarded reliable because they did not take into account that amorphous silicon dioxide, released during combustion of the substance, is formed in the hydrated state.

We have first determined the enthalpies of formation (ΔH_f^0) of hexamethylcyclotrisilazane (I) and octamethylcyclotetrasilazane (II) with $\text{R}=\text{CH}_3$, $n = 3$ and 4 respectively. For comparison, the ΔH_f^0 value for tetramethyldisilazane (HMe_2Si)₂NH (III) has also been measured. The purity of the compounds studied was over 99.7% (gas–liquid chromatography, melting

curves). The heats of combustion were measured in a precision calorimeter [7] with the heat value of $163.18 \pm 0.02 \text{ J } \Omega^{-1}$. The heats of evaporation (sublimation) were determined by the Knudsen effusion method in vacuum [7,8].

Combustion was performed by the method of explosive burning [7]. Samples (0.12–0.15 g) of the liquid compounds I–III were placed in a Terylene ampoule. The ampoule was attached to an iridium grille, 5 mm below which there was an iridium plate, and 30–40 mm below the plate an iridium crucible was placed into a ring electrode. A low-explosive substance having a high combustion rate (ultradispersed carbon) was introduced into the crucible. The burning carbon heated the plate onto which the bulk of the compound analyzed, which was not able to burn entirely, fell down, instantly vaporized and burnt in the atomized state. Solid compound II was mixed with ultradispersed carbon in a ratio of 1:1 in the iridium crucible. During combustion a slight explosion occurred and the mixture in the crucible completely burnt in the atomized state. The combustion products were analyzed by a technique described in [7,8]. The combustion completeness is over 99.0%. The obtained enthalpy of formation (ΔH_f^0), and

¹ For Part VI see [1].

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ΔH_v^0 enthalpy of evaporation of I–III are presented in Table 1.

In calculating the enthalpies of formation and atomization, use was made of the following ΔH_f^0 key values: $H_2O(l)$, -285.83 ± 0.04 kJ mol⁻¹ [9]; $CO_2(g)$, -393.514 ± 0.046 kJ mol⁻¹ [9]; $SiO_2(\text{anhydrous})$, -939.39 ± 0.52 kJ mol⁻¹ [7.8]; C, 716.967 ± 0.44 kJ mol⁻¹ [10]; H, 217.997 ± 0.006 kJ mol⁻¹ [10]; Si 450.0 ± 8.0 kJ mol⁻¹ [10]; N, 472.68 ± 0.12 kJ mol⁻¹ [10].

The enthalpies of formation and atomization were calculated by use of the Benson–Buss–Franklin [11,12] and Tatevskii [13] schemes. The results achieved are presented in Tables 2 and 3. For comparison the corresponding values for hexamethyldisilazane $Me_3SiNH-SiMe_3$ (IV) obtained previously [6] are given in these Tables.

Appropriate parameters (fragments of additive schemes) (Tables 4 and 5) were calculated by the least-squares method from measured enthalpies of formation and atomization of Si–N bond-containing compounds examined by us previously [6] and in the present work.

From the experimental enthalpies of formation and atomization and the calculated parameters of additive schemes for acyclic Si–N bond-containing compounds the energies E_c of formation of permethylated cyclotrisilazane and cyclosilazane rings were estimated to be 113 and 100 kJ mol⁻¹ respectively. These values indicate a marked difference in between the enthalpies of formation of the acyclic and endocyclic Si–N bond. As the molecule of octamethylcyclotetrasilazane is almost not strained [14], it should be accepted that the energy of the endocyclic Si–N bond is by 12.5 kJ mol⁻¹ (3.0 kcal mol⁻¹) lower than that of the acyclic bond.

Thus, if the energy of the acyclic Si–N bond in linear polyalkylsilazanes is taken, as the basis of our data, to be 318.5 ± 2 kJ mol⁻¹ (76 kcal mol⁻¹)¹, the energy of the endocyclic Si–N bond in higher oligopermethylcyclosilazanes is likely to be 306 ± 2 kJ mol⁻¹ (73 kcal mol⁻¹). If the strained energy of the cyclotrisi-

¹ According to [3], the Si–N bond energy in hexamethyldisilazane is 75.8 kcal mol⁻¹ (317 kJ mol⁻¹).

Table 1
Enthalpy of formation (ΔH_f^0) and enthalpy of evaporation (ΔH_v^0) for I–III

Compound		$-\Delta H_f^0(l)$ (kJ mol ⁻¹)	ΔH_v^0 (kJ mol ⁻¹)	$\Delta H_f^0(r)$ (kJ mol ⁻¹)
I	$(Me_2SiNH)_3$	610.0 ± 9.0	57.0 ± 1.0	553.0 ± 10.0
II	$(Me_2SiNH)_4$	680.0 ± 10.0	92.0 ± 1.5	788.0 ± 11.0
III	$(HMe_2Si)_2NH$	332.0 ± 8.0	44.0 ± 1.0	288.0 ± 9.0

Table 2
Enthalpies of formation, experimental ($\Delta H_f^0(g)$) and calculated by additive schemes, for I–IV

Compound		$-\Delta H_f^0$		
		Found	Calculated by Benson–Buss– Franklin scheme	Calculated by Tatevskii Scheme
I	$(Me_2SiNH)_3$	553.0 ± 10.0	666.0 ± 11.0	666.0 ± 11.0
II	$(Me_2SiNH)_4$	788.0 ± 11.0	888.0 ± 12.0	888.0 ± 12.0
III	$(HMe_2Si)_2NH$	288.0 ± 9.0	288.0 ± 10.0	288.0 ± 10.0
IV	$(Me_3Si)_2NH$	450.8 ± 10.0	451.7 ± 11.0	451.8 ± 11.0

Table 3
Enthalpies of atomization, experimental and calculated by additive schemes for I–IV

Compound		$\Delta H_a^0(g)$		
		Found	Calculated by Benson–Buss– Franklin scheme	Calculated by Tatevskii scheme
I	$(Me_2SiNH)_3$	12199.0 ± 9.0	12312.0 ± 10.0	12312.0 ± 10.0
II	$(Me_2SiNH)_4$	16316.6 ± 10.0	16416.0 ± 11.0	16416.0 ± 11.0
III	$(HMe_2Si)_2NH$	7797.0 ± 8.0	7797.0 ± 9.0	7797.0 ± 9.0
IV	$(Me_3Si)_2NH$	10265.4 ± 11.5	10266.3 ± 12.0	10266.4 ± 12.0

Table 4
Parameters of the Benson–Buss–Franklin additive scheme

Fragment	E_i (kJ mol ⁻¹)	$-H_i$ (kJ mol ⁻¹)
[Si–C(H) ₃]	1410.93	40.27
[(H)N–Si(C) ₂]	766.08	97.57
[Si–(C) ₂ –(N) ₂]	660.72	210.72
[(H)N ₂ (Si)]	621.42	–68.26

Table 5
Parameters of the Tatevskii additive scheme

Fragment	E_{ij} (kJ mol ⁻¹)	$-H_{ij}$ (kJ mol ⁻¹)
C ₁ –Si[NH]	1540.6	57.44
HN–Si[(C) ₂]	511.4	53.56
HN–Si[H(C)]	817.3	29.22

lazane ring (in accord with the cyclotrisiloxane ring [16]) is estimated to be 2.5 kcal mol⁻¹ (10.5 kJ mol⁻¹), the Si–N bond energy in its molecule is 70.5 kcal mol⁻¹ (295 kJ mol⁻¹). This is also shown by the difference between the enthalpies of formation of the Me₂SiNH group in (Me₂SiNH)₄ and (Me₂SiNH)₃ molecules:

$$\frac{788}{4} - \frac{553}{3} = 12.7 \text{ kJ mol}^{-1} = 30 \text{ kcal mol}^{-1}.$$

This is indicative of the fact that the Si–N bond energy in (Me₂SiNH)₃ is 3 kcal mol⁻¹ lower than in (Me₂SiNH)₄, being equal to 70.0 kcal mol⁻¹. Thus the Si–N bond energy in hexamethylcyclotrisilazane should be evaluated to be 70.0 ± 0.5 kcal mol⁻¹ or 293 ± 2 kJ mol⁻¹.

An analogous picture is observed with acyclic and cyclic permethylcyclotrisiloxanes [15–17]. The energies of the Si–O bond in low-strained rings of permethylated cyclotetrasiloxane and cyclopentasiloxane (strained energy, $E_s = 0.24$ and 0.25 kcal mol⁻¹)² are 105.9 and 106.6 kcal mol⁻¹ respectively. In the strained ring of hexamethylcyclotrisiloxane ($E_s = 2.5$ kcal mol⁻¹) the

² In Part V [17], E_s denoted the energy of the cyclotrisiloxane framework formation rather than the ring strain energy.

Si–O bond energy is 104.4 kcal mol⁻¹. In hexamethylcyclotrisiloxane and higher homologs the Si–O bond energy equals 107.5 kcal mol⁻¹ [17] and is taken as standard. This is consistent with the difference in the enthalpies of formation of the Me₂SiO group in (Me₂SiO)_n with $n = 3, 4, 5$ equal to 11.8 and 7.1 kJ mol⁻¹ or 2.8 and 1.7 kcal mol⁻¹ respectively. In agreement with the above data the thermal effect of the ring opening in hexamethylcyclotrisiloxane is 5.5 kcal mol⁻¹ whereas that in octamethylcyclotetrasiloxane and decamethylcyclopentasiloxane is as small as 0.2 kcal mol⁻¹ [16].

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