Thermochemistry of organosilicon compounds

VI *. Thermochemical properties of organosilicon compounds with a Si–N bond

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Abstract

We have evaluated the enthalpies of combustion and formation in the condensed and gaseous states, of fifteen organosilicon compounds containing an Si–N bond, of the general formula $R_{4-n}Si(NR'R'')_n$ where R = H, alkyl; R' = H, alkyl, $Si(CH_3)_3$; R'' = alkyl, $Si(CH_3)_3$. The enthalpies of atomization in the gaseous phase and parameters for evaluating the enthalpies of formation and atomization of the above compounds by use of the Franklin–Benson and Tatevskii schemes have been calculated. The Si–N bond energy ranges from 316.5 to 329 kJ mol^{-1}. In compounds containing an Si–N–Si group, the Si–N bond energy is lowest.

Introduction

Monomeric and polymeric organosilicon compounds having one or more Si–N bonds are of great theoretical and practical interest. However, their thermochemical constants are scarce in the literature and most of them are contradictory and need re-examination [1–6]. The Si–N bond energies calculated from experimental thermochemical data, have been evaluated within the range of 305.9 to 376.6 kJ mol^{-1} [1–5].

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Results and discussion

The enthalpies of combustion and evaporation have been measured for 15 monomeric organosilicon compounds with the Si–N bond, of the general formula $R_{4-n}Si(NR'R'')$ with R = H, alkyl; R' = H, alkyl, $Si(CH_3)_3$; R'' = alkyl, $Si(CH_3)_3$ (Table 1). The energies of fragments in the Franklin–Benson (Table 2) and the Tatevskii schemes (table 3) have been determined. From this the enthalpies of formation in the condensed state and the enthalpies of atomization in the gas phase have been calculated (Table 4).

In evaluating the enthalpies of formation and atomization use was made of the following key values (ΔH_f°, kJ mol^{-1} at 298.15 K):
-285.830 ± 0.042 (H$_2$O, liquid); -393.514 ± 0.13 (CO$_2$, gas) [8]; -939.39 ± 0.52

Table 1

Enthalpies of combustion, formation and evaporation of the investigated organosilicon compounds containing an Si–N bond at 298.15 K, kJ mol^{-1}

Compound	$-\Delta H^\circ$ (cycl. (liq.)	$-\Delta H_f^\circ$ (liq.)	ΔH°
HSi[N(C$_2$H$_5$)$_2$]$_3$	9684.2 ± 4.5	407.7 ± 5.0	58.4 ± 1.0
(CH$_3$)$_3$SiNHCH$_3$	4096.1 ± 5.1	275.2 ± 6.0	37.4 ± 0.8
(CH$_3$)$_3$SiN(CH$_3$)$_2$	4771.1 ± 5.0	279.6 ± 6.0	33.6 ± 0.8
(CH$_3$)$_3$SiN(C$_2$H$_5$)$_2$	6082.7 ± 5.2	326.7 ± 6.0	37.9 ± 0.8
(C$_2$H$_5$)$_3$SiN(C$_2$H$_5$)$_2$	8064.4 ± 4.5	383.0 ± 5.0	42.2 ± 1.0
(C$_2$H$_5$)$_3$SiNHCH$_2$CH$_2$CH$_3$	7107.7 ± 5.7	374.5 ± 6.0	41.5 ± 0.8
(C$_2$H$_5$)$_3$SiNHCH(CH$_3$)$_2$	7385.8 ± 5.5	382.3 ± 6.0	38.6 ± 0.8
(C$_2$H$_5$)$_3$SiNHC(CH$_3$)$_3$	8054.1 ± 6.5	393.3 ± 7.0	40.3 ± 0.9
(C$_2$H$_5$)$_3$SiN(CH$_2$CH$_2$CH$_2$CH$_3$)$_2$	10684.5 ± 6.3	480.3 ± 7.0	56.3 ± 1.0
(C$_2$H$_5$)$_3$SiN[CH(CH$_3$)CH$_2$CH$_3$]$_2$	10667.4 ± 7.5	497.4 ± 8.0	51.4 ± 0.9
(C$_2$H$_5$)$_3$SiNHCH(CH$_3$)CH$_2$CH$_2$CH$_3$	8694.6 ± 7.2	432.1 ± 8.0	46.9 ± 1.0
(C$_2$H$_5$)$_3$SiNH(CH$_2$)$_7$CH$_3$	10668.6 ± 7.8	496.2 ± 8.0	59.1 ± 1.0
[(CH$_3$)$_3$Si]$_2$NH	6462.2 ± 8.1	493.0 ± 9.0	42.2 ± 0.9
[(CH$_3$)$_3$Si]$_2$NCH$_3$	7140.5 ± 8.3	494.1 ± 9.0	38.1 ± 0.8
[(CH$_3$)$_3$Si]$_3$N	9498.2 ± 9.6	720.3 ± 10.0	54.3 ± 1.0

Note: [(CH$_3$)$_3$Si]$_3$N is a solid, its enthalpies of formation and sublimation were determined as described in ref. 7.

Table 2

Numeric contributions of fragments in the Franklin–Benson scheme, kJ mol^{-1}

Fragment	Value		Fragment	Value	
	E_i	$-H_i$		E_i	$-H_i$
C–(C)(H)$_3$	1414.93	44.27	Si–(C)$_3$(N)	589.20	139.20
C–(C)$_2$(H)$_2$	1173.46	20.80	Si–(N)$_3$(H)	931.00	263.00
C–(C)(Si)(H)$_2$	1166.26	13.60	N–(Si)(C)$_2$	369.40	−103.28
C–(N)(C)(H)$_2$	1174.42	21.76	N–(Si)(C)(H)	624.20	−66.48
C–(C)$_3$(N)	690.56	−26.11	N–(Si)$_2$(C)	365.20	−107.48
C–(C)$_2$(N)(H)	943.63	8.96	N–(Si)$_3$	359.40	−113.28
C–(Si)(H)$_3$	1410.93	40.27	N–(C)(H)$_2$	889.35	−19.32
C–(N)(H)$_3$	1414.93	44.27	N–(Si)$_2$(H)	621.42	−68.26

Table 3

Numeric contributions of fragments in the Tatevskii scheme, kJ mol^{-1}

Fragment	Value		Fragment	Value	
	E_{ij}	$-H_{ij}$		E_{ij}	$-H_{ij}$
C_1-C_2	2002.27	55.58	C_3-N	443.02	-26.10
C_2-C_2	1173.46	20.80	C_1-NH	1919.30	15.52
C_3-C_1	1728.77	46.55	C_2NH	1093.60	-15.85
C_1-C_4	1592.70	42.87	C_3-NH	822.80	-21.87
C_2-C_3	898.68	10.79	C_4-NH	664.20	-48.09
C_1-Si	1540.60	57.44	$Si-N$	320.00	49.94
C_2-Si	707.43	18.60	$Si-H$	325.10	-5.40
C_1-N	1540.50	12.28	$Si-NH$	511.40	53.56
C_2-N	712.46	-21.43			

(SiO$_2$ amorph. hydr.) [9,10]; 716.67 ± 0.44 (C, gas); 217.997 ± 0.006 (H, gas); 450.00 ± 8 (Si, gas); 472.68 ± 0.12 (N, gas) [8].

Calculation of the enthalpies of formation and atomization by additive schemes was performed by use of:

(i) the Franklin–Benson formula [11,12]

$$\Delta H_a^\circ \text{ (gas)} = \sum_{i=1}^{n} K_i E_i$$

$$\Delta H_f^\circ \text{ (gas)} = \sum_{i=1}^{n} K_i H_i$$

Here $H_i = -E_i + \Sigma \, \partial \Delta H_f^\circ \text{ (atom)}$

where H_i is the enthalpy of formation of a given fragment; E_i is the energy of the fragment, which takes into account the mutual effect of the atoms separated by not more than one atom in the molecular chain; K_i is the number of fragments; ∂ the number of moles of C, H, Si and N atoms.

For the compounds studied the fragments are as follows:

C-C$_2$-(H)$_2$, C-(C)-(Si)(H$_2$), C-(N)(H)$_3$, etc.

(ii) The Tatevskii formula [13]:

$$\Delta H_f^\circ \text{ (gas)} = \sum_{i,j=1}^{n} n_{ij} H_{ij}, \ i \leqslant j$$

$$\Delta H_a^\circ \text{ (gas)} = \sum_{i,j=1}^{4} n_{ij} E_{ij}, \ i \leqslant j$$

Here $H_{ij} = -E_{ij} + \Sigma \, \partial \Delta H_f^\circ \text{ (atom)}$

where E_{ij} is the energy of the fragment, which takes into account the mutual effect of the atoms separated by not more than one other atom in the molecular chain; n_{ij} is the number of fragments.

The substances studied contain the following fragments:

C$_i$-Si, Si-N, C$_i$-N, etc.

Table 4

Enthalpies of formation and atomization of organosilicon compounds containing Si–N group, measured and calculated by the Franklin–Benson and Tatevskii schemes at 298.15 K, kJ mol^{-1}

Compound	$-\Delta H_f^\circ$ (gas) (exp.)	ΔH_f° (gas) (calc.) [a]	$-\Delta H_f^\circ$ (gas) (calc.) [b]	ΔH_a° (exp.)	ΔH_a (calc.) [a]	ΔH_a (calc.) [b]
HSi[N(C₂H₅)₂]₃	349.6 ± 6.0	349.3	349.3	17575.3 ± 7.8	17575.3	17575.3
(CH₃)₃SiNHCH₃	237.8 ± 7.0	237.8	237.8	6861.1 ± 8.1	6861.1	6861.1
(CH₃)₃SiN(CH₃)₂	246.0 ± 7.7	245.3	246.8	8022.0 ± 8.5	8021.3	8022.8
(CH₃)₃SiN(C₂H₅)₂	288.8 ± 7.0	288.8	290.6	10379.1 ± 8.8	10370.1	10371.9
(C₂H₅)₃SiNHCH₂CH₂CH₃	340.8 ± 6.0	341.6	340.8	13880.1 ± 8.0	13880.9	13880.1
(C₂H₅)₃SiNHCH(CH₃)₂	333.0 ± 7.0	332.2	332.2	12719.6 ± 8.6	12719.8	12719.6
(C₂H₅)₃SiNHC(CH₃)₃	353.0 ± 8.0	353.0	353.0	13892.3 ± 9.0	13892.3	13892.3
(C₂H₅)₃SiN(CH₂CH₂CH₂CH₃)₂	424.0 ± 8.0	424.8	423.9	18574.0 ± 7.5	18574.7	18573.9
(C₂H₅)₃SiN[CH(CH₃)CH₂CH₃]₂	446.0 ± 9.0	446.1	446.1	18596.0 ± 10.0	18596.7	18596.1
(C₂H₅)₃SiNHCH(CH₃)CH₂CH₂CH₃	385.2 ± 9.0	385.4	384.3	15077.2 ± 10.2	15077.4	15076.3
(C₂H₅)₃SiNH(CH₂)₇CH₃	437.1 ± 9.0	437.2	437.0	18587.1 ± 9.9	18587.1	18586.9
[(CH₃)₃Si]₂NH	450.8 ± 10.0	451.7	451.8	10265.4 ± 11.5	10265.4	10266.4
[(CH₃)₃Si]₂NCH₃	456.0 ± 10.0	456.8	456.8	11423.3 ± 11.0	11424.1	11424.1
[(CH₃)₃Si]₃N	656.0 ± 11.0	666.8	666.8	14814.6 ± 12.5	14825.4	14825.4

[a] By the Franklin–Benson scheme. [b] By the Tatevskii scheme.

Table 5

Comparison of the experimental and published (Lit.) data on the enthalpies of formation in the gaseous state and the Si–N bond energies

Compound	$-\Delta H_f^{\circ}$, kJ mole^{-1}			E_{Si-N}, kJ mol^{-1}		
	Our data	Lit	Refs.	Our data	Lit.	Refs.
HSi[N(C₂H₅)₂]₃	349.6 ± 6.0	–		329	322.2 ± 20.9	5
(CH₃)₃SiNHCH₃	237.8 ± 7.0	227.2 ± 4.2	4	320	305.9	4
(CH₃)₃SiN(CH₃)₂	246.0 ± 7.7	247.7 ± 3.8	4	324	331.0	4
(CH₃)₃SiN(C₂H₅)₂	288.8 ± 7.0	251.04 ± 6.3	2	325	309.2 ± 4.2	2
					348.5	
(C₂H₅)₃SiN(C₂H₅)₂	340.8 ± 6.0	330.5 ± 6.3	5	327	376.6 ± 20.9	5
(C₂H₅)₃SiNHCH₂CH₂CH₃	333.0 ± 7.0	–		327	–	
(C₂H₅)₃SiNHCH(CH₃)₂	343.7 ± 7.0	–		328	–	
(C₂H₅)₃SiNHC(CH₃)₃	353.0 ± 8.0	–		319	–	
(C₂H₅)₃SiN(CH₂CH₂CH₂CH₃)₂	424.0 ± 8.0	–		326	–	
(C₂H₅)₃SiN[CH(CH₃)CH₂CH₃]₂	446.0 ± 9.0	–		326	–	
(C₂H₅)₃SiNHCH(CH₃)CH₂CH₂CH₃	385.2 ± 9.0	–		326	–	
(C₂H₅)₃SiNH(CH₂)₇CH₃	437.1 ± 9.0	–		327	–	
[(CH₃)₃Si]₂NH	450.8 ± 10.0	432.2 ± 7.1	2	319	322.6 ± 3.8	2
		476.6 ± 6.7	4		319.7	3
		477.0 ± 7.5	4		317.1	4
[(CH₃)₃Si]₂NCH₃	456.0 ± 10.0	448.5 ± 7.5	4	319.5	314.2	4
[(CH₃)₃Si]₃N	656.0 ± 11.0	670.7 ± 12.1	4	316.5	310.0	4

The numerical contributions of fragments in the Franklin–Benson (H_i, E_i) and Tatevskii schemes (H_{ij}, E_{ij}) were calculated by the least squares method, using the enthalpies of formation and atomization of tri- and tetrasilanes as well as those of alkylalkoxysilanes determined experimentally [7].

In Table 4 the experimental ΔH_f° and ΔH_a° values are summarized and compared with well-established values calculated by the Benson and Tatevskii schemes. From the experimental ΔH_f° values, the bond energies depending on the bond surrounding have been calculated (Table 5). The data of Table 5 provides strong evidence for the Si–N bond energy not being constant and not depending much on the nature of substituents attached to the Si and N atoms. In the compounds studied the Si–N bond energies vary from 316.5 to 329 kJ mol^{-1}, i.e. within a fairly narrow range.

The lowest Si–N bond energy value is observed in compounds containing a Si–N–Si group: in hexamethyl- and heptamethyldisilazane (319.0 and 319.5 kJ mol^{-1}, respectively) and N-(trimethylsilyl)hexamethyldisilazane (316.5 kJ mol^{-1}). This seems to be due to a lower Si–N bond order in compounds containing this group. Our experimental values of the enthalpies of formation of organosilicon compounds containing a Si–N bond, and the Si–N bond energies coincide, within the limits of experimental error, with analogous values obtained from the heats of hydrolysis [4], and can therefore be regarded as reliable.

Experimental

The purity of the substances studied, which was assessed by GLC and the melting point curves, exceeds 99.3%.

The heats of combustion were measured in a precision calorimeter [7] (calorific value $151.16 + 0.02$ J Ω^{-1}).

The heats of formation and sublimation were determined by means of calorimetry (DAK-1IA calorimeter) and the Knudsen effusion method on a vacuum installation. Liquid compounds (0.130–0.165 g sample) were burnt in Terylene ampoules with benzoic acid pellets (0.30–0.35 g). The procedure of burning of organosilicon compounds was described previously [7]. The degree of combustion was 98.5–99.8%.

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