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Thermochemistry of organosilicon compounds

IV *. Thermochemical properties of Si-substituted silacyclobutanes

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Abstract

The enthalpies of combustion of five Si-substituted silacyclobutanes have been determined and their heats of formation in the liquid and gas states at 298.15 K evaluated. The enthalpies of atomization in the gas phase and the parameters for evaluating the enthalpies of atomization and bonding energies by additive schemes have been calculated. For the compounds studied the strain energy of the silacyclobutane ring varies within the range 107–112 kJ mole^{-1}, increasing with the introduction of substituents to both the silicon and carbon atom. The substitution of carbon atoms in cyclobutane by silicon atoms reduces the ring strain energy.

Introduction

Si-substituted silacyclobutanes $RR'Si(CH_2)_3$ have been studied fairly thoroughly [1,2]. However, the thermochemical properties of these compounds which permit determination of the energy of their formation and the silacyclobutane ring strain, have not been determined until now. The available figures for enthalpies of formation of 1,1-dimethyl-1-silacyclobutane are rather contradictory [3–6] (cf. notes to Table 2).

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* For part III see ref. 16.

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Table 1

Enthalpies of combustion, formation, evaporation and atomization of Si-substituted silacyclobutanes at 298.15 K (kJ mole^{-1})

Compound	General formula	$-\Delta H_c^0$ liquid	$-\Delta H_f^0$ liquid	ΔH_v^0
1-methylsilacyclobutane	$C_4H_{10}Si$	3894.6	48.0	25,1
1,2-dimethylsilacyclobutane	$C_5H_{12}Si$	4503.8	118,1 [a]	33.1
1,1,2-trimethylsilacyclobutane	$C_6H_{14}Si$	5155.3	146.0	36.0
1,1,3-trimethylsilacyclobutane	$C_6H_{14}Si$	5152.8	148.5	35.5
1-methyl-1-vinylsilacyclobutane	$C_6H_{12}Si$	4974.4	41.1	33.1

[a] Literature data: 115.1 ∓ 5.4 kJ mole^{-1} [3].

Table 2

Enthalpies of formation, atomization and ring strain of silacyclobutane and its substituted forms, calculated by use of the Franklin–Benson and Tatevskii schemes at 298.15 K (kJ mole^{-1})

Compound	$-\Delta H_{f,g}^0$ exp.	$-\Delta H_{f,g}^0$ [a]	$E_{cycl.}$	$-\Delta H_{f,g}^0$ [a]	$E_{cycl.}$	$\Delta H_{a,exp.}^0$	ΔH_a^0 [a]	ΔH_a^0 [b]
Silacyclobutane	–	130.8	107.8	130.9	107.9	–	5619.5	5619.3
1-methylsilacyclobutane	23.0	130.8	107.8	130.9	107.9	5519.7	5619.5	5627.5
1,1-dimethylsilacyclobutane	85.0 [c]	193.7	108.7 [d]	193.7	108.7	6734.3	6843.0	6843.0
1,1,2-trimethylsilacyclobutane	110.0	219.4	109.4	217.6	107.6	7912.0	8021.4	8019.6
1,1,3-trimethylsilacyclobutane	113.0	225.2	112.2	220.2	107.2	7915.0	8027.1	8022.2
1-methyl-1-vinylsilacyclobutane	8.0	117.2	109.2	116.9	109.0	7374.0	7483.0	7483.0

[a] Calculated by the Franklin–Benson scheme. [b] Calculated by the Tatevskii scheme. [c] Literature data: −82.8 ∓ 5.9 [3]; −108.7 ∓ 6.0 [7]; −138 ∓ 11 [7] (kJ mole^{-1}). [d] Literature data: 94 ∓ 8 [7], 108.4 ∓ 8.4 [3]; calculated values: 103 (kJ mole^{-1}) [6].

Table 3

Energies of fragments in the Benson scheme for evaluating $\Delta H_{f,g}^0$ and $\Delta H_{a,g}^0$ of Si-substituted silacyclobutanes at 298.15 K (kJ mole^{-1})

Fragment	Values		Fragment	Values	
	$-H_i$	E_i		$-H_i$	E_i
[C–(C)(H)$_3$]	44.27	1414.93	[C–(Si)(H)$_3$]	40.27	1410.93
[C–(C)$_2$(H)$_2$]	20.8	1173.46	[Si–(C)$_3$(H)]	42.6	712.4
[C–(Si)(C)(H)$_2$]	13.6	1166.26	[Si–(C)$_3$(C$_\alpha$)]	65.2	515.2
[C–(C)$_2$(Si)(H)]	−5.0	929.67	[C–(C$_\alpha$)(H)$_2$]	−26.19	1126.47
[C–(C)$_3$(H)]	7.95	942.62	[C–(C$_\alpha$)(Si)(H)]	−10.1	924.42
			[Si–(C)$_4$]	65.2	515.2

Table 4

Energies of fragments in the Tatevskii scheme for evaluating $\Delta H_{f,g}^0$ and $\Delta H_{a,g}^0$ of Si-substituted silacyclobutanes at 298.15 K (kJ mole^{-1})

Fragment	Values		Fragment	Values	
	$-H_{ij}$	E_{ij}		$-H_{ij}$	E_{ij}
E_{C_1-Si}	57.44	1540.6	E_{C_2-Si}	18.6	707.43
E_{Si-H}	5.4	325.1	$E_{C_1-C_3}$	46.56	1728.77
E_{C_3-Si}	5.94	430.0	$E_{C_2-C_3}$	10.8	898.68
$E_{C\alpha_3-Si}$	76.4	500.2	$E_{C\alpha_2-C\alpha_3}$	−95.68	1680.1
$E_{C_2-C_2}$	20.8	1173.46			

We have measured the enthalpies of formation of five Si-substituted silacyclobutanes in the condensed and gas state (Table 1). The enthalpies of atomization of these compounds have been determined (Table 2) and fragments of the Franklin–Benson and Tatevskii additive schemes have been calculated (Tables 3 and 4).

Experimental

The heats of combustion were determined in a precision isothermal calorimeter equipped with a stationary bomb designed at the Institute of Chemical Physics, Academy of Sciences of the U.S.S.R. (calorific value 7863.37 ± 0.02 J ohm^{-1}).

The heats of evaporation and sublimation were determined calorimetrically (DAK 1-1A calorimeter).

The purity of the substances examined exceeded 99.3% (GLC).

The combustion of liquid organosilicon compounds and analysis of the products of combustion were carried out by techniques described previously in [5]. Substances (samples 0.13–0.165 g of weight) were burned in terylene ampoules. The completeness of combustion ranged from 98.8 to 99.5%.

The data obtained on enthalpies of formation, heats of evaporation and sublimation of Si-substituted silacyclobutanes are presented in Table 1.

In calculating the enthalpies of formation and atomization, use was made of the following key values, ΔH_f^0, kJ mole^{-1} at 298 K: -285.830 ∓ 0.042 (H_2O, liq) [8]; -939.39 ∓ 0.52 (SiO_2, am. hydr.) [9,10]; -393.514 ∓ 0.046 (CO_2, g) [8]; 716.67 ∓ 0.44 (C, g); 217.997 ∓ 0.006 (H, g) 450 ∓ 8 (Si, g) [8].

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

1. Benson and Franklin formula [11,12]: $\Delta H_a^0, \text{g} = \Sigma_{i=0}^n K_i E_i$; $\Delta H_f^0, \text{g} = \Sigma_{i=0}^n K_i H_i$. Here: $H_i = -E_i + \Sigma\Delta H_{\text{fC,g}}^0 + \Sigma\Delta H_{\text{fH,g}}^0 + \Sigma\Delta H_{\text{fSi,g}}^0$ where E_i are fragments taking into account the mutual effect of the atoms separated by not more than one other atom in the molecular chain; K_i is the number of fragments.

For the compounds studied the fragments are as follows: [C–(C)$(H)_3$], [C–(Si)$(H)_3$], etc.

2. Tatevskii formula [13,14]. $\Delta H_{\text{a,g}}^0 = \Sigma_{i,j=1;i \leqslant j}^n n_{ij} E_{ij}$; $\Delta H_{\text{f,g}}^0 = \Sigma_{i,j=1;i \leqslant j}^n n_{ij} \text{H}_{ij}$. Here: $H_{ij} = -E_{ij} + \Sigma\Delta H_{\text{fC,g}}^0 + \Sigma\Delta H_{\text{fH,g}}^0 + \Sigma\Delta H_{\text{fSi,g}}^0$ where E_{ij} are fragments taking into account the mutual effect of the atoms separated by not more than two other atoms in the molecular chain; n_{ij} is the number of fragments.

For the compounds studied the following fragments were used: $E_{C_1-C_2}$, E_{C_1-Si}, etc.

Discussion

From the experimental enthalpies of formation and atomization of tri-, tetraalkyl- and alkylalkoxysilanes reported in [5] the energies of fragments of the Franklin–Benson (Table 3) and Tatevskii schemes (Table 4) were determined by the least squares method. On the basis of the data obtained the enthalpies of formation and atomization of silacyclobutane $H_2Si(CH_2)_3$ were calculated to be -130.8 and 5619.5 kJ mole^{-1} in the Franklin–Benson scheme and -130.9 and 5619.3 kJ mole^{-1} in the Tatevskii scheme.

Using the enthalpy values found experimentally and those calculated by the above additive schemes, the ring strain energies in the compounds studied were estimated by the following formula: $E_{cycl} = \Delta H^0_{a,298.15;g,calc.} - \Delta H^0_{a,298.15,g,exp.}$ and $E_{cycl} = \Delta H^0_{f,298.15,g,exp.} - \Delta H^0_{f,298.15,g,calc.}$

The calculated ring strain energy values of silacyclobutane are 107.8 and 107.9 kJ mole^{-1} (from the above cited enthalpies of its formation).

Conclusions

Thus, the silacyclobutane four-membered ring is under considerable strain. Depending on the character of substitution, the ring strain energy varies within the range 107–112 kJ mole^{-1} and increases with the number of the ring substituents, especially when an alkyl substituent is introduced in position 3. Previously, however, it had been suggested [6,7] that the introduction of substituents into the silacyclobutane cycle does not affect its strain energy. Comparison of the strain energies of cyclobutane, silacyclobutane and 1,3-disilacyclobutane (109.6 [15], 107.8, 74.1 [3] kJ mole^{-1}, respectively) indicates that sequential substitution of the carbon atoms in cyclobutane by silicon atoms reduces the ring strain energy. This seems to be due to a greater lability of the C–Si–C valent angle compared with that of the C–C–C angle.

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