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## Thermochemistry of organosilicon compounds

### V \*. Thermochemical properties of perorganyloligocyclosiloxanes

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#### Abstract

The heats of combustion have been determined and enthalpies of formation in the condensed and gaseous states of twelve perorganyloligocyclosiloxanes  $[\text{RR}'\text{SiO}]_n$ , where  $n = 3-5$ , have been evaluated at 298.15 K in a precision isothermal calorimeter equipped with a stationary bomb. Additive schemes permitted the enthalpies of atomization of these compounds to be calculated and their ring strain energies estimated to be 74.0–85.0 with  $n = 3$ , 57.0–60.0 with  $n = 4$  and 40.0–44.0  $\text{kJ mol}^{-1}$  with  $n = 5$ . The ring strain energy of the *cis*-isomer  $[\text{RR}'\text{SO}]_3$  is higher than that of the *trans*-isomer.

#### Introduction

Perorganyloligocyclosiloxanes  $[\text{RR}'\text{SiO}]_n$  ( $n \geq 2$ ) are of great theoretical and practical interest. Compounds of this type with  $n = 2$  (tetraorganylcyclodisiloxanes) are not freely available and are only poorly understood (see for example, Ref. 1). Compounds with  $n = 3$  or 4, on the contrary, can be obtained on a large scale and are widely used in the production of organosilicon polymers [2]. Perorganyloligocyclosiloxanes  $[\text{RR}'\text{SiO}]_3$  have a planar strained ring, which accounts for a higher Si–O bond energy (to 38.0  $\text{kJ mol}^{-1}$ ) [3]. The cyclosiloxane ring in their homologues with  $n \geq 4$  is, in contrast, non-planar and almost unstrained. According to thermochemical data, the ring strain in  $[(\text{CH}_3)_2\text{SiO}]_n$  where  $n = 4$  and 5, is about 0.8  $\text{kJ mol}^{-1}$

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[4]. The ring strain energy depends also upon the nature of ring substituents and their mutual arrangement including that relative to the ring plane [2]. Thus, for example, the ring strain energies in  $[\text{CH}_3(\text{F}_3\text{CCH}_2\text{CH}_2)_2\text{SiO}]_n$  with  $n = 3-5$  are 21.9, 5.4 and 3.1  $\text{kJ mol}^{-1}$ , respectively. At the same time, the ring strain energies of *cis*- and *trans*-stereoisomers  $[\text{CH}_3(\text{C}_6\text{H}_5)\text{SiO}]_3$  are 113.0 and 92.0  $\text{kJ mol}^{-1}$ , respectively. For the *cis*-isomer  $[\text{CH}_3(\text{C}_6\text{H}_5)\text{SiO}]_4$  this value is 33.5  $\text{kJ mol}^{-1}$ , that for other three stereoisomers being 0  $\text{kJ mol}^{-1}$  [5]. For higher stereoisomers of perorganyloligocyclosiloxanes  $[\text{RR}'\text{SiO}]_n$  with  $n = 5$  the ring strain energy is practically zero, whereas their Si-O bond energy is nearly equal. The enthalpies of formation of perorganyloligocyclosiloxanes available in the literature [3,6-20] are contradictory and, therefore, need revising.

## Results and discussion

We have measured the enthalpies of formation of twelve perorganylsubstituted cyclotri-, cyclo tetra- and cyclopentasiloxanes in the condensed and gaseous states

Table 1

Enthalpies of combustion, formation and evaporation (sublimation) of perorganyloligocyclosiloxanes at 298.15 K ( $\text{kJ mol}^{-1}$ )

No.	Compound	$\Delta H_{\text{comb}}$	$\Delta H_f^\circ$	$\Delta H_v^\circ$ ( $\delta H_s^\circ$ )
I	Hexamethylcyclotrisiloxane ( $\text{C}_6\text{H}_{10}\text{O}_3\text{Si}_3$ ), solid	6130.0 ± 9.0	1622.0 ± 10.0	54.0 ± 0.9
II	<i>cis</i> -1,3,5-Trimethyltriphenylcyclotrisiloxane ( $\text{C}_{21}\text{H}_{24}\text{O}_3\text{Si}_3$ ), solid	13166.0 ± 9.0	1346.0 ± 10.0	122.0 ± 1.0
III	<i>trans</i> -1,3,5-Trimethyltriphenylcyclotrisiloxane ( $\text{C}_{21}\text{H}_{24}\text{O}_3\text{Si}_3$ ), solid	13147.0 ± 9.0	1365.0 ± 10.0	132.0 ± 1.2
IV	Hexaphenylcyclotrisiloxane ( $\text{C}_{36}\text{H}_{30}\text{O}_3\text{Si}_3$ ), solid	20254.0 ± 10.0	1019.0 ± 11.0	139.0 ± 1.2
V	Octamethylcyclotetrasiloxane ( $\text{C}_8\text{H}_{24}\text{O}_4\text{Si}_4$ ), liquid	8141.0 ± 9.0	2195.0 ± 10.0	57.0 ± 0.8
VI	1,1-Dimethylhexaphenylcyclotetrasiloxane ( $\text{C}_{38}\text{H}_{36}\text{O}_4\text{Si}_4$ ), solid	22261.0 ± 10.0	1595.0 ± 10.0	141.0 ± 1.2
VII	1,1-Diphenylhexamethylcyclotetrasiloxane ( $\text{C}_{18}\text{H}_{28}\text{O}_4\text{Si}_4$ ), solid	12845.0 ± 11.0	1997.0 ± 12.0	87.0 ± 1.0
VIII	Octaphenylcyclotetrasiloxane ( $\text{C}_{48}\text{H}_{40}\text{O}_4\text{Si}_4$ ), solid	26989.0 ± 11.0	1374.0 ± 12.0	148.0 ± 1.3
IX	1,3,5,7-Tetramethyltetraphenylcyclotetrasiloxane ( $\text{C}_{28}\text{H}_{32}\text{O}_4\text{Si}_4$ ), solid	17527.0 ± 10.0	1822.0 ± 11.0	137.0 ± 1.2
X	1,1,3,3-Tetramethyltetraphenylcyclotetrasiloxane ( $\text{C}_{28}\text{H}_{32}\text{O}_4\text{Si}_4$ ), solid	17519.0 ± 10.0	1830.0 ± 11.0	139.0 ± 1.2
XI	Decamethylcyclopentasiloxane ( $\text{C}_{10}\text{H}_{30}\text{O}_5\text{Si}_5$ ), liquid	10153.0 ± 11.0	2766.0 ± 12.0	59.0 ± 1.0
XII	1,3,5,7-Pentamethylcyclopentasiloxane ( $\text{C}_5\text{H}_{20}\text{O}_5\text{Si}_5$ ), liquid	7090.0 ± 12.0	2433.0 ± 13.0	47.0 ± 0.9

Table 2

Enthalpies of formation, atomization and ring strain energies of the perorganyloligocyclosiloxanes calculated by the Franklin-Benson and Tatevskii schemes at 298.15 K ( $\text{kJ mol}^{-1}$ )

Compound	$-\delta H_f^\circ$ (gas) exp.	$E_s$	$-\Delta H_f^\circ$ (gas) calc. by the Benson scheme	$-\Delta H_f^\circ$ (gas) calc. by the Tatevskii scheme	$\Delta H_a^\circ$ (exp.)	$E_s$	$\Delta H_f^\circ$ calc. by the Benson scheme	$\Delta H_f^\circ$ calc by the Tatevskii scheme
I	$1568.0 \pm 11.0$	80.0	1648.0	1648.0	11889.0	81.0	11970.0	11971.0
II	$1224.0 \pm 11.0$	83.0	1307.0	1306.0	23604.0	82.0	23686.0	23686.0
III	$1233.0 \pm 11.0$	74.0	1307.0	1306.0	23613.0	73.0	23686.0	23686.0
IV	$880.0 \pm 11.0$	85.0	965.0	964.0	35317.0	85.0	35402.0	35402.0
V	$2138.0 \pm 11.0$	60.0	2198.0	2198.0	15900.0	60.0	15960.0	15960.0
VI	$1454.0 \pm 12.0$	60.0	1514.0	1513.0	39332.0	60.0	39392.0	39392.0
VII	$1910.0 \pm 13.0$	60.0	1970.0	1970.0	23711.0	60.0	23771.0	23771.0
VIII	$1226.0 \pm 13.0$	60.0	1286.0	1286.0	47143.0	60.0	47203.0	47203.0
IX	$1685.0 \pm 12.0$	57.0	1742.0	1741.0	31524.0	57.0	31581.0	31581.0
X	$1691.0 \pm 12.0$	51.0	1742.0	1741.0	31530.0	51.0	31581.0	31581.0
XI	$2708.0 \pm 13.0$	40.0	2748.0	2748.0	19910.0	40.0	19950.0	19950.0
XII	$2386.0 \pm 14.0$	44.0	2430.0	2433.0	13826.0	46.0	13869.0	13872.0

Table 3

Energies of fragments in the Benson scheme for evaluating  $\Delta H_f^\circ$  (gas) and  $\Delta H_a^\circ$  (gas) of perorganyloligocyclosiloxanes at 298.15 K ( $\text{kJ mol}^{-1}$ )

Fragment	Values		Fragment	Values	
	$-H_i$	$E_i$		$-H_i$	$E_i$
[C-(Si)(H) <sub>3</sub> ]	40.27	1410.93	[O-(Si) <sub>2</sub> ]	397.93	647.1
[C <sub>b</sub> -(C <sub>b</sub> ) <sub>2</sub> Si]	-4.65	712.0	[Si-(O) <sub>2</sub> (C <sub>2</sub> ) <sub>2</sub> ]	71.0	521.0
[C <sub>b</sub> -(C <sub>b</sub> ) <sub>2</sub> (H)]	-13.81	920.86	[Si-(C)(O) <sub>2</sub> (H)]	47.8	715.8

(Table 1). Besides, the enthalpies of atomization of these compounds have been determined (Table 2) and fragments of the Franklin-Benson (Table 3) and Tatevskii additive schemes (Table 4) have been calculated.

In calculation of the enthalpies of formation and atomization use was made of the following key values:  $\Delta H_f^\circ$ ,  $\text{kJ mol}^{-1}$  at 298.15 K:  $-285.830 \pm 0.042$  ( $\text{H}_2\text{O}$ , liq.) [21];  $-939.39 \pm 0.52$  ( $\text{SiO}_2$ , amorph. hydr.) [22,23];  $-393.514 \pm 0.046$  ( $\text{CO}_2$ , gas) [21];  $716.67 \pm 0.44$  (C, gas);  $217.997 \pm 0.006$  (H, gas);  $249.17 \pm 0.10$  (O, gas);  $450.00 \pm 8.00$  (Si, gas) [21].

For calculating the enthalpies of formation and atomization by additive schemes use was made of the formulas of Benson [24] and Franklin [25] (in the first approximation) and Tatevskii [26,27] (in second approximation). On the basis of the experimental enthalpies of formation and atomization of trialkyl-, tetraalkyl- and alkylalkoxysilanes, previously published in [22], the energies of fragments of the above schemes were determined by the least squares method. The ring strain energies,  $E_s$ , of the substances studied were calculated by the following formula:

$$E_s = \Delta H_a^\circ (298.15 \text{ (gas)}) \text{ calc.} - \Delta H_a^\circ (298.15 \text{ (gas)}) \text{ exp.}$$

$$E_s = \Delta H_f^\circ (298.15 \text{ (gas)}) \text{ exp.} - \Delta H_f^\circ (298.15 \text{ (gas)}) \text{ calc.}$$

These energy values are presented in Table 2. Table 2 shows the ring strain energies of the perorganylcyclotrisiloxanes (I, II, IV) to vary from 80 to 85  $\text{kJ mol}^{-1}$ . This energy increases when the methyl groups are substituted by phenyl groups in going from hexamethylcyclotrisiloxane to hexaphenylcyclotrisiloxane. However, the ring strain energy of *trans*-1,3,5-trimethyltriphenylcyclotrisiloxane (III) with perturbed molecular symmetry ( $74.0 \text{ kJ mol}^{-1}$ ) is markedly lower than that of the *cis*-isomer ( $83.0 \text{ kJ mol}^{-1}$ ). This seem to be due to the smaller effect of non-valent interactions of phenyl groups. The ring strain energy in the perorganyl-

Table 4

Energies of fragments in the Tatevskii scheme for calculating  $\Delta H_f^\circ$  (gas) and  $\Delta H_a^\circ$  (gas) of perorganyloligosiloxanes at 298.15 K ( $\text{kJ mol}^{-1}$ )

Fragment	Values		Fragment	Values	
	$-H_{ij}$	$E_{ij}$		$-H_{ij}$	$E_{ij}$
C <sub>1</sub> -Si	57.44	1540.60	C <sub>b3</sub> -Si	53.7	345.51
C <sub>b2</sub> -C <sub>b2</sub>	-13.81	920.86	O-Si	217.30	454.38
C <sub>b3</sub> -C <sub>b2</sub>	-27.57	708.51	Si-H	-5.40	325.1

Table 5

Comparison of our enthalpies of formation of the perorganyloligocyclosiloxanes in the condensed state ( $\text{kJ mol}^{-1}$ ) at 298.15 K with the literature data

Compound	$\Delta H_f^\circ$		Refs.
	Our values	Literature data	
I	1622.0 $\pm$ 10.0	1656.9 $\pm$ 20.9	6-8
		1648.3 $\pm$ 8.7	13
II	1346.08 $\pm$ 10.0	1357.3 $\pm$ 7.2	10, 11
		1347.3 $\pm$ 5.9	19, 20
		1431.8 $\pm$ 19.2	14, 15
III	1365.0 $\pm$ 10.0	1383.6 $\pm$ 15.1	10, 11
		1445.9 $\pm$ 18.4	12, 14
IV	1019.0 $\pm$ 11.0	941.4 $\pm$ 20.9	6-8
V	2195.0 $\pm$ 10.0	2271.9 $\pm$ 8.4	3
VI	1595.0 $\pm$ 10.0	1628.0 $\pm$ 10.0	17
VII	1997.0 $\pm$ 12.0	2133.4 $\pm$ 6.2	17
VIII	1374.0 $\pm$ 12.0	1329.8 $\pm$ 6.0	18
IX	1822.0 $\pm$ 11.0	1835.0 $\pm$ 7.2	10, 11
		1867.6 $\pm$ 8.0	9
		1895.4 $\pm$ 20.9	12, 15
X	1830.0 $\pm$ 11.0	1822.9 $\pm$ 7.1	10, 11
XI	2766.0 $\pm$ 12.0	2874.04 $\pm$ 8.4	3
XII	2433.0 $\pm$ 13.0	2472.7 $\pm$ 12.6	9

cyclotetrasiloxanes (X-IX) is much lower ( $60 \text{ kJ mol}^{-1}$ ). This value is even smaller in 1,1,3,3-tetramethyltetraphenylcyclotetrasiloxane ( $51 \text{ kJ mol}^{-1}$ ) in which not all substituents of the same type ( $\text{CH}_3$  or  $\text{C}_6\text{H}_5$ ) are located on the same side of the ring. And, finally, the ring strain energy of the pentasiloxane ring (compounds XI, XII) is even lower ( $40\text{--}44 \text{ kJ mol}^{-1}$ ). These thermochemical data concerning the strain of cyclosiloxane rings are in agreement with the existing concepts [2]. They indicate that the rings in  $[\text{RR}'\text{SiO}]_n$  with  $n \geq 4$  are still slightly strained, if it is assumed, in the first approximation, that the Si-O bond energy does not depend on the ring size.

In Table 5 our data are compared with the literature values of enthalpies of formation of perorganyloligocyclosiloxanes in the condensed state. This Table shows that our  $\Delta H_f^\circ$  (cond, 298.15) values are consistent within the error of measurement, with the results obtained by combustion in the presence of fluoro-organic compounds and, therefore, they may be considered reliable. At the same time, in two cases our ring strain energies in compounds (II, III and IX) (Table 2) differ greatly from previously published values ( $51.8$ ,  $66.8$  and  $134.7 \text{ kJ mol}^{-1}$ , respectively) [11]. Therefore, the ring strain energy in the 1,3,5,7-tetramethyltetraphenylcyclotetrasiloxane reported in [11] should be considered wrong.

## Experimental

Combustion of the substances was carried out in a precision isothermal calorimeter equipped with a stationary bomb, designed at the Institute of Chemical Physics, Academy of Sciences of the USSR. The calorific value of the calorimeter determined by burning of standard benzoic acid was  $782.91 \pm 0.02 \text{ kJ mol}^{-1}$ .

The perorganyloligocyclosiloxanes under investigation were obtained at the Institute of Chemistry of Silicates (Leningrad), and purified by fractionate distillations over sodium metal. Their purity, assessed from GLC and the melting point curves, exceeds 99.3%.

The heats of evaporation of liquid cyclosiloxanes were determined with a DAK 1 = 1A microcalorimeter according to the technique described in [28]. The heats of sublimation of solids were measured by the Knudsen effusion method [28].

The method for burning liquid and solid organosilicon compounds and analyzing the combustion products have been described previously [20,22]. The degree of combustion was from 98.8 to 99.5%.

The enthalpies of combustion, formation and evaporation (sublimation) are presented in Table 1.

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