

# Ab Initio Study of Silyloxonium Ions

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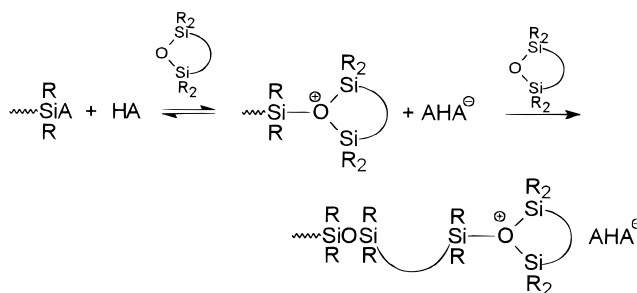
The geometries and proton and silylenium cation ( $\text{H}_3\text{Si}^+$ ) affinities as well as ring strain energies of several hydrogen-substituted cyclic siloxanes, cyclotrisiloxane ( $\text{H}_2\text{SiO}$ )<sub>3</sub> (**5a**), cyclotetrasiloxane ( $\text{H}_2\text{SiO}$ )<sub>4</sub> (**6a**), and 1,3-oxadisilacyclopentane (**7a**), were calculated by ab initio quantum-mechanical methods using the polarized 6-31\* basis set. Protonation and silylenium cation addition to siloxanes lead to secondary and tertiary silyloxonium ions, respectively. The calculated strain energies follow the order: **7a** > **5a** > **6a**  $\approx$  0. Upon protonation or silylation, the strain in the five-membered ring of **7b** and **7c** is significantly reduced, while in the cyclotrisiloxane silyloxonium ions **5b,c** the strain is preserved. The endocyclic Si–O bonds in **7a** and **5a** are weakened upon protonation or addition of  $\text{H}_3\text{Si}^+$  more than the exocyclic bonds and are therefore predicted to be cleaved more readily by nucleophiles, resulting in a ring opening rather than in splitting of the exocyclic  $\text{SiH}_3$  group. **7a** is by ca. 10 kcal/mol more basic than the other siloxanes due to the angular strain in the five-membered ring. Its basicity is comparable to that of dialkyl ethers and alkoxy silanes. A linear correlation was found between the gas-phase proton and  $\text{H}_3\text{Si}^+$  affinities. On the basis of SCRF calculations interaction with solvent (cyclohexane or  $\text{CH}_2\text{Cl}_2$ ) has only a moderate effect on the energies of protonation and ring-opening reactions. The role of silyloxonium ions as possible active centers in the cationic ring-opening polymerization of cyclosiloxanes is discussed in light of the calculated basicities and ring strain energies. The calculations suggest that the polymerizations of the cyclic monomers **5a**, **6a**, and **7a** should reveal different kinetic and thermodynamic behavior. **7a** is predicted to be the most reactive monomer, and its polymerization is the most favored thermodynamically.

## Introduction

Silyloxonium ions are possible intermediates in reactions of electrophilic silicon reagents, such as silyl iodides and triflates, with ethers and alcohols.<sup>1</sup> In analogy to the polymerization mechanism of cyclic ethers and acetals,<sup>2</sup> tertiary silyloxonium ions have been postulated to be the active centers of chain growth in the cationic polymerization of cyclosiloxanes (Scheme 1).<sup>3</sup> The mechanism of this process has been studied for more than 40 years, but it still remains controversial.<sup>3</sup>

The main difficulty in detecting the silyloxonium species in the reaction mixture is their high electrophi-

Scheme 1



licity. They react rapidly with nucleophiles present in solution. However, there is evidence for the existence of silyloxonium ions in model “non-nucleophilic” systems at low temperatures.<sup>4,5</sup> Recently, the trisilyloxonium ions **1–3** have been obtained via addition of a “trimethylsilylenium cation equivalent” to hexamethyldisiloxane, hexamethylcyclotrisiloxane ( $((\text{CH}_3)_2\text{SiO})_3$ ; **D<sub>3</sub>**), and octamethylcyclotetrasiloxane ( $((\text{CH}_3)_2\text{SiO})_4$ ; **D<sub>4</sub>**), respectively (D stands for a dimethylsiloxane unit).<sup>6</sup> The ion **1** has been shown to initiate the polymerization of **D<sub>3</sub>** and **D<sub>4</sub>**.<sup>6</sup> These results strongly support the suggestion that silyloxonium ions play an active role in the cationic polymerization of cyclosiloxanes.

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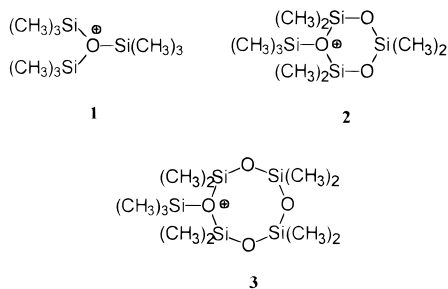
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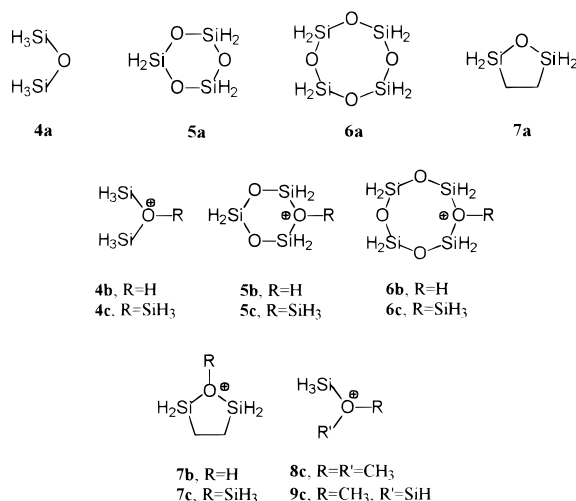
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Because of their high reactivity, silyloxonium ions are difficult to study experimentally. To gain further insight into the chemistry of silyloxonium ions, we have carried out ab initio quantum-mechanical calculations on the protonation and silylation reactions of several simple model siloxanes: the parent disiloxane  $\text{H}_3\text{-SiOSiH}_3$  (**4a**) and the three cyclic siloxanes cyclotrisiloxane ( $(\text{H}_2\text{SiO})_3$ ; **5a**), cyclotetrasiloxane ( $(\text{H}_2\text{SiO})_4$ ; **6a**), and 1-oxa-2,5-disilacyclopentane (**7a**). Little is known



experimentally about the chemistry of hydrogen-substituted siloxanes, because they are generally much more reactive than methyl-substituted siloxanes. However, we believe that they are good models for the methyl-substituted systems because in many reactions they behave similarly.<sup>3f,7</sup> In particular, hydrogen-substituted cyclosiloxanes readily polymerize in the presence of cationic initiators. Thus, theoretical studies of these simple models may provide information useful for understanding their own chemistry as well as the chemistry of their alkyl-substituted analogues.

In this paper we study computationally a variety of properties of siloxanes, such as their basicity, nucleophilicity, and ring strain, which determine the kinetics and thermodynamics of the cationic ring-opening process. Although the results of our calculations apply strictly only to reactions in the gas phase, we believe that the computational results may be helpful in the interpretation of the polymerization mechanism in solution, at least in inert solvents with poor solvating ability. Since NMR is the most important experimental technique used for studying silyloxonium ions and related species in solution, the  $^{29}\text{Si}$  NMR chemical shieldings of the studied silyloxonium ions were also

computed. These values may be helpful in the identification of such species in reaction mixtures.

## Theoretical Methods

Ab initio calculations have been carried out using standard techniques,<sup>8</sup> as implemented in the Gaussian 94 series of programs.<sup>9</sup> Geometry optimizations, harmonic frequencies, and zero-point vibrational energies were calculated with the polarized 6-31G\* basis set.<sup>9</sup> All structures were identified as true local minima on the energy potential surface by their Hessian matrices. The vibrational components of the thermal energy were scaled by the usual factor of 0.893.<sup>8</sup> Single-point calculations, which include part of the electron correlation, were performed using the Møller–Plesset perturbation theory up to fourth order (using the frozen-core approximation).<sup>10</sup> This level of theory, denoted as MP4SDTQ/6-31G\*//HF/6-31G\*, was used for energy comparisons, except for the cyclotetrasiloxane derivative **6c**, for which the MP2/6-31G\*//HF/6-31G\* energy was used. The orbital and bond analyses were performed with both the Mulliken<sup>11</sup> and the natural bond orbital (NBO) methods.<sup>12</sup> Calculations of the  $^{29}\text{Si}$  NMR chemical shieldings were carried out with the GIAO<sup>13a</sup> and IGAIM<sup>13b</sup> methods implemented in Gaussian 94,<sup>9</sup> using the B3LYP hybrid density functional method,<sup>14</sup> the 6-311+G\*\* basis set, and the HF/6-31G\* optimized geometries. Solvation calculations (HF/6-31G\*) were performed using an Onsager model and an Isodensity Polarized Continuum Model (IPCM) (employing the default isodensity value of 0.0004 au for the cavity surface) implemented within a self-consistent reaction field (SCRF) method in Gaussian 94.<sup>15</sup> The total energies of all the calculated species are given in the Supporting Information.

## Results and Discussion

**Geometries.** The calculated HF/6-31G\* equilibrium geometries of the neutral, protonated, and silylated

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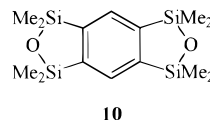
siloxanes, **4a–c** through **7a–c** as well as of the silylated dimethyl ether **8c** and methoxysilane **9c** are shown in Figure 1.

**(a) Neutral Siloxanes.** The structures of siloxanes **4a–6a** were studied previously at various levels of ab initio methods.<sup>16,17</sup> The geometry of disiloxane **4a** was optimized at 6-31G\*,<sup>16a,b</sup> and at MP2(full)/6-31G\*<sup>16c</sup> as well as with several other basis sets,<sup>16d–i</sup> providing a good basis for judging the reliability of the various methods. The geometry of the cyclotrisiloxane **5a** was optimized previously with the 3-21G,<sup>17a</sup> 3-21G\*\*,<sup>17b,c</sup> and 6-31G<sup>17d</sup> basis sets, while the geometry of cyclotetrasiloxane **6a** was optimized with the relatively small 3-21G<sup>17a</sup> and 3-21G\*\*<sup>17b,c</sup> basis sets. During the preparation of this paper, the HF/6-31G\* and HF/6-311G(d,p) optimized geometries of **5a** and **6a** were also reported.<sup>17c</sup>

At 6-31G\* disiloxane **4a** has  $C_{2v}$  symmetry and an Si–O bond length of 1.626 Å.<sup>16b</sup> The Si–O–Si angle of 170.0° calculated at 6-31G\* is substantially larger than the experimental electron diffraction value of 143.1°.<sup>18</sup> Previous studies showed that methods including electron correlation are required to reproduce correctly the experimental Si–O–Si angle.<sup>16a,c,h</sup> However, as the calculated barrier for linearization of the Si–O–Si bond angle is less than 0.5 kcal/mol at 6-31G\*,<sup>16a,h</sup> the energetic error which may be introduced by the overestimated Si–O–Si angle is small. Cyclotrisiloxane **5a** was calculated at 6-31G\* to be planar with  $D_{3h}$  symmetry, in agreement with earlier calculations<sup>17b–e</sup> and with the electron diffraction data for the fully methylated analogue (Me<sub>2</sub>SiO)<sub>3</sub>(D<sub>3</sub>).<sup>19</sup> The calculated Si–O bond lengths of 1.640 Å and the Si–O–Si bond angles of 133.5° are close to the experimental values for D<sub>3</sub> (1.635 Å and 131.6°, respectively).<sup>19</sup>

It was more difficult to locate the minimum energy geometry of the eight-membered siloxane ring **6a**. The potential energy surface of **6a** is flat, with several local minima of similar energy. In most previous calculations a  $D_{4h}$  symmetry was assumed.<sup>17a,b</sup> although the electron diffraction data for both (H<sub>2</sub>SiO)<sub>4</sub> and (Me<sub>2</sub>SiO)<sub>4</sub> showed that the  $S_4$  conformation is the most stable.<sup>19,20</sup> We have performed several optimizations starting from different conformations, but all of them converged to the  $D_{4h}$  structure. This result is in contrast to ref 17e, in which four minima ( $D_{4h}$ ,  $S_4$ ,  $C_{2v}$ (Si), and  $C_{2v}$ (O)), very close in energy, were found. However, the  $D_{4h}$  structure is predicted to be the global minimum when the large 6-311G(d,p) basis set is used,<sup>17e</sup> in agreement with our calculations. This inconsistency, in particular our failure to reproduce the  $S_4$  geometry, probably arises from the very flat potential energy surface of **6a**. However, the calculated Si–O bond length of 1.626 Å and the calculated Si–O–Si bond angle of 159.6° are in reasonable agreement with the electron diffraction data (1.628 Å and 148.6°) for the  $S_4$  conformation.<sup>20</sup> Since the energy difference at 6-31G\* between  $D_{4h}$  and  $S_4$  conformations of (H<sub>2</sub>SiO)<sub>4</sub> is about 0.25 kcal/mol,<sup>17e</sup> we used the  $D_{4h}$  structure for energy calculations, assuming that the resulting error in energy is small.

1-Oxa-2,5-disilacyclopentane **7a** has a twisted “half-chair”  $C_2$ -symmetry structure with a O–Si–C–C dihedral angle of 26.1°. The Si–O–Si angle is exceptionally small (117.2°) as a result of the ring constraints. In accord with the known inverse bond length/bond angle relationship,<sup>16a</sup> the Si–O bond in **7a** is significantly longer (1.657 Å) than in the other siloxanes and is similar to that calculated for the strained cyclodisiloxane (H<sub>2</sub>SiO)<sub>2</sub> (1.671 Å at 6-31G\*).<sup>17a</sup> Experimental structural data for **7a** are not available, but the computed values are close to those found by X-ray analysis for **10** ( $r(\text{Si–O}) = 1.647$  Å,  $\angle\text{Si–O–Si} = 118.2^\circ$ ).<sup>21</sup>



**(b) Protonated Siloxanes (Secondary Oxonium Ions).** The most important geometrical parameters of the siloxanes and their protonated derivatives are listed in Table 1. All the protonated siloxanes have planar  $\equiv\text{Si}_2\text{OH}^+$  skeletons, in accord with previous studies.<sup>16b</sup> This is in contrast to protonated dialkyl ethers that have pyramidal geometries.<sup>22</sup> The Si–O bonds lengthen upon protonation by about 0.15–0.18 Å, reaching values of ca. 1.8 Å, in agreement with earlier calculations for disiloxane and alkylsilyl ethers.<sup>16b</sup> No experimental geometries are available for protonated siloxanes, but a similar Si–O bond length (1.78 Å) was found in an X-ray study of protonated tri-*tert*-butylsilanol.<sup>24</sup> For comparison, at MP2(full)/6-31G\*  $r(\text{Si–O})$  in H<sub>3</sub>SiOH<sub>2</sub><sup>+</sup> is 1.867 Å, 0.197 Å longer than in H<sub>3</sub>SiOH (1.670 Å).<sup>16c</sup>

**(c) Tertiary Silyloxonium Ions.** The structural changes which occur upon H<sub>3</sub>Si<sup>+</sup> addition to siloxanes are similar (although somewhat smaller) to those occurring upon protonation. The trisilyloxonium ions **4c–7c** have a planar  $\equiv\text{Si}_2\text{OSi}(\text{H}_3)^+$  skeleton, in agreement with earlier calculations.<sup>6,17b</sup> The silylated Si–O bonds are elongated, reaching values similar to those found in the corresponding protonated structures. The endocyclic Si–O bonds at the oxonium center in **5c–7c** are slightly longer than the exocyclic bonds.

The cyclotrisiloxane ring in **5c** becomes nonplanar upon H<sub>3</sub>Si<sup>+</sup> addition ( $C_s$  symmetry). The dihedral angle between the plane defined by the oxonium fragment  $\equiv\text{Si}_2\text{OSi}(\text{H}_3)^+$  and the plane of the ring is 22°. The silylated cyclotetrasiloxane **6c** and oxadisilacyclopentane **7c** have puckered  $C_1$  symmetry structures with structural parameters very similar to those of the protonated analogues **6b** and **7b** (Figure 1).

The mixed methylsilyloxonium ions **8c** and **9c** have slightly pyramidal structures (the deviations from planarity are 18.3 and 6° for **8c** and **9c**, respectively).

**NMR Calculations.** Since NMR has been, so far, the only tool used for the identification of silyloxonium ions, we have calculated <sup>29</sup>Si NMR chemical shifts of the aforementioned compounds, and the results are given in Table 2.

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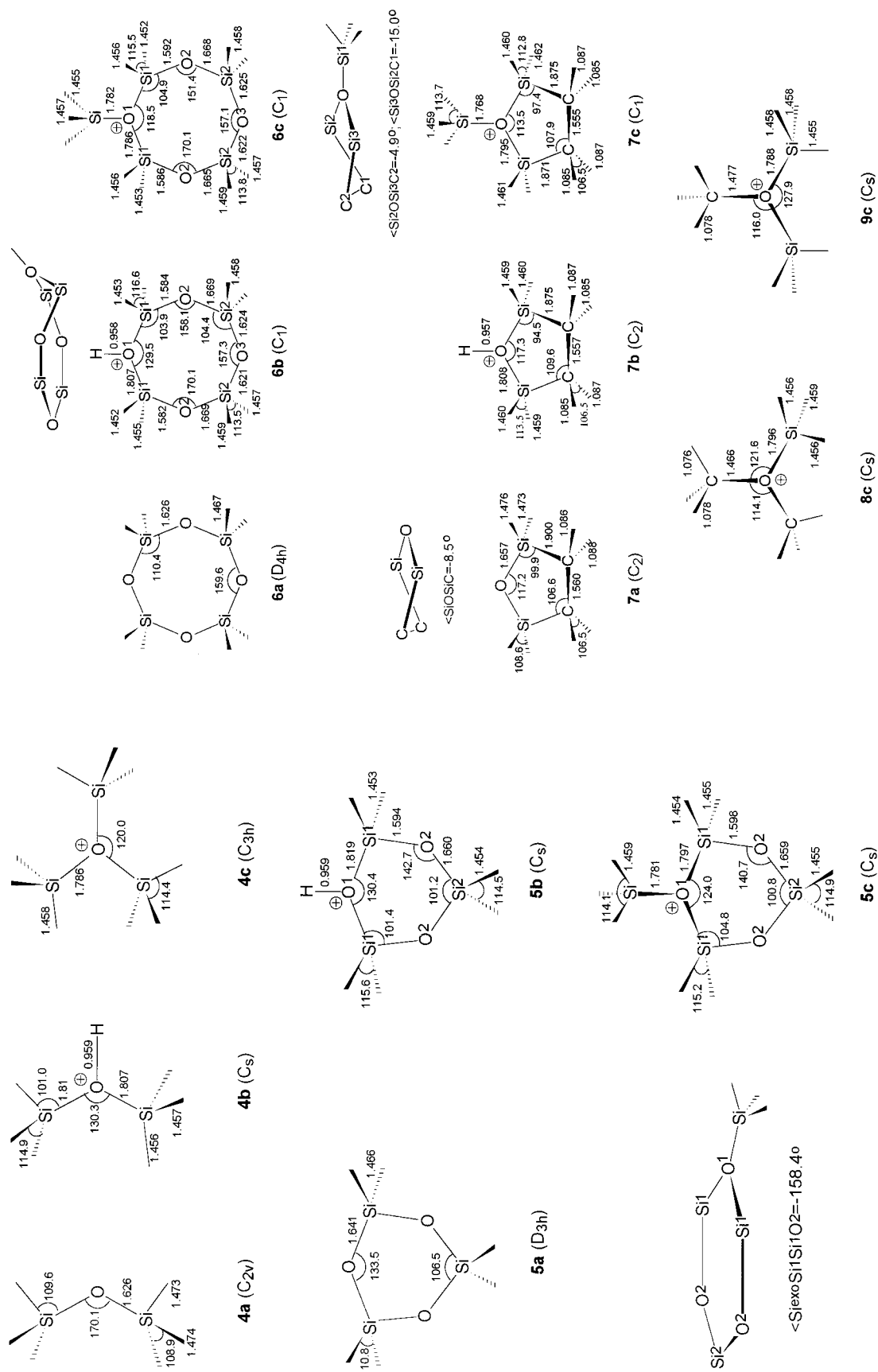
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**Figure 1.** Optimized geometries (6-31G\*) of model siloxanes **4a–7a** and of silyloxonium ions **4b–7b** and **4c–9c**.

**Table 1. Calculated Geometrical Parameters<sup>a</sup> of the SiOSi Unit in Siloxanes 4a–7a, Protonated Siloxanes 4b–7b, and Silylated Siloxanes 4c–7c**

species	param	siloxane		
		( <i>na</i> )	<i>na</i> + H <sup>+</sup>	<i>na</i> + SiH <sub>3</sub> <sup>+</sup>
H <sub>3</sub> SiOSiH <sub>3</sub> ( <b>4a</b> )	Si–O	1.626	1.807, 1.811	1.786
	Si–H	1.474	1.456	1.458
	Si–O–Si	170.0	130.3	120.0
	H–Si–H	108.9	114.7	114.3
(H <sub>2</sub> SiO) <sub>3</sub> ( <b>5a</b> )	Si–O	1.640	1.819	1.797
	Si–H	1.466	1.453	1.454
	Si–O–Si	133.5	130.4	124.0
	O–Si–O	106.5	101.4	104.8
(H <sub>2</sub> SiO) <sub>4</sub> ( <b>6a</b> )	Si–O	1.626	1.806	1.785
	Si–H	1.467	1.453	1.454
	Si–O–Si	159.6	129.5	118.5
	O–Si–O	110.4	103.9, 106.7	104.9, 106.2
(CH <sub>2</sub> SiH <sub>2</sub> ) <sub>2</sub> O ( <b>7a</b> )	Si–O	1.657	1.808	1.808
	Si–H	1.476	1.459	1.460
	Si–O–Si	117.2	117.3	113.5
	O–Si–C	99.9	94.5	97.4
	H–Si–H	108.6	113.5	112.8

<sup>a</sup> Bond distances in angstroms and bond angles in degrees.**Table 2. GIAO and IGAIM <sup>29</sup>Si NMR Chemical Shifts (Relative to TMS<sup>a</sup>) of Siloxanes and Silyloxonium Ions Calculated Using B3LYP/6-311+G\*\*//6-31G\***

species	GIAO	IGAIM	exptl <sup>b</sup>
<b>4a</b>	–50.9	–45.8	–38.0 (7.0)
<b>4b</b>	17.1	21.7	(22.9) <sup>c</sup>
<b>4c</b>	11.0	16.3	(51.1) <sup>d</sup>
<b>5a</b>	–41.0	–36.3	(–9.2)
<b>5b</b>			
Si <sup>1</sup>	–12.7	–7.9	
Si <sup>2</sup>	–29.6	–24.9	
<b>5c</b>			
Si <sup>exo</sup>	–13.0	–7.9	(50.2) <sup>d</sup>
Si <sup>1</sup>	–21.1	–15.8	(10.0)
Si <sup>2</sup>	–31.3	–26.5	(–9.6)
<b>6a</b>	–60.2	–54.9	–47.2 <sup>e</sup> (–19.4)
<b>8c</b>	29.0	32.6	(66.9) <sup>f</sup>
<b>9c</b>	20.1	24.4	(59.0) <sup>g</sup>

<sup>a</sup>  $\delta$ (TMS) = 339.5 ppm (GIAO), 343.5 ppm (IGAIM). <sup>b</sup> Values in parentheses correspond to the permethyl-substituted analogues.<sup>24</sup> <sup>c</sup> Reference 3. <sup>d</sup> Reference 5. <sup>e</sup> Reference 7. <sup>f</sup> Chemical shift in Me<sub>3</sub>SiOEt<sub>2</sub><sup>+</sup>.<sup>4</sup> <sup>g</sup> Chemical shift in (Me<sub>3</sub>Si)<sub>2</sub>OEt<sup>+</sup>.<sup>4</sup>

The calculated <sup>29</sup>Si chemical shifts  $\delta$  (at B3LYP/6-311+G\*\*//HF/6-31G\*), of H<sub>3</sub>SiOSiH<sub>3</sub> are –50.0 ppm (GIAO) and –46.2 ppm (IGAIM). These values are 8–12 ppm higher than the reported experimental value of –38.0 ppm.<sup>24</sup> However, calculations using the MP2/6-31G\* optimized geometry gave <sup>29</sup>Si chemical shifts of –41.4 ppm (GIAO) and –37.0 ppm (IGAIM), in very good agreement with experiment. This suggests that for correct replacement of the magnetic properties of siloxanes, the correct Si–O–Si angle should be used. The measured chemical shift of Me<sub>3</sub>SiOSiMe<sub>3</sub> is 6.8 ppm, ca. 45 ppm downfield from that of **4a**.<sup>24</sup> In order to test the reliability of the calculated <sup>29</sup>Si chemical shifts of **4b,c** and of **5a–c**, we compared them with the well-known experimental chemical shifts of their methyl-substituted analogues, assuming that substitution of Si–H by Si–Me is additive and is independent of the siloxane structure. This assumption can be supported by comparison of known chemical shifts of linear and cyclic oligosiloxanes with those of their methylated analogues. The SiH<sub>2</sub> groups in linear and unstrained cyclic siloxanes appear in the range –48 to –52 ppm,

**Table 3. Calculated Charges (6-31G\*) around the Oxonium Center in Model Siloxanes According to Mulliken and NBO Population Analysis<sup>a</sup>**

		Mulliken			NBO		
		a	b	c	a	b	c
<b>4</b>	H(O)		0.55			0.58	
	O	–0.84	–0.95	–1.02	–1.35	–1.16	–1.32
	Si	0.92	0.91	0.91	1.47	1.37	1.36
	H(Si)	–0.17	–0.06	–0.08	–0.27	–0.19	–0.19
	SiH <sub>3</sub> <sup>b</sup>	0.42	0.7	0.67	0.67	0.78	0.78
<b>5</b>	H <sup>1</sup>		0.54			0.57	
	Si <sup>exo</sup>			0.91			1.35
	H <sub>3</sub> Si <sup>exo</sup>			0.66			0.76
	O <sup>1</sup>	–0.87	–0.96	–1.03	–1.35	–1.18	–1.35
	Si <sup>1</sup>	1.21	1.22	1.22	1.93	1.9	1.89
	H(Si <sup>1</sup> )	–0.17	–0.09	–0.09	–0.29	–0.24	–0.24
	Si <sup>1</sup> H <sub>2</sub> <sup>b</sup>	0.87	1.04	1.03	1.35	1.42	1.41
<b>6</b>	H <sup>1</sup>		0.54			0.57	
	Si <sup>exo</sup>			0.9			1.36
	H <sub>3</sub> Si <sup>exo</sup>			0.65			0.64
	O <sup>1</sup>	–0.84	–0.95	–1.02	–1.37	–1.18	–1.34
	Si <sup>1</sup>	1.2	1.21	1.23	1.95	1.89	1.89
	H(Si <sup>1</sup> )	–0.18	–0.1	–0.09	0.29	0.23	–0.21
	Si <sup>1</sup> H <sub>2</sub> <sup>b</sup>	0.84	1.01	1.0	1.37	1.45	1.49
<b>7</b>	H <sup>1</sup>		0.55			0.58	
	Si <sup>exo</sup>			0.91			1.37
	H <sub>3</sub> Si <sup>exo</sup>			0.66			0.75
	O <sup>1</sup>	–0.87	–0.95	–1.02	–1.32	–1.16	–1.33
	Si <sup>2</sup>	1.02	1.01	1.02	1.66	1.61	1.61
	H(Si <sup>2</sup> )	–0.17	–0.08	–0.08	–0.27	–0.21	–0.21
	Si <sup>2</sup> H <sub>2</sub> <sup>b</sup>	0.69	0.86	0.89	1.13	1.2	1.2

<sup>a</sup> For atom numbering see Chart 1. <sup>b</sup> Charge on the entire group.

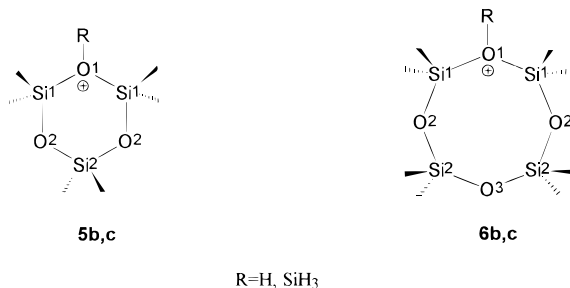
whereas SiHMe groups appear at –34 to –37 ppm and SiMe<sub>2</sub> groups at –19 to –24 ppm.<sup>7,24</sup> Thus, substitution of one H by Me shifts the <sup>29</sup>Si signal by 13–15 ppm downfield. Disiloxanes R<sub>3</sub>SiOSiR<sub>3</sub>, where R = H or Me, obey this correction as well.<sup>24</sup> Further support for this assumption is provided by the fact that the difference between the calculated chemical shift of **5a** and that measured for D<sub>3</sub> is 31.8 ppm (GIAO) and 27.0 ppm (IGAIM), as expected for the substitution of two Si–H bonds by two Si–Me groups.

For silyloxonium cations the change in the <sup>29</sup>Si chemical shift due to substitution of Si–H by Si–Me is difficult to determine because of the lack of experimental data. For instance, according to IGAIM calculations, the <sup>29</sup>Si signal of (H<sub>3</sub>Si)<sub>3</sub>O<sup>+</sup> is shielded by 35 ppm compared to that of (Me<sub>3</sub>Si)<sub>3</sub>O<sup>+</sup>.<sup>6</sup> This difference between the <sup>29</sup>Si chemical shifts of the exocyclic silicon atoms in **5c** and **2** is 58 ppm (IGAIM), while the corresponding difference between the endocyclic Si<sup>1</sup> atoms in these species is 26 ppm.<sup>6</sup> Calculations suggest that in the silylated disiloxane **4c** the Si atoms are more shielded than those in the corresponding protonated analogue **4b**. This is in contrast to the data reported for (Me<sub>3</sub>Si)<sub>2</sub>OH<sup>+</sup> and (Me<sub>3</sub>Si)<sub>3</sub>O<sup>+</sup> (Table 2).<sup>4,6</sup>

**Charge Distribution and Orbital Analysis.** The atomic charges in all the studied species were calculated using both the Mulliken population analysis<sup>11</sup> and the natural population analysis (NPA), which is based on natural bond orbital (NBO) theory.<sup>12</sup> The results are collected in Table 3, and the numbering system is given in Chart 1. The two methods gave different absolute values (as is well-known) but similar qualitative results, and they are therefore discussed together.

The calculations show that the charge at the silicon atoms directly bonded to the oxonium oxygen is approximately the same as in the corresponding neutral

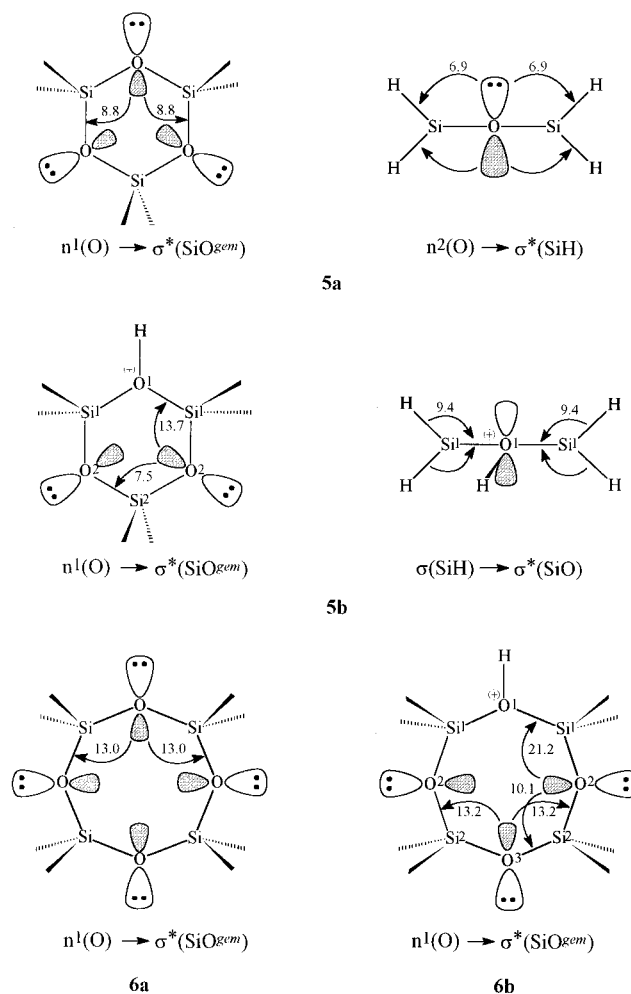
Chart 1



siloxane. The major change upon protonation of silylation occurs at the peripheral hydrogens, which become less negatively charged. The total charge on each of the H<sub>3</sub>Si groups in disiloxane **4a** becomes less negative by 0.11e (NPA) as a result of protonation or silylation. Similar results are observed for the cyclic systems **5–7**. The positive charge on the exocyclic Si atom in **5c–7c** is considerably smaller than that on the Si<sup>1</sup> atoms within the ring (Table 3).

NPA shows that in neutral siloxanes electron delocalization from bonding to antibonding orbitals ("non-Lewis structures") contributes 0.6% (**4a**, **7a**) to 0.85% (**5a**, **6a**) of the total electron density. Thus, stabilization of the molecular structure associated with delocalization effects is somewhat larger in oligosiloxanes, such as **5a** and **6a**, than in compounds having only one isolated SiOSi linkage (**4a** and **7a**), since the energy of the  $n(\text{O}) \rightarrow \sigma^*(\text{Si}-\text{O})$  interaction is larger than that of the  $\sigma(\text{Si}-\text{H}) \rightarrow \sigma^*(\text{Si}-\text{O})$  interaction. The contribution from these delocalization interactions is slightly reduced upon protonation and silylation (ca. 0.4% of the total electron density in **4b** and **7b** and 0.8% in **5b** and **6b**). This is also reflected in the calculated delocalization energies (obtained by zeroing all orbital interactions and recalculating the energy of the altered Fock matrix<sup>12</sup>) of siloxanes and of the corresponding oxonium ions. For example, the total delocalization energies for **4a–c** are 146, 108, and 174 kcal/mol (73, 54, and 58 kcal per Si–O bond), respectively. The delocalization pattern of the other siloxanes is more complicated, making detailed analysis difficult. However, protonation or silylation always reduces the total delocalization stabilization energy of the siloxane. We find, as noted previously,<sup>16a</sup> that the d orbitals on Si do not participate significantly in electron delocalization; the d(Si) orbitals being populated by only 0.05–0.06 electron (NBO).

The strongest delocalizations (according to NBO analysis) in neutral siloxanes XH<sub>2</sub>SiOSiH<sub>2</sub>X (X = H, O, C) are those involving donation of electrons from the oxygen lone pairs to the antibonding  $\sigma^*(\text{Si}-\text{H})$  and  $\sigma^*(\text{Si}-\text{X})$  orbitals. In the silyloxonium ions the direction of electron transfer is reversed. The strongest interactions in this case are those in which the  $\beta$ - $n(\text{O})$  (in **5b,c** and **6b,c**)  $\sigma(\text{Si}-\text{H})$ , and  $\sigma(\text{Si}-\text{X})$  orbitals donate electrons into the  $\sigma^*(\text{Si}-\text{O})$  antibonding orbitals of the oxonium center. The other interactions, not involving the oxonium center, are considerably weaker. The dominant delocalization interactions in cyclosiloxanes **5a** and **6a** as well as in their protonated forms, **5b** and **6b**, together with the corresponding second-order stabilization energies (kcal/mol), are shown in Figure 2. The unsymmetrical second-order energies of the  $n(\text{O}) \rightarrow \sigma^*(\text{Si}-\text{O})$  interactions illustrate polarization of the molecule induced by the positive charge (Figure 2).

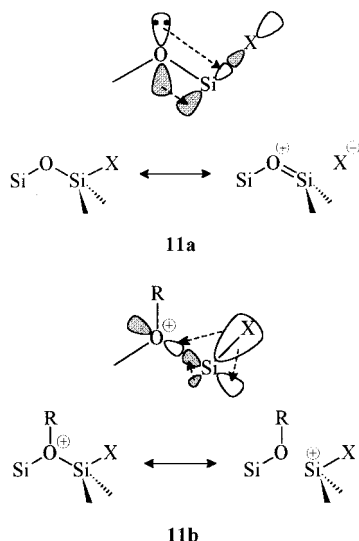


**Figure 2.** The strongest delocalization interactions occurring in the cyclosiloxanes **5a**, **5b**, **6a** and **6b**, according to the NBO second-order perturbative analysis (for clarity only representative interactions of a series of symmetrical interactions are drawn). The numbers on the arrows are the energies associated with the interactions (kcal/mol).

The elongation and weakening of the Si–O bonds at the silyloxonium center can be attributed to two cooperative effects. The first is the electrostatic repulsion between the SiH<sub>2</sub>X moieties (SiH<sub>3</sub> in **4b** and **4c**) around the oxonium center. In a nucleophilic substitution step (e.g., in the propagation step of polymerization), this effect is amplified by attractive interactions between the SiH<sub>2</sub>X groups and the electron-rich nucleophile. The second effect is the hyperconjugation involving electron transfer into the Si–O antibonding orbitals at the oxonium center, as is illustrated in terms of resonance structures in Scheme 2.

The contribution of "no bond" resonance structures of type **11b** to silyloxonium species is reflected by changes in the geometry of the SiH<sub>2</sub>X groups. Thus, the Si–H bonds shorten by ca 0.02 Å upon addition of H<sup>+</sup> or SiH<sub>3</sub><sup>+</sup>, reaching values similar to those in SiH<sub>3</sub><sup>+</sup> (1.454 Å), and the H–Si–H angle adopts intermediate values (115.6° in **4b**, 114.4° in **4c**) between those in neutral **4a** (109.0°) and in SiH<sub>3</sub><sup>+</sup> (120°). In cyclosiloxanes **5c** and **6c** the Si–O bonds geminal to the oxonium center (Si<sup>1</sup>–O<sup>2</sup>) are also considerably shorter than in neutral siloxanes (Figure 1). These geometric features suggest that the silyl groups bonded to the oxonium center have partial silylenium cation (SiH<sub>3</sub><sup>+</sup> or SiH<sub>2</sub>X<sup>+</sup>)

Scheme 2



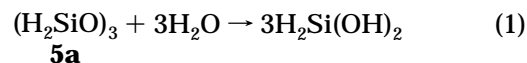
character. The endocyclic  $\text{Si}^1\text{--O}^1$  bonds at the oxonium center of **5c**–**7c** are longer than the exocyclic  $\text{Si--O}$  bonds (Figure 1). In **5c** and **6c** this can be explained by increased electron occupancy of the  $\sigma^*(\text{Si}^1\text{--O}^1)$  antibonding orbitals caused by the stronger  $n(\text{O}^2)\text{--}\sigma^*(\text{Si}^1\text{--O}^1)$  interactions. Indeed, the NBO occupancy of the endocyclic  $\sigma^*(\text{Si}^1\text{--O}^1)$  orbitals in **5c** and **6c** is 0.08 e, while that of  $\sigma^*(\text{Si}^{\text{exo}}\text{--O}^1)$  is only 0.04 e. In **7c**, where the  $\sigma(\text{Si}^1\text{--H})\text{--}\sigma^*(\text{Si}^1\text{--O}^1)$  and  $\sigma(\text{Si}^1\text{--C})\text{--}\sigma^*(\text{Si}^1\text{--O}^1)$  interactions have similar energies, these antibonding orbitals have similar occupancies (0.042 and 0.036 e, respectively). Due to the acute  $\text{SiOSi}$  angle in the five-membered ring and the resulting exceptionally short 1.3– $\text{Si}\cdots\text{Si}$  distance (2.83 Å in **7a**, 3.03 in **5a**, 3.20 Å in **6a**) strong electrostatic repulsion between the  $\text{SiH}_2$  groups is induced, causing the elongation of the endocyclic  $\text{Si--O}$  bonds.

The bond length differences  $\Delta r = r^{\text{endo}}(\text{Si--O}) - r^{\text{exo}}(\text{Si--O})$  for **5c**–**7c** are 0.016, 0.004, and 0.027 Å, respectively. The longer  $\text{Si}^1\text{--O}^1$  bonds and the higher net positive charge on the endocyclic  $\text{Si}^1$  atoms compared to the exocyclic Si (Figure 1, Table 3) suggest that **nucleophilic attack should occur preferentially at a ring Si atom, resulting in ring cleavage of 7c and 5c rather than in the splitting of the exocyclic  $\text{SiH}_3$  group.**

**Ring Strain of Cyclosiloxanes.** The ring strain of a cyclosiloxane monomer is believed to be the most important factor determining both the thermodynamics and the kinetics of its polymerization.<sup>3</sup> Strain energies of hydrogen-substituted cyclosiloxanes are not known but are expected to be not very different from those in the dimethylsiloxane analogues, since the steric effect of methyl groups is small.<sup>3f</sup> Studies of the equilibria between cyclic species and linear chains for various polysiloxane systems  $[\text{R}'\text{R}''\text{SiO}]_x$  showed that the proportion of small cyclics in the undiluted equilibrium mixture increases with the increasing size of the substituents, because the repulsive interaction between ligands at the neighboring silicon atoms in small cyclosiloxane rings is reduced compared to that in a siloxane chain.<sup>3a</sup> This results in a decrease in the total ring strain, measured as the enthalpy of the ring-opening reaction. Thus, the small steric effect of methyl groups is expected to slightly diminish the strain in

dimethyl cyclosiloxanes compared to that in dihydrogen cyclosiloxanes. However, the strain in permethylcyclosiloxanes is subject to some controversy. For example, according to calorimetric measurements of equilibration reactions (i.e. catalytic decomposition of the starting siloxane leading to the thermodynamic mixture of cyclic and open chain polysiloxanes),<sup>3a,b</sup> the strain energy of the  $\text{D}_3$  ring is about 2–4 kcal/mol and  $\text{D}_4$  is practically strainless (0.25 kcal/mol).<sup>25a,b</sup> In contrast, combustion enthalpy measurements gave strain energies of 19 kcal/mol for  $\text{D}_3$  and 14 kcal/mol for  $\text{D}_4$ .<sup>25c</sup> The latter values are, however, inconsistent with the thermodynamic data for the polymerization of cyclosiloxanes<sup>3</sup> and with the data for other heterocyclic monomers.<sup>2</sup> For example, the strain energies of tetrahydrofuran ( $(\text{CH}_2)_4\text{O}$ ) and trioxane ( $(\text{CH}_2\text{O})_3$ ) are 5.5 and 4.4 kcal/mol, respectively.<sup>2</sup> Cyclosiloxanes are considered to be less strained than cyclic ethers and acetals of the same ring size because of the greater flexibility of the  $\text{SiOSi}$  linkage. Thus, the values reported in ref 25c seem to be too high.

Theoretical work on the ring strain in cyclosiloxanes is sparse.<sup>17a,b,d</sup> First, we note that the comparison of experimental data with calculations must be treated with care, because the equilibration reaction studied experimentally leads to a mixture of linear and cyclic siloxanes and only the average thermodynamic features of the reaction can be experimentally evaluated. Moreover, it is important to choose isodesmic reactions, which minimize the influence of other factors. For example, the energy of reaction 1, which can be suggested as

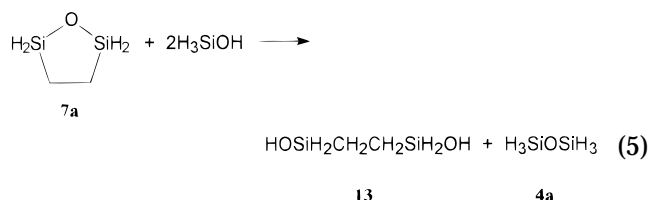
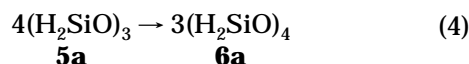
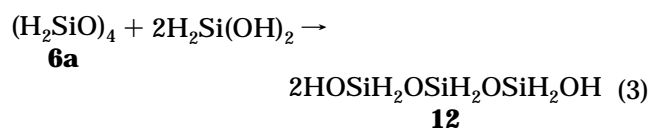
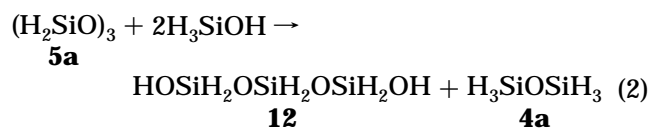


measuring the strain in **5a**, is 19 kcal/mol at 6-31G.<sup>17d</sup> Comparison with the equilibration energy of  $\text{D}_3$  suggests that this value is too high. One of the reasons for this is that reaction 1 indeed involves the ring opening and the consequent strain relief but it also includes the energy involved in the bond separation processes. Thus, in addition to the strain arising from bond and angle deformations, other effects such as the additional stabilization of the  $-\text{OSiO}-$  grouping in cyclosiloxane and in silanediol  $\text{H}_2\text{Si}(\text{OH})_2$  must be also considered. These interactions, which give rise to the anomeric effect, have been studied in silanediol and silanetriol, and the stabilization energy associated with the anomeric effect in silanediol was found to be ca. 6–7 kcal/mol.<sup>26</sup> The magnitude of this effect in siloxanes has not been studied quantitatively so far.

In order to evaluate the ring strain of **5a**–**7a**, we considered the isodesmic equations (2)–(5), which minimize the aforementioned problems. The enthalpies of these reactions are based on MP4/6-31G\*/HF/6-31G\* energies and on thermal corrections obtained from frequency calculations at HF/6-31G\*. The computed thermodynamic quantities are listed in Table 4.

According to eq 2, the “strain energy” of **5a** ( $-\Delta H_{298}$ ) is 6.5 kcal/mol. However, this value probably is slightly

(25) (a) Piccoli, W. A.; Haberland, G. G.; Merker, R. L. *J. Am. Chem. Soc.* **1960**, *82*, 1883. (b) Yuzhelevsky, Yu. A.; Sokolov, V. V.; Tagyeva, L. V.; Kagan, E. G. *Vysokomol. Soedin., Ser. B* **1971**, *2*, 95. (c) Voronkov, M. G.; Klyuchnikov, V. A.; Mironenko, E. V.; Shvets, G. N.; Danilova, T. F.; Khudobin, Y. I. *J. Organomet. Chem.* **1991**, *406*, 91. (26) (a) Apeloig, Y.; Stanger, A. *J. Organomet. Chem.* **1988**, *346*, 305. (b) Reed, A. E.; Schade, C.; Schleyer, P. v. R.; Kamath, P. V.; Chandrasekhar, J. *J. Chem. Soc., Chem. Commun.* **1988**, 67.



overestimated because the electronic interactions between the silanol end functions and the siloxane chain stabilize **12** to some extent.

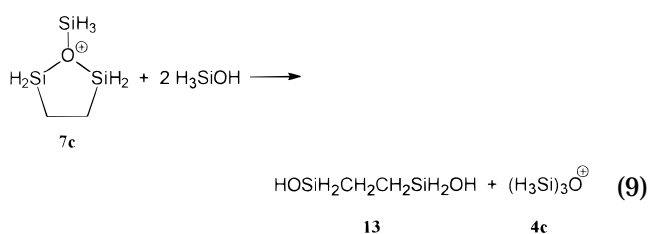
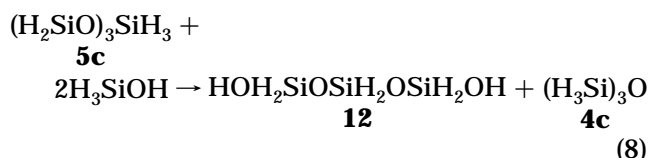
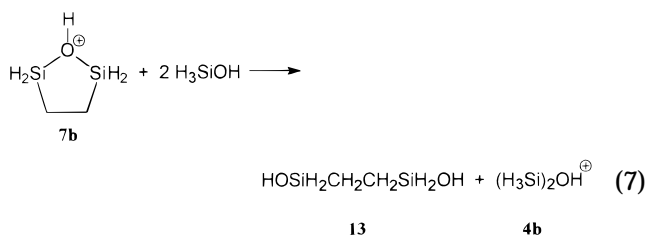
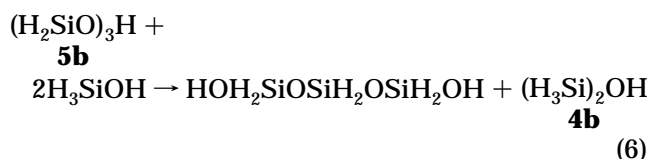
The energy of ring opening of cyclotetrasiloxane **6a** (eq 3) is  $-2.1$  kcal/mol. The small negative value indicates that either the cyclotetrasiloxane ring is not entirely strainless or that **12** is slightly stabilized by the silanol end groups, as discussed above.

The most appropriate reaction to compute the strain energy of **5a** seems to be the conversion of cyclotrisiloxane into a larger unstrained ring like cyclotetrasiloxane (eq 4).<sup>25b</sup> The energy released in this reaction (for 4 mol of **5a**) is 19.7 kcal (4.9 kcal/mol, 1.6 kcal per SiO bond) at MP4/6-31G\*/HF/6-31G\* and 26.4 kcal at HF/6-31G\* (74.2 kcal, 17.7 kcal/mol at 3-21G<sup>17a</sup>). Our best estimate of the ring strain of **5a** (which includes thermal corrections to the electronic energy) is  $-\Delta H_{298} = 18.1/4 = 4.5$  kcal/mol (1.5 kcal per SiO bond) (Table 4). This result agrees well with the experimentally measured strain for D<sub>3</sub> (2–4 kcal/mol).<sup>25a,b</sup>

The strain in **7a** calculated according to reaction 5 is 7.4 kcal/mol. This value is similar to the ring strain of the methyl-substituted analogue of **7a**, 1-oxa-2,5-bis(dimethylsila)cyclopentane, of 8–12 kcal/mol (based on the heat of equilibration of this monomer and the thermodynamic mixture of its linear and cyclic oligomers).<sup>25a</sup> Thus, **7a** is ca. 1–3 kcal/mol more strained than **5a** (using eqs 2 and 4, respectively).

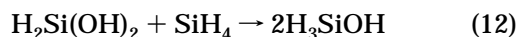
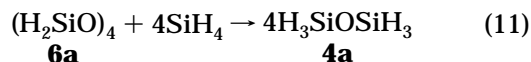
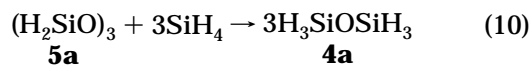
The fact that protonated and silylated siloxanes have geometries different from those of the corresponding neutral siloxanes implies that their strain energies may be different. The strain of a cyclic silyloxonium ion affects its stationary concentration in the reaction mixture and, consequently, the rate of polymerization of the corresponding monomer.<sup>2</sup> For example, it was shown that different reactivities of silyloxonium ions, which depend on the ring size, determine the kinetics of polymerization of cyclic silaethers.<sup>27</sup>

The strain energies of the protonated cyclosiloxanes **5b** and **7b** were computed by eqs 6 and 7, which are analogous to eqs 2 and 5, respectively. The strain energies of the silylated derivatives **5c** and **7c** were calculated according to eqs 8 and 9. The results are given in Table 4.



The protonation and silylation of the cyclosiloxane causes similar changes in its strain (Table 4). Thus, the protonation and silylation of cyclotrisiloxane **5a** increases its strain energy by 1.5 kcal/mol (compare eqs 6 and 8 with eq 2). In contrast, the enthalpies of reactions 7 and 9 are positive, which suggests that **7b** and **7c** are slightly better stabilized (by ca. 3 kcal/mol) than the corresponding open-chain analogues. The latter results probably reflect the contribution of stabilizing stereoelectronic effects in **13** and may also be partially due to an inadequate level of theory. Thus, we conclude that the ring strain in cyclotrisiloxane remains nearly unchanged upon protonation or silylation, while the strain in **7a** is largely released in the corresponding oxonium ions **7b** and **7c**.

Finally, we note that the presence of the silaacetal OSiO bonds considerably stabilize cyclic siloxanes via the anomeric effect, analogous to that occurring in silanediol,<sup>26</sup> as may be concluded from the calculated energies of the bond separation equations (10) and (11)



The calculated enthalpy of reaction 10 ( $\Delta H_{298} = -21.8$  kcal/mol) indicates that the geminal interactions in each silaacetal OSiO group contribute 7.3 kcal/mol to the total stabilization of **5a**. The analogous stabilization energy in **6a** ( $\Delta H_{298} = -35.1$  kcal/mol) is 8.8 kcal per OSiO linkage (eq 11). For comparison, the bond separation enthalpy in  $\text{H}_2\text{Si(OH)}_2$  (eq 12) is 9.3 kcal/mol.

**Basicity and Silicophilicity of Siloxanes.** The rate of propagation in the cationic polymerization of



**Table 4. Calculated Energies (kcal/mol) of Eq 2–11<sup>a</sup>**

eq	$\Delta E(\text{HF})$	$\Delta E(\text{MP2})$	$\Delta E(\text{MP4})$	$\Delta E_{298}^b$	$\Delta H_{298}^c$
2	-8.6	-8.2	-7.9	1.4	-6.5
3	-1.2	-3.0	-3.2	1.1	-2.1
4	-26.4	-21.0	-19.7	1.6	-18.1
5	-10.4	-8.7	-8.3	0.9	-7.4
6	-7.5	-9.6	-9.6	1.6	-8.0
7	3.3	2.6	2.5	0.2	2.7
8	-7.7	-9.1	-9.0	1.4	-7.6
9	3.6	2.8	2.6	0.4	3.0
10	12.3	17.8	19.6	2.2	21.8
11	25.2	30.7	32.7	2.4	35.1

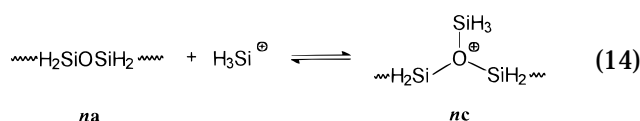
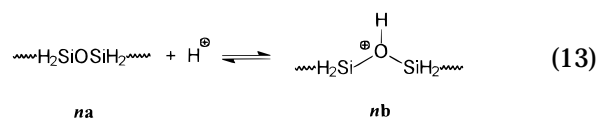
<sup>a</sup> Using the 6-31G\* basis set. For the species involved in eqs 2–11 and not referred to in the text the following energies were used: for **12**,  $E(\text{MP4/6-31G}^*/\text{HF/6-31G}^*) = -1172.146\,99$  hartrees,  $\Delta E_{298} = 62.6$  kcal/mol; for **13**,  $E(\text{MP4/6-31G}^*/\text{HF/6-31G}^*) = -810.050\,23$  hartrees,  $\Delta E_{298} = 76.4$  kcal/mol. <sup>b</sup> Thermal correction to the electronic energy, including ZPE. <sup>c</sup> Based on the MP4/6-31G\*//HF/6-31G\* energies.

heterocycles is proportional to the nucleophilicity of the monomer.<sup>2</sup> Since nucleophilicity is a kinetic property, specific for a given reaction, and since no general order of nucleophilicities is known, basicities are often used to predict the reactivities of various monomers.<sup>2</sup> Although this is a rather crude approach, it has yielded satisfactory results explaining various phenomena of the cationic polymerization of heterocycles.<sup>2</sup> We have therefore calculated the proton affinities as well as the silylenium cation affinities and silicophilicities (i.e., reactivity toward silicon atom) of the model siloxanes **4a–7a**.

The question of the basicity of siloxanes was addressed in a variety of experimental and theoretical studies.<sup>16a–c,28–31</sup> The much lower basicity of disiloxanes compared to isostructural dialkyl ethers, both in the gas phase and in solution, is well recognized experimentally<sup>29</sup> and theoretically.<sup>16a,b</sup> This behavior was rationalized by the lower energy and the smaller coefficient on oxygen in the HOMO of siloxanes compared to dialkyl ethers, both resulting from delocalization of the oxygen lone pairs into the  $\pi(\text{SiH}_3)$  and  $\pi^*(\text{SiH}_3)$  orbitals.<sup>16a</sup> Alkylsilyl ethers represent an intermediate case, being slightly less basic than dialkyl ethers but more basic than the corresponding disiloxanes.<sup>16b</sup> Previous calculations were limited to disiloxanes (containing only one SiOSi bond), and we extend this study to compounds having several siloxane bonds.

The gas-phase proton affinity (PA) and basicity of a molecule are defined as the negative of the enthalpy,  $-\Delta H_{298}$ , and of the free energy,  $-\Delta G_{298}$ , respectively, for the corresponding protonation reaction (eq 13). We calculated these species using MP4/6-31G\*//HF/6-31G\* energies (except where stated otherwise) and standard thermodynamic relationships.<sup>8,16b</sup>

Reaction 13 models the first step of initiation of the polymerization process, which involves protonation of



$n=4-7$ ;  $\text{---H}_2\text{Si}$  denotes either a  $\text{SiH}_3$  group or a  $\text{SiH}_2$  unit within a ring

the siloxane bond in the monomer (or partial charge transfer via a hydrogen bond to an acid).<sup>29b</sup>

The silylenium cation affinity and the silicophilicity of various siloxanes are computed analogously, as the negative of the enthalpy and of the free energy, respectively, for the addition of a silylenium cation to siloxanes (eq 14). Silylenium cation constitutes the simplest model for the electrophilic silicon. Equation 14 can therefore be viewed as a model for the propagation step, which involves a nucleophilic attack of the monomer on the electrophilic silicon atom in the active propagation center (silyloxonium ions, Scheme 1). To compare the silylenium affinities of siloxanes with those of ethers and mixed silylalkyl ethers, we have also calculated the energies of  $\text{H}_3\text{Si}^+$  addition to dimethyl ether (**8a**) and methoxysilane,  $\text{CH}_3\text{OSiH}_3$  (**9a**).

The absolute and relative proton affinities (PA) as well as the relative basicities of **4a–9a**, calculated at various theoretical levels, are collected in Tables 5 and 6.

The calculated absolute  $\text{PA}_{298}$  of the parent siloxane **4a** is 185.3 kcal/mol.  $\text{PA}_0$  is 183.8 kcal/mol, 4.8 kcal/mol higher than the value calculated according to G1 theory using MP2(full)/6-31G\* optimized geometries.<sup>16c</sup> Although the MP4/6-31G\*//HF/6-31G\* level of theory cannot accurately reproduce the absolute proton affinities of siloxanes, it is expected to give reliable values of the relative PA's and basicities, as errors tend to partially cancel in such comparisons.

The calculated PA order is **7a** > **8a**  $\approx$  **9a** > **6a**  $\geq$  **4a**  $\geq$  **5** (Table 6). The proton affinity of oxadisilacyclopentane **7a** (196 kcal/mol at MP4/6-31G\*//HF/6-31G\* and 197.5 kcal/mol at MP3/6-31G\*//HF/6-31G\* is 10.7 kcal/mol higher than that of **4a** and is almost as high as that of tetrahydrofuran ( $\text{PA}_{298} = 198.8$  kcal/mol at MP3/6-31G\*//HF/6-31G\*).<sup>32</sup> Siloxanes **4a**, **5a**, and **6a** have similar PA's. The PA of **6a** is 2.4 kcal/mol higher, while PA of **5a** is -1.6 kcal/mol lower than that of **4a**. The order of basicities is similar; the only difference is that **5a** is slightly more basic than **6a** and **4a**, due to a distinct increase in the entropy of cyclotrisiloxane **5a** upon protonation (Table 5).

The calculated silyl affinities and silicophilicities of **4a–9a** are given in Tables 7 and 8. The absolute silyl affinities are some 120 kcal/mol lower than the corresponding PA's. The  $\text{Me}_3\text{Si}^+$  affinities of  $\text{Et}_2\text{O}$ ,  $\text{EtO-SiMe}_3$ , and  $(\text{Me}_3\text{Si})_2\text{O}$  calculated previously<sup>6</sup> are about 20 kcal/mol lower than the  $\text{H}_3\text{Si}^+$  affinities of  $(\text{CH}_3)_2\text{O}$ ,  $\text{CH}_3\text{OSiH}_3$ , and  $(\text{H}_3\text{Si})_2\text{O}$ , respectively. The silyl and proton affinities of **4a–9a** are linearly correlated with a slope close to 1 (slope = 0.984,  $r = 0.990$ ; Figure 3). A

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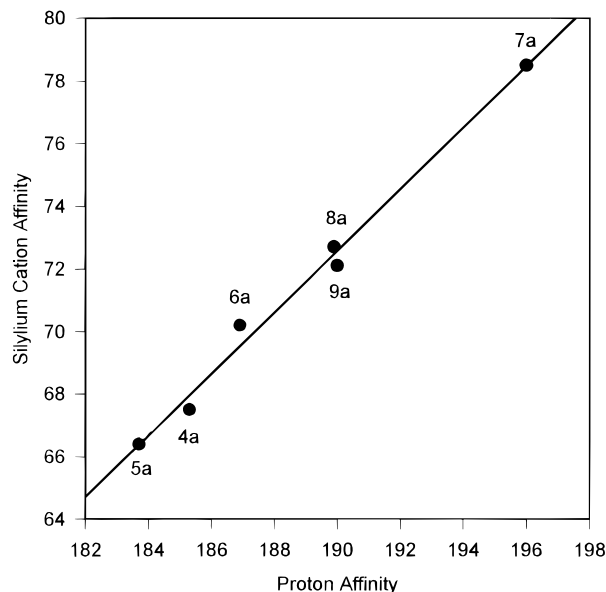
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**Table 5. Calculated Proton Affinities (6-31G\*) of Model Oxygen Bases (Eq 13) (kcal/mol)<sup>a</sup>**

base	$\Delta E_0^e(\text{HF})$	$\Delta E_0^e(\text{MP2})$	$\Delta E_0^e(\text{MP3})$	$\Delta E_0^e(\text{MP4})$	$\Delta E_{298}^b$	$\Delta H_{298}^c$	$\Delta S$ (cal/(mol K))	$\Delta G_{298}^c$
<b>4a</b>	-189.6	-189.2	-191.8	-191.1	5.8	-185.3	-27.9	-177.0
<b>5a</b>	-190.7	-187.8	-190.4	-189.3	5.6	-183.7	-14.1	-179.5
<b>6a</b>	-192.8	-192.6	-194.7	-194.4	5.7	-188.7	-36.1	-178.0
<b>7a</b>	-203.4	-200.5	-203.4	-201.9	5.9	-196.0	-23.2	-189.1
<b>8a<sup>d</sup></b>	-199.3	-195.2	-197.1	-196.5	6.5	-189.9	-21.8	-183.4
<b>9a<sup>d</sup></b>	-197.9	-194.6	-197.1	-196.1	6.1	-190.0	-21.8	-183.5

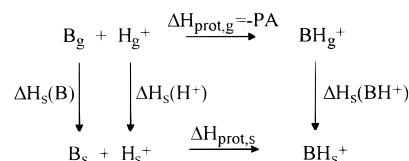
<sup>a</sup>  $S(\text{H}^+) = 26.039$  cal/(mol K).<sup>35</sup> <sup>b</sup>  $\Delta E_{298} = E_{298}^{\text{vib}} + \Delta E_{298}^{\text{rot}} + \Delta E_{298}^{\text{trans}} + \Delta(\text{PV})$ ;  $\Delta E_{298}^{\text{vib}}$  scaled by 0.893.<sup>8</sup> <sup>c</sup> Based on the MP4/6-31G\*/6-31G\* energies. <sup>d</sup> HF, MP2, and MP3 values taken from ref 16b.

**Figure 3.** Plot of the silylenium cation affinity vs the proton affinity of several siloxanes (kcal/mol).

similar correlation is found between the silicophilicity and basicity scale. This is in accord with the linear relationship between proton and  $\text{Me}_3\text{Si}^+$  affinities found previously by ICR measurements.<sup>31</sup> The linear correlation between proton and silyl affinities suggests that the electronic demands of both cations are similar; that is, they induce analogous changes in the electronic structure of a siloxane base. The lower energy of interaction with silylenium cation is mainly due to the higher thermodynamic stability of  $\text{H}_3\text{Si}^+$  relative to  $\text{H}^+$ . Thus, protonation causes greater changes in the molecular structure of a siloxane than does silylation. Cyclotrisiloxane **5a** is 4 kcal/mol more silicophilic than **4a**. This is consistent with the known high reactivity of its permethylated analogue.<sup>3</sup>

The high basicity and silicophilicity of oxadisilacyclopentane **7a** results from two main factors. (i) The geometry of the five-membered ring does not allow optimal orbital overlap. Consequently, the  $n(\text{O}) \rightarrow \sigma^*(\text{Si}-\text{X})$  delocalization is diminished (the total NBO delocalization energy associated with these interactions is 35.3 kcal/mol in **7a**, compared to 47.9 and 42.4 kcal/mol in **4a** and **5a**, respectively), and the oxygen lone pairs are thus more localized. The calculated energy of the HOMO is higher than in other siloxanes (-11.3 eV in **7a**, compared to -12.1 eV in **4a** and -11.8 eV in **5a**). (ii) The enthalpy of protonation or silylation of **7a** involves an energy gain due to the release of ring strain.

**Studies of the Protonation of Siloxanes in Solution.** Since polymerization is usually carried out in solution, we have attempted to estimate computationally the effect of solvation on the thermodynamics of the

**Scheme 3****Table 6. Relative Basicities (6-31G\*) of Model Oxygen Bases Calculated Using Disiloxane 4a as a Reference Base (kcal/mol)**

base	$\Delta E_0^e(\text{HF})$	$\Delta E_0^e(\text{MP2})$	$\Delta E_0^e(\text{MP3})$	$\Delta E_0^e(\text{MP4})$	$\Delta H_{298}^a$	$\Delta G_{298}^a$
<b>4a</b>	0	0	0	0	0	0
<b>5a</b>	1.1	-1.4	-1.4	-1.8	-1.6	2.5
<b>6a</b>	3.2	3.5	3.3	3.4	2.4	1.1
<b>7a</b>	13.8	11.3	11.6	10.8	10.7	12.1
<b>8a<sup>b</sup></b>	9.7	6.0	5.3	5.4	4.6	6.4
<b>9a<sup>b</sup></b>	8.3	5.4	5.3	5.0	4.7	6.5

<sup>a</sup> Based on the MP4/6-31G\*/6-31G\* energies. <sup>b</sup> HF, MP2, and MP3 values taken from ref 16b.

protonation reaction employing a SCRF method.<sup>15</sup> As model solvents for calculations we chose cyclohexane ( $\epsilon = 2.0$ ) and dichloromethane ( $\epsilon = 8.9$ ), which have been commonly used in mechanistic studies of polymerization processes and which are believed to simulate closely the true conditions of polymerization.<sup>3</sup> The thermodynamic cycle shown in Scheme 3 was considered:<sup>33</sup>

$$\Delta H_{\text{prot},s} = -\text{PA} + \Delta H_s(\text{BH}^+) - \Delta H_s(\text{B}) - \Delta H_s(\text{H}^+) \quad (15)$$

The energy of solvation of ions may be expressed as a sum of two components: (i) the neutral term (involving cavitation and dispersion-repulsion interactions) and (ii) the electrostatic term (eq 16).<sup>33</sup>

$$\Delta H_s(\text{BH}^+) = \text{neutral term} + \text{electrostatic term} \approx \Delta H_s(\text{B}) + \Delta H_s^{\text{el}}(\text{BH}^+) \quad (16)$$

The first term was found to be nearly the same for neutral and protonated amines in water (the difference being less than 0.2 kcal/mol); therefore, it seems reasonable to assume that this is also true for siloxanes in cyclohexane and dichloromethane.<sup>33b</sup> Thus

$$\Delta H_{\text{prot},s} = -\text{PA} + \Delta H_s^{\text{el}}(\text{BH}^+) - \Delta H_s^{\text{el}}(\text{B}) - \Delta H_s(\text{H}^+) \quad (17)$$

The equilibrium geometries calculated for **4a** and **5a** in cyclohexane and dichloromethane using the Onsager dipole model are almost identical with the gas-phase geometries (differences in bond lengths and angles are less than 0.001 Å and less than 0.1°, respectively, except

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**Table 7. Calculated Thermodynamic Properties (6-31G\*) for the Addition of H<sub>3</sub>Si<sup>+</sup> to Model Oxygen Bases (Eq 15) (kcal/mol)<sup>a</sup>**

base	$\Delta E_0^e(\text{HF})$	$\Delta E_0^e(\text{MP2})$	$\Delta E_0^e(\text{MP3})$	$\Delta E_0^e(\text{MP4})$	$\Delta E_{298}^b$	$\Delta H_{298}^c$	$\Delta S$ (cal/(mol K))	$\Delta G_{298}^c$
<b>4a</b>	-59.7	-69.5	-69.0	-70.0	2.5	-67.5	-45.3	-54.0
<b>5a</b>	-60.0	-68.6	-67.9	-68.8	2.4	-66.4	-28.3	-58.0
<b>6a<sup>d</sup></b>	-61.7	-72.7			2.5	-70.2	-49.8	-55.3
<b>7a</b>	-73.8	-81.0	-80.7	-81.0	2.5	-78.5	-32.5	-68.8
<b>8a</b>	-70.0	-75.8	-74.3	-75.4	2.7	-72.7	-28.9	-64.1
<b>9a</b>	-67.7	-74.8	-74.0	-74.7	2.6	-72.1	-28.5	-63.6

<sup>a</sup> SiH<sub>3</sub><sup>+</sup>:  $E_0^e(\text{HF}) = -290.328\ 91$ ;  $E_0^e(\text{MP2}) = -290.391\ 21$ ;  $E_0^e(\text{MP3}) = -290.406\ 03$ .  $E_0^e(\text{MP4}) = -290.410\ 57$ ;  $\Delta E_{298} = 15.4$  kcal/mol;  $S = 48.88$  cal/(mol K). <sup>b</sup>  $\Delta E_{298} = E_{298}^{\text{vib}} + \Delta E_{298}^{\text{rot}} + \Delta E_{298}^{\text{trans}} + \Delta(\text{PV})$ ;  $\Delta E_{298}^{\text{vib}}$  scaled by 0.893.<sup>8</sup> <sup>c</sup> Based on the MP4/6-31G\*/6-31G\* energies, unless stated otherwise. <sup>d</sup>  $\Delta H$  and  $\Delta G$  were calculated using MP2/6-31G\* values.

**Table 8. Relative Silicophilicities (6-31G\*) of Model Oxygen Bases 4a–9a, using Disiloxane 4a as a Reference (kcal/mol)**

base	$\Delta E_0^e(\text{HF})$	$\Delta E_0^e(\text{MP2})$	$\Delta E_0^e(\text{MP3})$	$\Delta E_0^e(\text{MP4})$	$\Delta H_{298}^a$	$\Delta G_{298}^a$
<b>4a</b>	0	0	0	0	0	0
<b>5a</b>	0.3	-0.9	-1.1	-1.2	-1.1	4.0
<b>6a<sup>b</sup></b>	2.0	3.2			2.7	1.3
<b>7a</b>	14.1	11.5	11.7	11.0	11.0	14.8
<b>8a</b>	10.3	6.3	5.3	5.4	5.2	10.1
<b>9a</b>	8.0	5.3	5.0	4.7	4.6	9.6

<sup>a</sup> Based on the MP4/6-31G\*/6-31G\* energies, unless stated otherwise. <sup>b</sup>  $\Delta H$  and  $\Delta G$  were calculated using the MP2/6-31G\* values.

for the Si–O–Si angle, which decreases from 170.0° in the gas phase to 168.9° in C<sub>6</sub>H<sub>12</sub> and 167.6° in CH<sub>2</sub>Cl. This is not surprising, as the dipole moments of siloxanes are close to zero. Changes in the equilibrium geometries of protonated siloxanes **4b** and **5b** upon solvation are somewhat larger (differences in bond lengths and bond angles are less than 0.005 Å and 0.2°, respectively). However, these changes do not significantly affect the energies of the protonated species. For example, the energies calculated for **5b** in CH<sub>2</sub>Cl<sub>2</sub> using gas-phase and SCRF geometries differ by only 0.3 kcal/mol. In view of the above, the gas-phase geometries were used for calculations of the solvent effects. Moreover, the thermal corrections to enthalpy and free energy calculated for **4a** and **4b** in solution are very similar to those calculated in the gas phase ( $(\Delta E_{298})_s < 0.1$  kcal/mol,  $T\Delta S_s < 0.2$  kcal/mol). Assuming that this holds also for **5a–7a**, the following approximation can be made:

$$\Delta H_s^{\text{el}}(\text{BH}^+) = H_s^{\text{el}}(\text{BH}^+) - H_g^{\text{el}}(\text{BH}^+) \approx E_s^{\text{el}}(\text{BH}^+) - E_g^{\text{el}}(\text{BH}^+) \quad (18)$$

Hence, the relative proton affinity in solution of the bases B<sub>1</sub> and B is given by eq 19. The relative basicities

$$\Delta H_{\text{prot},s}(\text{B}) - \Delta H_{\text{prot},s}(\text{B}_1) = -\Delta\text{PA} + \Delta E_s^{\text{el}}(\text{BH}^+) - \Delta E_s^{\text{el}}(\text{B}_1\text{H}^+) - (\Delta E_s^{\text{el}}(\text{B}) - \Delta E_s^{\text{el}}(\text{B}_1)) \quad (19)$$

( $\Delta G_{\text{prot},s}(\text{B}) - \Delta G_{\text{prot},s}(\text{B}_1)$ ) of siloxanes in solution were calculated from an equation analogous to eq 19. The results of such calculations for **4a–7a** are presented in Table 9.

The basicity order of siloxanes in both cyclohexane and in dichloromethane is **7a** > **4a** > **5a** > **6a**. The differences between the two solvents are small (Table 9). In the gas phase, the order is **7a** > **5a** > **6a** > **4a**. As in the gas phase, also in solution **7a** is much more basic than the other siloxanes, which indicates the dominance of structural effects (mostly angular strain)

in this case. The basicity order of the other siloxanes in solution is different from that in the gas phase, **4a** being more basic in solution than **5a** and **6a**.

Since no experimental data are available for hydrogen-substituted siloxanes, the closest comparison which can be made is with dimethylsiloxanes. In the gas phase, the basicity of methyl siloxanes relative to their H analogues is mainly determined by their higher polarizability, which increases with increasing size of the molecule.<sup>16a,b,30</sup> In solution, the basicity order of dimethylsiloxanes was measured by two types of reactions: first, as constants for hydrogen bonding with phenol in CCl<sub>4</sub><sup>29a</sup> and with CF<sub>3</sub>COOH in CH<sub>2</sub>Cl<sub>2</sub>.<sup>29b</sup> In these experiments the basicity order D<sub>3</sub> > D<sub>4</sub> > (Me<sub>3</sub>-Si)<sub>2</sub>O was found. On the other hand, the interaction of dimethylsiloxanes with CF<sub>3</sub>SO<sub>3</sub>H in the presence of a reference base (hindered amine) in C<sub>6</sub>H<sub>6</sub> gave the basicity order (Me<sub>3</sub>Si)<sub>2</sub>O > D<sub>3</sub> ≈ D<sub>4</sub>.<sup>29c</sup> The different basicity order is not unexpected, as the reactions used for these measurements are significantly different. In hydrogen bonding (e.g. with phenol) only partial proton transfer occurs, whereas interaction with CF<sub>3</sub>SO<sub>3</sub>H, which is one of the strongest protonic acids, involves a much larger degree of proton transfer, resulting probably in ion-pair formation. The reaction with CF<sub>3</sub>SO<sub>3</sub>H probably models more closely the “full” protonation considered here, and indeed, the basicity order measured using CF<sub>3</sub>SO<sub>3</sub>H corresponds well to the basicity order calculated by us. These studies clearly show that the basicities of siloxanes depend on the reaction system, particularly on the polarity and donor–acceptor properties of the solvent and on the strength of a reference acid used for such measurements.<sup>29</sup>

**Implications of the Calculations for the Polymerization Mechanism of Cyclic Siloxanes.** The differences in basicities are expected to cause changes in the kinetics and mechanism of polymerization. For example, the basicity of a cyclic monomer relative to that of a siloxane oxygen within a polymer chain determines the proportion of propagation vs undesired chain scission. Oxadisilacyclopentane **7a**, the most basic and more silicophilic among the cyclosiloxanes discussed here, is expected to be the most reactive monomer. Its high strain energy indicates that polymer formation is strongly thermodynamically favored. Cyclotrisiloxane **5a** is expected to be less reactive, but its moderate ring strain also highly favors polymerization. In contrast, cyclotetrasiloxane **6a** has basicity and silicophilicity similar to that of the siloxane chain (which is modeled by **4a**) and the enthalpy of its ring-opening reaction is close to zero. Hence, the polymerization of **6a** is expected to lead to equilibration, i.e., to a thermodynamic mixture of cyclic and linear siloxanes, as is

**Table 9. Relative Proton Affinities and Basicities of Siloxanes in Cyclohexane and Dichloromethane Calculated Using the IPCM Model**

	solvent ( $\epsilon$ )	$\mu$ (D)	$-E_s^{\text{el}}$ (hartrees)	$E_g^{\text{el}} - E_s^{\text{el}}$ (kcal/mol)	$\Delta(\Delta H_{\text{prot},s})$ (kcal/mol)	$\Delta(\Delta G_{\text{prot},s})$ (kcal/mol)
<b>4a</b>	C <sub>6</sub> H <sub>12</sub> (2.0)	0.16	656.259 02	0	0	0
<b>4b</b>			656.561 23	31.8		
<b>5a</b>		0	1 095.121 24	2.1	-5.3	-1.2
<b>5b</b>			1 095.425 14	30.2		
<b>6a</b>		0	1 460.175 69	0.2	-1.9	-3.2
<b>6b</b>			1 460.482 87	27.7		
<b>7a</b>	CH <sub>2</sub> Cl <sub>2</sub> (8.9)	1.84	733.179 09	1.4	7.3	8.7
<b>7b</b>			733.548 44	29.8		
<b>4a</b>		0.19	656.260 77	1.1	0	0
<b>4b</b>			656.655 00	58.8		
<b>5a</b>		0.09	1 095.130 32	5.7	-7.3	-3.2
<b>5b</b>			1 095.516 35	57.2		
<b>7a</b>		2.24	733.182 31	3.4	4.8	6.2
<b>7b</b>			733.588 92	55.2		

indeed found for D<sub>4</sub>.<sup>3</sup> These conclusions correspond well to the observed features of dihydrogen siloxane equilibration.<sup>3f,7</sup> The order of the reactivities predicted on this basis, **7a** > **5a** > **6a**, is the same as that observed for the dimethylsiloxane analogues.

The relatively low basicity and silicophilicity of cyclotrisiloxane **5a** and the relatively high strain energies of **5b** and **5c** imply that the equilibrium constants for silyloxonium ions formation are small and therefore the stationary concentration of the silyloxonium species in the polymerization of **5a** is predicted to be very low. From this it is possible to conclude that the alternative pathways of propagation (not involving silyloxonium ions), such as insertion of the monomer into the activated ester end group, can compete effectively with the silyloxonium pathway.<sup>3</sup> In contrast, the ring strain in **7a** is released upon silyloxonium ion formation; therefore, the stationary concentrations of the oxonium ions **7b** and **7c** are expected to be relatively high. Various acid–base equilibria, which complicate the polymerization of D<sub>3</sub> and D<sub>4</sub> because of the low basicity of these monomers,<sup>3d,e,29b</sup> should be less important in the case of the more basic oxadisilacyclopentane. The kinetics of polymerization of this monomer should therefore be simpler and should resemble the kinetics of polymeri-

zation of THF. Preliminary data from the Łódź laboratory on the polymerization of oxatetramethyldisilacyclopentane indeed confirm these predictions.<sup>34</sup>

The calculations in solution reveal also some variations in ring strain energies due to different energies of interaction with solvent. Thus, the HF/6-31G\* strain energy of **5a** calculated from eq 4 decreases from -26.4 kcal (6.6 kcal/mol) in the gas phase to -18.7 kcal (4.7 kcal/mol) in cyclohexane.

Another important finding of the calculations is that nucleophilic attack on a silylated cyclosiloxane **5c** or **7c** is predicted to cleave the endocyclic Si–O bonds more easily than the exocyclic Si–O bond. This expected to favor ring opening and propagation over transfer of the exocyclic H<sub>3</sub>Si<sup>+</sup> group to another molecule of monomer or to an oxygen in a chain.

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**Supporting Information Available:** Table 10, giving the absolute energies of calculated species (1 page). Ordering information is given on any current masthead page.

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