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Trisilyloxonium Ions: Preparation, NMR Spectroscopy, *ab Initio*/IGLO Studies, and Their Role in Cationic Polymerization of Cyclosiloxanes[1]

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Abstract: Trisilyloxonium ions, key intermediates in understanding the mechanism of cationic polymerization of cyclosiloxanes, were for the first time prepared by reacting trimethysilane with trityl tetrakis(pentafluorophenyl)-borate (**TPFPB**) in the presence of siloxanes and directly observed by NMR spectroscopy at −70 °C. Polymerization or oligomerization of siloxanes can be initiated by *in-situ* formed trisilyloxonium ions. The mechanism of the reactions is discussed. Structural parameters and ^{29}Si NMR chemical shifts of a number of silyloxonium ions were calculated by *ab initio*/IGLO methods. The results are in good agreement with the obtained experimental data.

Introduction

Although the cationic polymerization of cyclosiloxanes is a widely used industrial process in the manufacture of polysiloxanes, the mechanism of the reaction is not yet well established.[2] The main problem is the lack of knowledge of the nature of the intermediates involved in the polymer propagation. Trisilyloxonium ions were postulated by some investigators as possible intermediates.[2e−h] However, existence of such intermediate ions has never been proven and its intermediacy was questioned by other investigators because of low nucleophilicity of the oxygen atom in siloxanes.[2b]

Mono- and disilyloxonium ions were reported for the first time from this laboratory[3] either by protonation or methylation of silyl ethers or siloxanes. However, trisilyloxonium ions could not be prepared by a similar approach. It has been long known that organohydrosilanes readily transfer hydrides to carbocations, such as trityl cation (so called Corey hydride transfer).[4] Recently this approach was explored by several groups to obtain silylated onium and arenium ions.[5] Kira, Sakurai, et al. reported the generation of mono- and disilyloxonium ions by using such an approach as an alternative to the alkylation of silyl ethers.[5a] Recently the X-ray crystal structure of protonated *tert*-butyldimethylsilanol was reported by Reed, Bau, et al.[6]

In the course of our studies on silyl-substituted carbenium ions and silyl onium ions,[3,5fg,7] we now report the preparation and NMR spectroscopic characterization of long-lived trisilyloxonium ions. The structural geometries, dissociation energies, and ^{29}Si NMR chemical shifts of a series of mono-, di-, and trisilyloxonium ions were also calculated by *ab initio*/IGLO methods. The calculated results were compared with the experimentally observed data. The role of these ions in the polymerization of siloxanes is also discussed.

Experimental Section

All NMR spectra were recorded on a Varian Unity-300 NMR spectrometer and the chemical shifts (^{1}H, ^{13}C, and ^{29}Si) referenced to tetramethylsilane. Gel permeation chromatography (GPC) of polysiloxanes was performed on a Waters system with toluene as eluent and the molecular weight was calibrated with a polysiloxane standard.

Trityl tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (Ph_3C^+**TFPB**) and trityl tetrakis(pentafluorophenyl)borate (Ph_3C^+ **TPFPB**) were prepared according to modified literature methods.[8,9] All other chemicals were purchased from Aldrich Chemical Co. Dichloromethane was distilled over calcium hydride before use.

Preparation of Silyloxonium Ions and Their NMR Studies. One hundred milligrams of the corresponding trityl salt and 0.5 mmol of siloxane were dissolved in 0.5 mL of dry CD_2Cl_2 in a 5-mm NMR tube under argon atmosphere. The tube was cooled to −78 °C still under argon and 0.2 mmol of trimethylsilane was introduced to the mixture under rapid vortex stirring. The tube was then sealed and maintained at −78 °C for several hours until the completion of the reaction. The NMR spectra of the samples were recorded at −70 °C.

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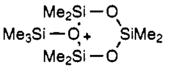
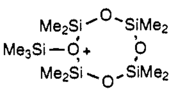
Table 1. NMR Chemical Shifts of Some Silyloxonium Ions and Their Precursors

compounds		^{29}Si, ppm exp	^{29}Si, ppm calcd	^1H, ppm	^{13}C, ppm exp	^{13}C, ppm calcd	ref
$(Me_3Si)_3O^+$	**3**	51.1	51.9	0.71	4.33	4.23	this work
$(Me_3Si)_2O$		7.0	5.1	0.10	1.38	2.00	this work
	**5**	50.2 10.0 −9.6					this work
	**6**	51.5 9.7 −7.9		0.70 0.52 0.32	3.58 0.33 −2.74		this work
$Me_3SiO^+Et_2$	**1**	66.9	69.9	0.61[a]	−1.1[a]	−0.5[a]	5a
$(Me_3Si)_2O^+Et$	**2**	59.0	59.3			1.13[a]	5a

[a] $(CH_3)_3Si$.

Polymerization of the Siloxanes. The procedure for the preparation of the silyloxonium ion was similar to that described. The mole ratio of siloxanes to trityl-**TPFPB** was 250 (for cyclosiloxanes) and 50 (for hexamethyldisiloxane, **HMSO**). Trimethylsilane was introduced into the mixture at 0 °C. After 2 h at 0 °C, a small portion of the reaction mixture was transferred to a NMR tube to determine the extent of polymerization. The reaction mixture was warmed to room temperature and maintained under stirring for 20 h to complete polymerization before quenching with methanol. The polymers were extracted with pentane, washed with methanol, and dried.

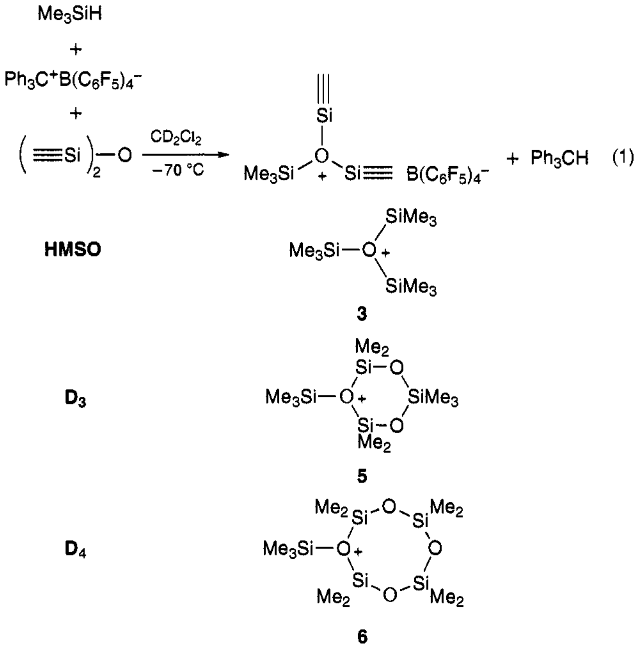
Calculational Methods. *Ab initio* calculations were carried out by using the GAUSSIAN-92[10] package of programs. Restricted Hartree–Fock calculations were performed throughout. Optimized geometries were obtained at the HF/6-31G* level. Single-point calculations using HF/6-31G* geometries were carried out at the MP2/6-31G* level and are denoted by MP2/6-31G*//HF/6-31G*. Vibrational frequencies at the HF/3-21G//HF/3-21G level were used to characterize stationary points as minima and to evaluate zero-point vibrational energies (ZPE) which are scaled by a factor of 0.89.[11]

IGLO calculations were performed according to the reported method[12] at the IGLO II′ level using HF/6-31G* optimized geometries. Huzinaga[13] Gaussian lobes were used as follows. Basis II′: Si, 11s 7p 2d contracted to [51111111, 211111, 11], d exponent 1.4 and 0.35; C and O, 9s 5p 1d contracted to [51111, 2111, 1], d exponent 1.0; H, 3s contracted to [21].

Results and Discussion

Long-Lived Trisilyloxonium Ions. Initially, we examined the reaction of trimethylsilane with the trityl-**TFPB** salt, in the presence of 10 equiv of **HMSO**. Experiments were carried out at −78 °C in dichloromethane-d_2 under argon. ^{29}Si NMR spectra of the reaction mixture were recorded at −70 °C, −60 °C, −20 °C and room temperature, respectively. Only the signals associated with the corresponding trimethylfluorosilane and disiloxane were observed. No tris(trimethylsilyl)oxonium ion **3** was detected. When triethylsilane was used in the above experiments in combination with **HMSO**, a small amount of trimethyltriethyldisiloxane was detected indicating the intermediacy of mixed trisilyloxonium ion, although it was too unstable to be observed. On the other hand, it was reported by Kira, Sakurai, et al. that in the presence of diethyl ether, the reaction of trimethylsilane with trityl-**TFPB** yielded diethyl(trimethylsilyl)oxonium ion **1**[5a] observable even at −30 °C. It is clear that trisilyloxonium ions such as **3** are much less stable than silyoxonium ion **1**. The unstable trisilyloxonium ions abstract fluoride anion from **TFPB** to give fluorosilanes and disiloxanes.

When trityl-**TPFPB** salt, in which fluorine atoms on the phenyl rings are less nucleophilic, was used instead of trityl-**TFPB** to react with trimethysilane in the presence of **HMSO** (3–5 equiv), ion **3** was formed, as evidenced by ^{29}Si, ^1H, and ^{13}C NMR spectroscopy at −70 °C (eq 1).



(1)

The ^{29}Si resonance for **3** ($\delta^{29}Si$ 51) is deshielded compared to **HMSO** (deshielded by 43.4 ppm), but it is more shielded than those in silyloxonium ions **1** and **2** (see Table 1). Ion **3** generated under these conditions is quite stable at −70 °C. No significant changes were observed in its NMR spectra after standing for several hours at this temperature. Upon raising the temperature, the ^{29}Si signals of **3** and excess **HMSO** disappeared. An intense peak of tetramethylsilane (**TMS**) appeared, accompanied by that of trimethylchlorosilane. The yield of **TMS** was determined by ^1H NMR to be 41% relative to added **HMSO**. GC/MS analysis of the reaction mixture revealed $Me_3SiO-(Me_2SiO)_n-SiMe_3$ ($n = 1-3$) and cyclosiloxanes $\overline{-(Me_2SiO)_n-}$ ($n = 3-6$) as major silicon-containing products apart from **TMS**. The reaction was performed independently with **HMSO**/trityl-**TPFPB** = 50/1 in CH_2Cl_2, initially at 0 °C and then at room temperature. After 24 h, a series of oligomers, mainly in the form of $Me_3SiO-(Me_2SiO)_n-SiMe_3$ and $\overline{-(Me_2SiO)_n-}$, were obtained in 38% overall yield.

To explain the siloxane oligomerization, two mechanisms can be considered (Scheme 1). Mechanism 1 involves nucleophilic attack of **HMSO** on silyloxonium ion **A** to form pentacoordinate silicon species **B**, followed by 1,3-methyl transfer and elimination of **TMS** to give **C**. Propagation is achieved by repeating steps 1 and 2 leading to **D**, which may undergo intramolecular ring closure to produce cyclosiloxanes (path a) or release a silicenium ion to **HMSO**, giving linear oligomers (path b). Abstraction of Cl^- from the solvent by silyloxonium ions yields Me_3SiCl whose formation inhibits the oligomerization. Alternatively, **C** can be formed through the intermediacy of **B′** (Mechanism 2). Mechanism 1 is more likely to account for the reaction, because pentacoordinated silicon species are well-

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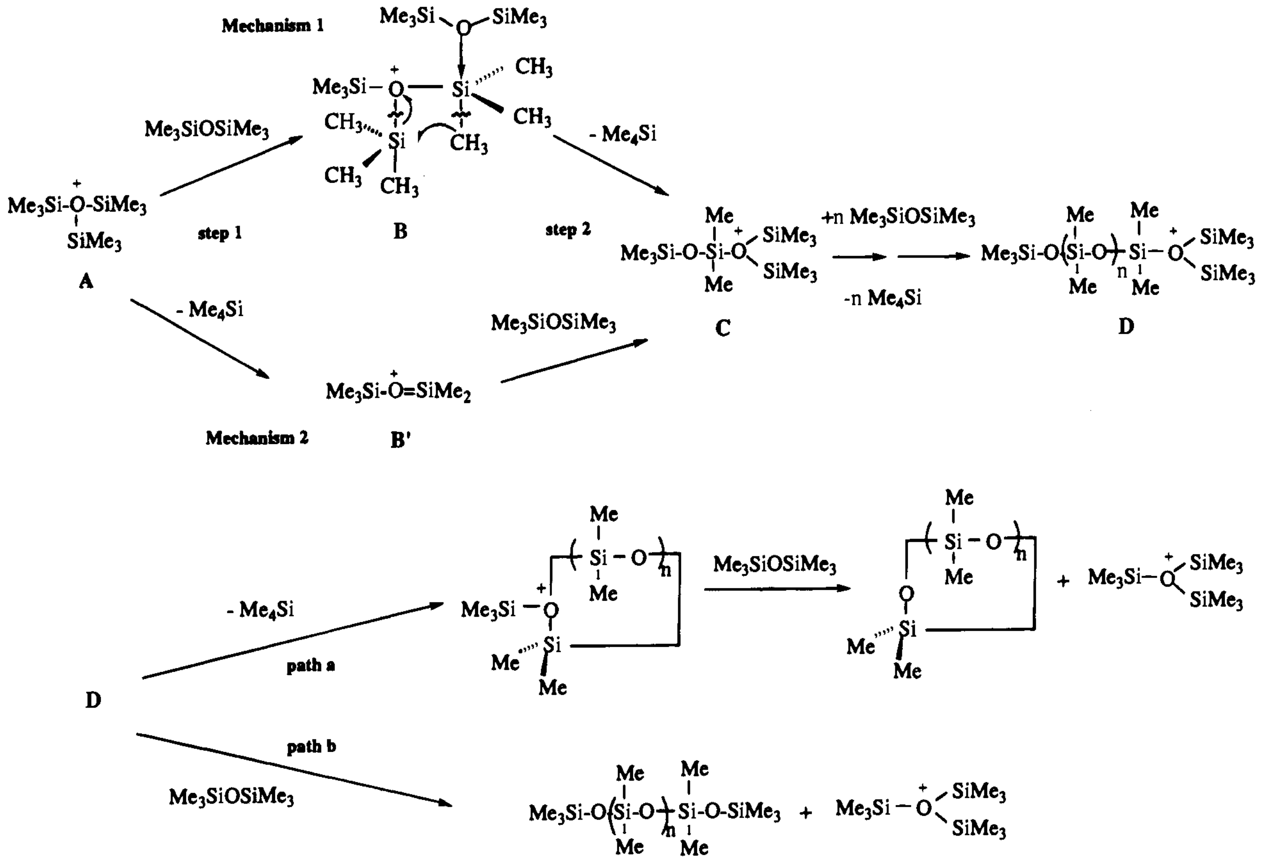
Scheme 1



known to be involved as intermediates in nucleophilic substitution on silicon,[14] particularly with cleavage of the silicon–carbon bond[15] and a similar 1,3-methyl transfer was observed in the solvolysis of chlorotris(trimethylsilyl)methyldimethylsilane.[16]

In another independent experiment, HMSO was added at −78 °C to a toluene-d_8 solution of trimethylsilyltoluenium ion,[5f,g] which was prepared by reacting trimethylsilane with trityl-**TPFPB** in toluene-d_8. The ^{29}Si NMR at −40 °C showed one peak at δ ^{29}Si 57, shifted upfield from that of the trimethylsilyltoluenium ion observed at δ ^{29}Si 74. The chemical shift is deshelded 6 ppm from that observed for ion **3** in CD_2Cl_2 solution (δ ^{29}Si 51). The peak at δ ^{29}Si 57 ppm thus may be due to an average signal for the mixture of trimethylsilyltoluenium ion and ion **3** undergoing rapid exchange on the NMR time scale. The survival of the trimethylsilyltoluenium ion in the equilibrium mixture with ion **3** confirms once again that toluene is highly nucleophilic toward the silyl cation.

The main objective of our studies on trisilyloxonium ions is to better understand the cationic ring-opening polymerization of cyclosiloxanes. Consequently, we have also studied silyloxonium ions generated from cyclosiloxanes. Under similar conditions as described (eq 1), trimethylsilane was added to a dichloromethane-d_2 solution of the trityl salt of **TPFPB** in the presence of hexamethylcyclotrisiloxane (**D**$_3$) or octamethylcyclotetrasiloxane (**D**$_4$). ^{29}Si NMR spectra of the resulting solution at −70 °C demonstrated the formation of the corresponding trisilyloxonium ions (**5** and **6**) (Table 1). Raising the temperature resulted in polymerization of the excess cyclosiloxanes.

Table 2. Polymerization of **D**$_3$ and **D**$_4$ in CH_2Cl_2 (2 mol/L), I/M = 0.4%

			final product ratio[b]			
monomer	initiator	rate[a] (%)	linear	cyclic	10^4M_w[c]	10^4M_n[c]
D$_3$	**A**	80	85	15	7.3	6.7
	B	95	80	20	15.1	12.5
D$_4$	**A**	43	>95	<5	9.4	8.7
	B	28	93	7	26.0	22.1

[a] Monomer consumption determined by ^{1}H NMR after 2 h at 0 °C. [b] Determined by GPC on final isolated polymers (quenching with MeOH after 24 h at ambient temperature). [c] Linear polymers.

Trisilyloxonium-Initiated Polymerization. Polymerization of **D**$_3$ and **D**$_4$ was carried out in dichloromethane, using trimethylsilane with trityl-**TPFPB** as initiators (I/M = 0.4%) (eq 2). Both reactions were monitored by ^{1}H NMR. After 2 h

$$\overline{-(\mathrm{Me_2SiO})_n-}\ \xrightarrow[\mathrm{CH_2Cl_2,\ 0\ ^\circ C-r.t.}]{\text{initiators}}\ -(\mathrm{Me_2SiO})_x- + \overline{-(\mathrm{Me_2SiO})_y-} \qquad (2)$$

D3 ($n = 3$)
D4 (n=4)

initiators: **A** $\mathrm{Me_3SiH/Ph_3C^+}$**TPFPB**$^-$
B CF_3SO_3H

at 0 °C, 80% **D3** and 43% **D4** were polymerized. The polymerization was complete after the mixture was left standing over night and polysiloxanes were isolated in more than 90% yield (Table 2). GPC of obtained polysiloxanes showed M_w quite close to that expected from the I/M ratio and very low polydispersity (M_w/M_n < 1.5). The mechanism for this ring-

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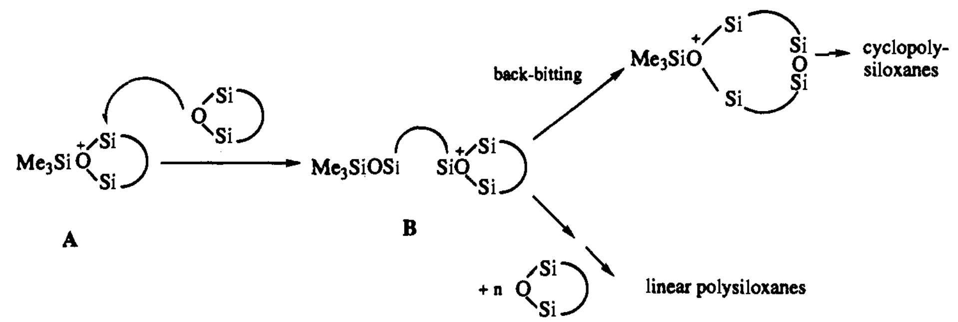
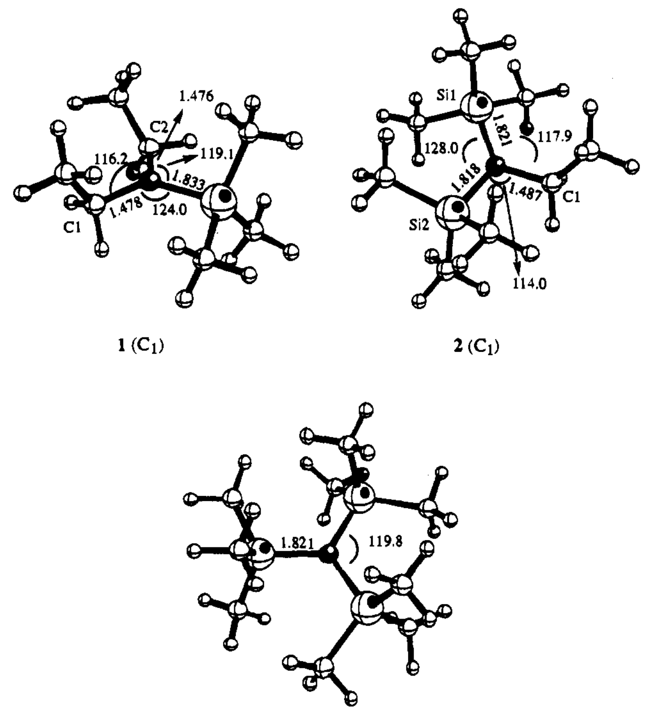
Scheme 2





1 (C_1) 2 (C_1)

3 (C_3)

Figure 1. HF/6-31G* optimized geometries of ions **1**–**3**.

opening polymerization is suggested to involve attack of cyclosiloxane on *in-situ* formed ion A accompanied by ring-opening to give species **B**. Repeat of this step leads to polysiloxanes (Scheme 2).

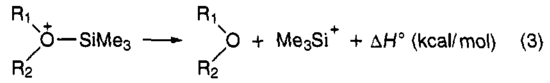
For comparison, triflic acid catalyzed polymerizations were also carried out under similar conditions. The results are given in Table 2. As the reaction rates are comparable, trisilyloxonium ions are quite probably involved in the acid-initiated polymerization. However, more detailed studies are needed to fully understand the role of trisilyloxonium ions in such polymerization reactions.

***Ab Initio*/IGLO Studies.** To investigate the effect of the silyl group on the nature and stability of silyloxonium ions, we carried out *ab initio* calculations on trimethylsilyldiethyl oxonium ion **1**, bis(trimethylsilyl)ethyl oxonium ion **2**, and tris(trimethylsilyl) oxonium ion **3**. Ions **1** and **2** had been observed previously by Kira, Sakurai, et al. by NMR spectroscopy in the reaction mixture at low temperature.

The central oxygen atom in each of the calculated ions **1**, **2**, and **3** is found almost in the plane of three adjacent atoms (Figure 1). The C–O bonds of ions **1** and **2** have similar lengths (1.48 Å) as those calculated for trialkyloxonium ions (1.47 Å).[17] The Si–O bond lengths of the ions range from 1.818 to 1.833 Å. They are some 0.2 Å longer than that of hexamethyldisiloxane (**HMSO**) (1.63 Å).[18a] Reed, Bau, et al. found in an X-ray structure study of a protonated silanol the Si–O bond length of 1.78 Å and suggested that this lengthening of the bond is an indication of predominance of silyl cation character over onium ion character.[6] We believe, however, that the lengthening of the Si–O bond only reflects the decrease in participation of the p-electrons of oxygen in the Si–O bond as the oxygen is positively charged.[18] In addition Si–O bonds in most siloxanes, silyl ether, or silanols are much shorter than expected from the Schomaker–Stevenson rule, explained by (p–d) π back-bonding or a higher than estimated electronegativity difference.[18] Interestingly the Si–O bond lengths in silyloxonium ions are much closer to that expected from the Schomaker–Stevenson rule (1.77 Å).

The C_1OC_2 angle (116°) of ion **1** is slightly higher than that in dialkyl ether (i.e. 113° for dimethyl ether[17]). On the other hand, the C_1OSi or C_2OSi angle of **1** is close to that in silyl ethers, thus the ion is not very strained. In contrast, the SiOSi angle of ion **3** is forced to be around 120° (compared to 148° in **HMSO**[18a]) and the resulting high strain of the ion may be one of the reasons for its instability.

To examine this suggestion, the dissociation energies of the silyloxonium ions **1**–**3** (eq 3) were calculated at the MP2/6-



$$R_1R_2\overset{+}{O}{-}SiMe_3 \longrightarrow R_1R_2O + Me_3Si^+ + \Delta H^\circ\ (\text{kcal/mol}) \quad (3)$$

1: $R_1 = R_2 = Et$	56.1
2: $R_1 = Et$, $R_2 = SiMe_3$	57.4
3: $R_1 = R_2 = SiMe_3$	49.2

31G*//HF/6-31G* + ZPE (HF/3-21G//HF/3-21G) level. Ion **3** needs 7–8 kcal/mol less energy for dissociation into disiloxane and trimethylsilyl cation compared to the dissociation of ions **1** and **2** into respective ethers and the trimethylsilyl cation. The results indicate that the formation of very stable and less bent disiloxane may be the plausible driving force for the decomposition of ion **3**.

The ^{13}C and ^{29}Si NMR chemical shifts of ions **1**–**3** were calculated at the IGLO II' level using HF/6-31G* geometries. The calculated ^{29}Si and ^{13}C NMR chemical shifts of the ions **1**, **2**, and **3** are in close agreement with the experimental data (Table 1), confirming the true oxonium ion nature of these species. Thus the calculated ^{29}Si NMR chemical shift of **3** is 51.9 ppm and it compares rather well with the experimental value of δ ^{29}Si 51.0. The calculated ^{13}C NMR chemical shift of 4.23 ppm also agrees well with the experimental value of 4.33 ppm. Similarly, the calculated ^{29}Si NMR chemical shifts of **1** and **2**

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are 69.9 and 59.3 ppm, respectively, and they agree well with the corresponding experimental values of 66.9 and 59.0 ppm. The calculated and experimental data also reveal that the increase in the number of silyl groups linked to oxygen atom results in more shielding of ^{29}Si NMR chemical shifts in the siloxonium ions. This indicates a better charge-sharing ability of the trimethylsilyl group compared to that of an ethyl group in the oxonium ions.[19] However, the observation of very limited changes of ^{29}Si NMR chemical shifts of these ions indicates their true oxonium ion nature.

In summary, we have been able to generate and characterize by means of NMR spectroscopy the first long-lived trisilyloxonium ions. Our studies on their behavior demonstrated that they are very reasonably electrophilic silicon species and can initiate polymerization of siloxanes. We have also carried out *ab initio*/IGLO studies on a series of silyloxonium ions and rationalized their relatively low stability. This work helps to better understand the mechanism of the cationic polymerization reactions of cyclosiloxanes and has potential for the preparation of polysiloxanes containing block or graft copolymers. Further studies are underway to demonstrate this potential.

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