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Experimental and Theoretical Characterization of FSi(OCH₃)₂(OCH₂)⁻: A Gas Phase Fluoride−Siloxirane Adduct

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Abstract: The structural characteristics and reactivity of the gas-phase FSi(OCH₃)₂(OCH₂)⁻ ion were investigated by a combination of *ab initio* calculations and FT-ICR techniques. The theoretical calculations for different possible structures reveal that carbanion and alkoxide ion type structures lead to ring closure upon geometry optimization to yield two different cyclic fluoride−siloxirane structures. The FSi(OCH₃)₂(*cyc*-OCH₂)⁻ ions containing the elusive siloxirane ring are estimated to be extremely stable with respect to F⁻ (69 kcal mol⁻¹) dissociation in agreement with earlier calculations on simpler systems. Experimentally, this ion is formed as a minor product (7%) in the gas-phase ion/molecule reaction of F⁻ with Si(OMe)₄ and is observed to undergo readily fluoride transfer to the parent neutral. This strongly suggests an ion with a structure corresponding to a fluoride adduct of a siloxirane species. Reaction of FSi(OCH₃)₂(OCH₂)⁻ with BF₃, hexafluorobenzene, and gas-phase acids more acidic than ethanol further suggests that this ion is capable of reacting as an alkoxide type nucleophile or base. This latter behavior has been associated with the possibility of ring opening of the siloxirane in the collision complex that mediates this ion/molecule reaction.

Siloxiranes (**I**) are among the simplest cyclic organosilane systems which, unlike their well-known carbon analogs, have eluded systematic chemical and structural characterization.

(I)
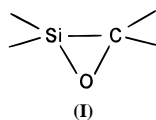
Results from recent theoretical and experimental studies have contributed to the revival of the discussion regarding the potential stability of these three-membered moieties. For example, the thermal decomposition of gaseous Si(OMe)₄ has been claimed to proceed initially by elimination of MeOH and (MeO)₂Si(*cyc*-OCH₂).[1] While this latter product defied isolation in the high-temperature reaction, this fact was attributed to a rearrangement of the siloxirane species to MeOSi(O)OEt.

The idea that siloxiranes may rearrange to more stable forms finds support in molecular orbital calculations of model systems. The extensive set of *ab initio* calculations carried out for simple Si−O−H−C-containing molecules at the MP4(SDTQ)/6-31G**//HF/6-31G** level with empirical bond additivity parameter corrections is particularly useful in deriving conclusions about the thermochemistry of these compounds.[1,2] This theoretical approach has been shown to yield heats of formation in excellent agreement with the few experimentally known values for Si-containing compounds and provide a guideline for bond energies in these systems. Calculations for siloxiranes such as (HO)₂Si-(*cyc*-OCH₂) at this level do suggest that this species could be prone to undergo interconversion to more stable structures as claimed in ref 1.

The thermodynamic stability of three-membered cyclic silanes and of heterocyclopropanes in general is a subject of much interest because of the presumed role of strain energy on the enthalpy content.[3] High-quality *ab initio* calculations predict silacyclopropane to have a much higher strain energy than cyclopropane, while negligible differences are computed for higher cyclic organosilanes and cycloalkanes.[4] On the other hand, the successful spectroscopic identification of such exotic species as silacyclopropyne,[5] for which the strain energy is estimated to be in the range of 100 kcal mol⁻¹, suggests that this effect alone may not be the only source of the apparent difficulty in isolating siloxiranes.

Siloxirane type intermediates have long been recognized to mediate molecular rearrangements leading to silicon migration from carbon to oxygen,[6] and *vice versa*.[7]

The mechanism involving ring closure for the transient anionic intermediate is expected to be favored by the ability of Si to form hypervalent species of the kind typically associated with

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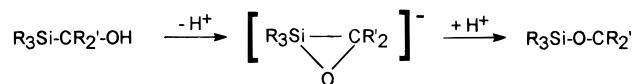[†] Present address: Institute of Chemistry, University of Campinas, Campinas, SP, Brazil.

[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1997.

(1) Chu, J. C. S.; Soller, R.; Lin, M. C.; Melius, C. F. *J. Phys. Chem.* **1995,** *99,* 663.

(2) (a) Ho, P.; Melius, C. F. *J. Phys. Chem.* **1995,** *99,* 2166. (b) For the procedure used to develop empirical bond additivity corrections, see: Allendorf, M. D.; Melius, C. F. *J. Phys. Chem.* **1992,** *96,* 428.

(3) (a) For a qualitative discussion on heterocyclopropanes, see: Driess, M.; Grützmacher, H. *Angew. Chem., Int. Ed. Engl.* **1996,** *35,* 828. (b) For thermochemical aspects of strain energy, see: Benson, S. W. *Thermochemical Kinetics*; 2nd ed.; John Wiley & Sons, Inc.: New York, 1976; pp 60−63.

(4) Boatz, J. A.; Gordon, M. S.; Hildebrandt, R. L. *J. Am. Chem. Soc.* **1988,** *110,* 352.

(5) (a) Maier, G.; Reisenauer, H. P.; Pacl, H. *Angew. Chem., Int. Ed. Engl.* **1994,** *33,* 1248. (b) Maier, G.; Pacl, H.; Reisenauer, H. P.; Meudt, A.; Janoschek, R. *J. Am. Chem. Soc.* **1995,** *117,* 12712. (c) For a theoretical description, see: Sherril, C. D.; Brandow, C. G.; Allen, W. D.; Schaefer, J. F., III *J. Am. Chem. Soc.* **1996,** *118,* 7158.
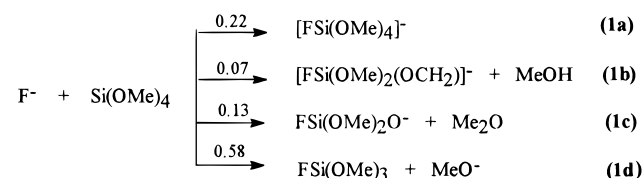
(6) For reviews on these rearrangements and pertinent literature, see: (a) Brook, A. G. *Acc. Chem. Res.* **1974,** *7,* 77. (b) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths: London, 1981; Chapter 5.

(7) West, R.; Lowe, R.; Stewart, H. F.; Wright, A. *J. Am. Chem. Soc.* **1971,** *93,* 282.

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nucleophilic substitution at a Si center.[8] Theoretical calculations confirm the notion that neutral siloxiranes should be strongly stabilized by addition of an anion like fluoride to the silicon center.[9] This is actually a common feature of cyclic silanes for which attachment to F⁻ is proposed to lead to significant stabilization.[10] Gas-phase experimental measurements have indeed corroborated this prediction, and a fluoride affinity of 40 ± 5 kcal mol⁻¹ has been established for 1,1-dimethylsilacyclobutane.[11]

The investigation of intrinsic properties of covalently bound ionic intermediates and of molecules stabilized by binding to an anion has been one of the most important domains of gas-phase ion chemistry. For simple silicon-containing species, gas-phase studies have already provided a unique view of the reactivity of simple organosilanes and a wealth of important thermochemical data.[12] Thus, it is conceivable that ionic siloxiranes intermediates, such as those responsible for Brook type rearrangements,[6] may be identified in the gas phase by a judicious choice of experimental conditions. It is already known that three-, four-, and five-membered species are likely to mediate the reactions of silyl anions, and α-silyl carbanions, with CO_2 and N_2O in the gas phase.[13]

The gas-phase reaction of F⁻ with $Si(OMe)_4$ was the subject of an early study in a flowing afterglow tube and shown to proceed exclusively by addition of F⁻ with the subsequent formation of a pentacoordinated adduct, $FSi(OMe)_4^-$.[14] This same reaction studied in our laboratories at lower pressures and under ion cyclotron resonance (ICR) conditions reveals a much richer chemistry which presumably arises from unimolecular elimination processes of energy rich pentacoordinated adduct ions.[15] The reported product distribution for this case is shown in reaction **1**. The rather unique reaction leading to the

$$F^- \ + \ Si(OMe)_4 \begin{array}{l} \xrightarrow{\ 0.22\ } [FSi(OMe)_4]^- \hspace{2.5cm} \textbf{(1a)} \\ \xrightarrow{\ 0.07\ } [FSi(OMe)_2(OCH_2)]^- \ + \ MeOH \hspace{0.5cm} \textbf{(1b)} \\ \xrightarrow{\ 0.13\ } FSi(OMe)_2O^- \ + \ Me_2O \hspace{1.3cm} \textbf{(1c)} \\ \xrightarrow{\ 0.58\ } FSi(OMe)_3 \ + \ MeO^- \hspace{1.5cm} \textbf{(1d)} \end{array}$$

$FSi(OMe)_2(OCH_2)^-$ ion (of unknown structure), and its possible connection with siloxirane chemistry, prompted us to explore the reactivity and structure of this ion by a combination of experimental and theoretical techniques. It should be emphasized that this behavior is very specific of the reactions of F⁻ since products similar to that of reaction 1b are not observed in reactions with much stronger gas-phase bases.[15,16]

This paper initially describes the results of *ab initio* calculations carried out for the $FSi(OMe)_2(OCH_2)^-$ ion. These calculations predict the cyclic siloxirane–fluoride structure to be the most stable form. In the second part, the experimental

investigation of gas-phase ion/molecule reactions of the $FSi(OMe)_2(OCH_2)^-$ ion unveils an unusually rich chemistry.

Computational Procedure

The first approach toward the structural elucidation of the product ion of reaction 1b was to consider possible isomeric forms of $FSi(OMe)_2(OCH_2)^-$ which would be consistent with mechanistic considerations of reaction 1.[15] Four different species, **II–V**, were considered as likely candidates to arise from $FSi(OMe)_4^-$ by elimination of MeOH. These proposed structures and the outcome of the

(II)   (III)   (IV)   (V)
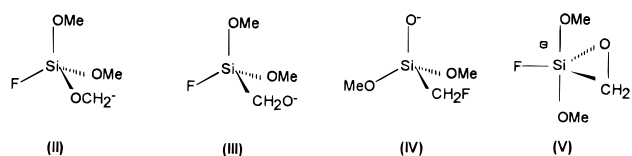
calculations played an important role in the design of ion/molecule reactions which could provide experimental insight into the structure of the anion and a test of the theoretical predictions.

High-level *ab initio* calculations for Si species are usually limited to small systems which can be handled by G2 methodology[17] or extensive correlation-consistent polarized valence basis sets.[18] For more complex species, one approach has been to mimic these molecules by model systems with some of the substituents replaced by H atoms. Another approach has been to use more modest basis sets which allow calculations to be carried out to the MP4 level but for which empirical corrections are essential to obtain the correct thermochemistry.[1,2] For our case, it was deemed more appropriate (a) to consider species which exhibited different atom connectivities but which could correspond to the actual experimentally observed ion and (b) to develop an appropriate basis set for the anionic species at hand.

Ab initio calculations for ions **II–V** and some of the related neutral systems were carried out using the GAMESS[19] suite of programs. All calculations were performed in the cluster of work stations located at the CENAPAD-SP computing facilities of the University of Campinas. The size of the systems represented by structures **II–V** precluded the possibility of using very large basis sets or extending the calculations to the highest levels of theory with our present computational facilities. Yet, the study of systems **II–V** can be carried out with the help of recent methods which are capable of generating good-quality basis sets for anionic systems while circumventing some of the computational limitations.[20]

The basic methodology used to obtain high-quality theoretical results for these systems was to adapt the double ζ valence set (DZV) of primitive basis functions[21] with the help of the generator coordinate method (GCM).[22] The GCM is a valuable tool in molecular orbital calculations since it actually introduces a quality test for the basis set used in a given atomic or molecular environment. In this method, monoelectronic functions, $\psi(1)$, are considered to be integral transforms of the type

$$\psi(1) = \int f(\alpha)\, \varphi(1,\alpha)\, d\alpha$$

where $f(\alpha)$ constitutes the so-called weight function, $\varphi(1,\alpha)$ represents the generator function of Gaussian type orbitals (GTO), and integration is performed over the space of the generator coordinate α, or exponent

(8) Corriu, R. Mechanisms of Nucleophilic Substitution at Silicon. In *Journal of Organometallic Chemistry Library 9, Organometallic Chemistry Reviews*; Seyferth, D., Ed.; Elsevier: Amsterdam, 1980; pp 357–373.

(9) Schlegel, H. B.; Skancke, P. N. *J. Am. Chem. Soc.* **1993**, *115*, 10916.

(10) Skancke, P. N. *J. Phys. Chem.* **1994**, *98*, 3154.

(11) Sullivan, S. A.; DePuy, C. H.; Damrauer, R. *J. Am. Chem. Soc.* **1981**, *103*, 480.

(12) For comprehensive reviews, see: (a) Schwarz, H. In *The Chemistry of Organic Silicon Compounds, Part 1;* Patai, S., Rappoport, Z., Eds.; John Wiley and Sons: Chichester, 1989; pp 445–510. (b) Damrauer, R.; Hankin, J. A. *Chem. Rev.* **1995**, *95*, 1137.

(13) DePuy, C. H.; Damrauer, R.; Bowie, J. H.; Sheldon, J. C. *Acc. Chem. Res.* **1987**, *20*, 127.

(14) DePuy, C. H.; Bierbaum, V. M.; Flippin, L. A.; Grabowski, J. J.; King, G. K.; Schmitt; R. J.; Sullivan, S. A. *J. Am. Chem. Soc.* **1980**, *102*, 5012.

(15) Silva, M. L. P.; Riveros, J. M. *J. Mass Spectrom.* **1995**, *30*, 733.

(16) (a) Damrauer, R.; Krempp, M. *Organometallics* **1990**, *9*, 999. (b) Krempp, M.; Damrauer, R. *Organometallics* **1995**, *14*, 170.

(17) Schlegel, H. B.; Darling, C. L. *J. Phys. Chem.* **1993**, *97*, 8207.

(18) Nicholas, J. B.; Feyereisen, M. *J. Chem. Phys.* **1995**, *103*, 8031.

(19) GAMESS: Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. J.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.

(20) (a) Morgon, N. H.; Custodio, R.; Riveros, J. M. *Chem. Phys. Lett.* **1995**, *235*, 436. (b) Morgon, N. H.; Linnert, H. V.; Riveros, J. M. *J. Phys. Chem.* **1995**, *99*, 11667. (c) Morgon, N. H. *J. Phys. Chem.* **1995**, *99*, 17832.

(21) Dunning, T. H., Jr.; Hay, P. J. In *Methods of Electronic Structure Theory*; Shaefer, H. F., III, Ed., Plenum Press: New York, 1977; Chapter 1, pp 1–27.

(22) (a) Custodio, R.; Goddard, J. D.; Giordan, M.; Morgon, N. H. *Can. J. Chem.* **1992**, *70*, 580. (b) Custodio, R.; Giordan, M.; Morgon, N. H.; Goddard, J. D. *Int. J. Quantum Chem.* **1992**, *42*, 411.

of the GTOs. The existence of weight functions (amounting to the graphical representation of the linear combination of atomic orbital functions) is an essential condition for using the GCM. An explicit analysis of the behavior of the weight functions by the GCM is then used as a criterion for adjusting the set of atomic functions necessary to obtain a proper description of the electronic cloud.

The actual calculations required the internal electrons of all atoms other than H to be represented by an effective core potential (ECP). Under these conditions, the combination of the generator coordinate method with an effective core potential is used to define the cutoff point for the pseudopotential. For the valence electrons, the GCM actually yields the choice of primitive diffuse functions to be added to the original basis set for a correct description of anions.

The internal electrons of Si were represented by the effective core potential of Stevens, Basch, and Krauss (SBK),[23] while the valence region was corrected by addition of diffuse functions following the procedure described before[20] and outlined above. The resulting basis set for Si was then ECP+7s5p1d (effective core potential for the inner electrons and a 7s, 5p, and 1d primitive basis function set for the outer electrons). The weight functions of the DZV primitive 1s, 2s, and 2p atomic orbitals of Si, including all of the electrons (ae), display a normal asymptotic behavior with decreasing values of α as shown and need no further correction. However, this condition is not obeyed for small values of α by the valence orbitals 3s and 3p. Since anionic systems require corrections to account for the diffuse nature of the electronic cloud, the GCM in conjunction with the effective core potential is used to define the cutoff point at which the internal electrons are represented by a pseudopotential. Addition of extra diffuse functions then leads to a correct description of the valence orbitals, and the result of this procedure was then verified in atomic and molecular environments.

A similar approach was used for other atoms which may bear anionic character in structures **II**−**V**. Thus, the descriptions of the outer electrons were corrected with the addition of diffuse functions for C, in the CH_2^- moiety of **II**, and O and F in $FSi(OMe)_2CH_2O^-$ (**III**), $(CH_2F)Si(OMe)_2O^-$ (**IV**), and $[FSi(OMe)_2(cyc\text{-}CH_2O)]^-$ (**V**) and represented by an ECP+8s7p1d basis set. For the other atoms, the original double ζ basis functions augmented with polarization functions (p on H and d on other atoms) were used and are here identified as the DZV** basis set.

Computational Results

The generator coordinate method is known to be capable of generating basis sets of extremely good quality. For simple systems, calculations carried out to high levels of theory (in terms of corrections for correlation energy) and with considerably more refined basis sets by the GCM than those used in the present case yield gas-phase acidities comparable to or better[24] than those obtained with the G2 method which is often used as the benchmark in this field.[25]

The quality of the basis set developed for this work was first tested on simple Si-containing systems relevant to the problem at hand. For example, the proton affinity of SiH_3^- is estimated to be 377 kcal mol^{-1} with our basis sets in calculations carried out for geometries optimized at the Hartree−Fock level, energies calculated at the MP2 level, and correcting for zero-point vibrational energies. This calculation compares well with values of 378 kcal mol^{-1}, obtained using MP2(FULL)//HF/6-31++G-(d,p), and 375 kcal mol^{-1} at the MP4SDTQ//HF/6-311++G-(2df,p) level.[26] In all cases, the calculations are above the experimental $\Delta H°_{acid}(SiH_4) = 372.8 \pm 2$ kcal mol^{-1}.[27]

The fluoride affinity (FA) of silacyclopropane, $c\text{-}H_2Si(CH_2)_2$, was also calculated with the present basis set according to the formal definition,

$$FA = E[c\text{-}H_2Si(CH_2)_2] + E(F^-) - E[c\text{-}H_2FSi(CH_2)_2]^-$$

A value of 42.6 kcal mol^{-1} was obtained after correction for zero-point vibrational energies with vibrational frequencies scaled by 0.89. Our result is comparable to values of 43.8 kcal mol^{-1} obtained at the MP2//HF/6-31++G* level and 44.8 kcal mol^{-1} obtained at the MP2//HF/MC-311++G* level.[10] Likewise, the calculated Si−C, Si−H, C−C, and C−H bond distances for $c\text{-}H_2Si(CH_2)_2$ and $[c\text{-}H_2FSi(CH_2)_2]^-$ differ on the average by 0.03 Å with those obtained for the calculations at the MP2//HF/6-31++G* level and by 0.02 Å with those obtained at the MP2//HF/MC-311++G* level of ref 10. Furthermore, our calculated H−C−Si, H−C−C, H−Si−C and F−Si−C angles were found to differ on the average by 0.2° and 0.3° with the two levels of calculation previously discussed.[10]

Similar agreement was found between calculations using our basis set and those previously reported for the case of SiF_3^-,[26] and SiOH.[28]

The good agreement with experiment and with previous *ab initio* calculations on molecular Si-containing species illustrates the fact that the basis sets developed here for larger Si environments fare well when adapted to much simpler molecular species.

The initial search of the best geometries for species **II**−**V** had to contend with the likelihood of several local minima due to conformations arising from rotation of the groups. For species **V**, near-axial or near-equatorial arrangements could also be envisioned as a result of distorted trigonal bipyramid geometries. For simple hypervalent Si species like SiH_4X^- and SiH_3XY^-, calculations reveal that the preferred conformation for F and OMe groups cannot be established *a priori* in multiply substituted siliconates.[29] These considerations led us to carry out an initial analysis with the most probable structures chosen by using the genetic algorithm of SPARTAN.[30] These structures were then optimized at the *ab initio* level.

The initial structures assumed for **II** and **III** were found to lead to ring closure upon geometry optimization but to yield different isomeric structures of **V**. Thus, at this level of calculation **II** and **III** are not predicted to be local minima in the energy surface. The carbanion structure **II** yields a siloxirane-containing siliconate ion which is identified in Figure 1 as structure **V(II)**. By comparison, the alkoxide structure **III** results in the siloxirane-containing siliconate anion labeled **V-(III)**. Given the complexity of the systems under consideration, no attempt was made to find the transition state connecting structures **V(II)** and **V(III)**. Figure 1 shows the optimized geometric parameters obtained for all ionic species, while Figure 2 shows the optimized geometries obtained for different neutral systems used in comparing thermochemical data. These include $Si(OMe)_4$ (usually known as TMOS), $FSi(OMe)_3$, $FSi(OMe)_2$-$(cyc\text{-}CH_2O)$, $(MeO)_2Si(cyc\text{-}CH_2O)$, and $FSi(OMe)_2(CH_2OH)$.

The fact that structures **II** and **III** could not be established as local minima is not altogether surprising. The earlier calculations[9] for the much simpler $FH_2SiCH_2O^-$ and $FH_2SiOCH_2^-$ systems established the alkoxide and carbanion structures to be shallow minima (14.5 and 23.7 kcal mol^{-1}, respectively, above the corresponding siloxirane anions) displaying very low energy barriers for ring closure (2.0 and 1.9 kcal

(23) Stevens, W. J.; Basch, H.; Krauss, M. *J. Chem. Phys.* **1984**, *81*, 6086.

(24) Morgon, N. H. Manuscript in preparation.

(25) Smith, B. J.; Radom, L. J. *J. Phys. Chem.* **1991**, *95*, 10549.

(26) Rodrigues, C. F.; Hopkinson, A. C. *Can. J. Chem.* **1992**, *70*, 2234.

(27) Wetzel, D. M.; Salomon, K. E.; Berger, S.; Brauman, J. I. *J. Am. Chem. Soc.* **1989**, *111*, 3835.

(28) Allendorf, M. K.; Melius, C. F.; Ho, P.; Zachariah, M. R. *J. Phys. Chem.* **1995**, *99*, 15285.

(29) Gordon, M. S.; Davis, L. P.; Burggraff, L. W. In *Advances in Gas Phase Ion Chemistry*; Adams, N. G., Babcock, L. M., Eds.; JAI Press Inc.: Greenwich, CT, 1992; pp 203−223.

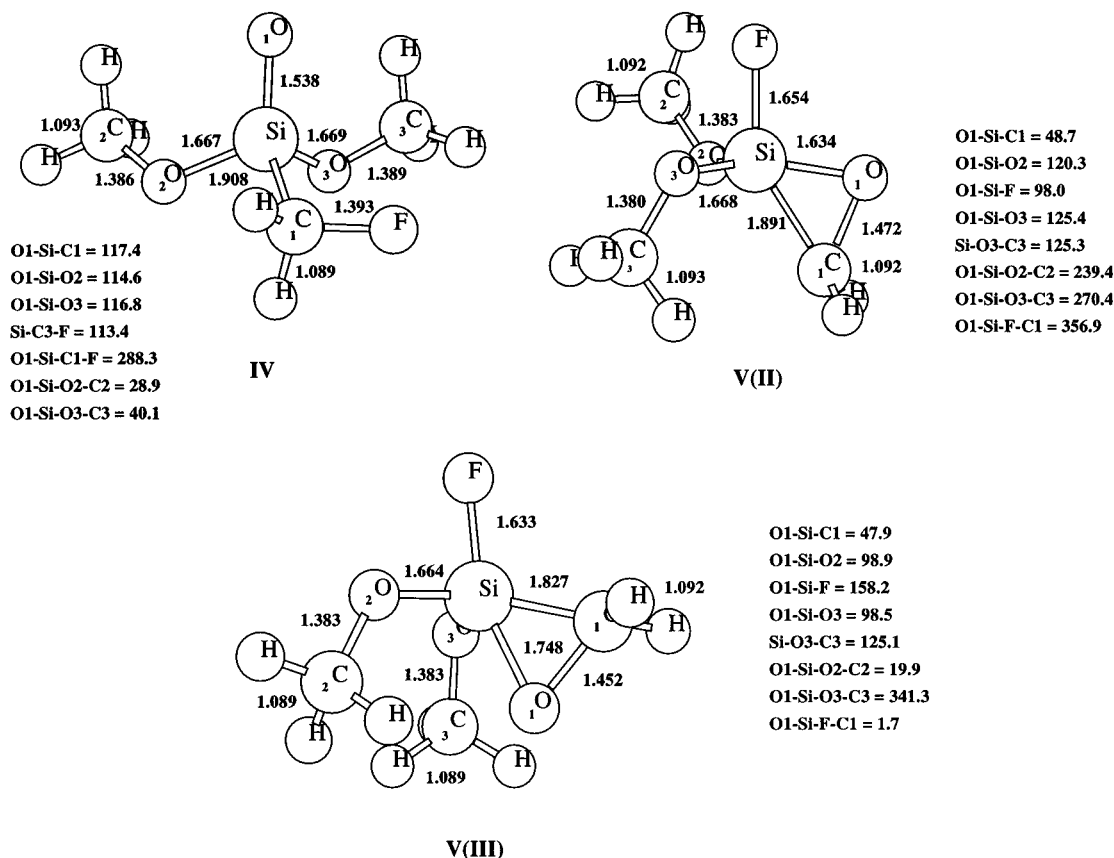(30) SPARTAN version 4.0, Wavefunction, Inc., 18401 Von Karman Ave., #370, Irvine, CA 92715.

O1-Si-C1 = 117.4
O1-Si-O2 = 114.6
O1-Si-O3 = 116.8
Si-C3-F = 113.4
O1-Si-C1-F = 288.3
O1-Si-O2-C2 = 28.9
O1-Si-O3-C3 = 40.1

IV

O1-Si-C1 = 48.7
O1-Si-O2 = 120.3
O1-Si-F = 98.0
O1-Si-O3 = 125.4
Si-O3-C3 = 125.3
O1-Si-O2-C2 = 239.4
O1-Si-O3-C3 = 270.4
O1-Si-F-C1 = 356.9

V(II)

O1-Si-C1 = 47.9
O1-Si-O2 = 98.9
O1-Si-F = 158.2
O1-Si-O3 = 98.5
Si-O3-C3 = 125.1
O1-Si-O2-C2 = 19.9
O1-Si-O3-C3 = 341.3
O1-Si-F-C1 = 1.7

V(III)

Figure 1. Optimized geometries for (MeO)₂Si(CH₂F)O⁻ (**IV**) and for the two isomeric forms of FSi(OMe)₂(*cyc*-CH₂O)⁻ , **V(II)** and **V(III)**.

mol⁻¹, respectively). For those systems, ring closure was also claimed to yield two different conformational isomers of [FH₂-Si(*cyc*-CH₂O)]⁻ with significant differences in Si−C and Si−O bond distances as in our case. The transition state for inter-conversion between these two species was found in ref 9 to involve a mechanism resembling a pseudorotation.

The geometric parameters obtained for the siloxirane moiety in our calculations bear strong similarities to those obtained in ref 9. A much shorter Si−O bond (1.634 Å) is calculated for the anion originating from the carbanion, **V(II)**, than for **V-(III)** (1.748 Å). By comparison, the FH₂Si(*cyc*-CH₂O)⁻ orig-inating by ring closure of the carbanion was calculated to have a Si−O bond distance of 1.660 Å as opposed to a bond distance of 1.775 Å in the siloxirane anion obtained by ring closure of the alkoxide structure.⁹ Likewise, our calculated Si-*cyc*C bond distance of 1.891 Å is much longer in **V(II)** than in **V(III)**, where Si−*cyc*-C = 1.827 Å. The equivalent anions FH₂Si-(*cyc*-CH₂O)⁻ were calculated in ref 9 to have Si−*cyc*-C bond distances of 1.927 and 1.833 Å, respectively. Finally, the calculated O−Si−C angles in the siloxirane moiety are similar within 1° of those previously calculated.

The geometric parameters obtained for TMOS reveal Si−O and C−O bond distances of 1.612 and 1.403 Å, respectively. These values should be compared with bond distances of 1.623 and 1.404 Å obtained in ref 2.

Table 1 lists the relative energies at the MP2 level for the different ion structures including zero-point vibrational energy and thermal corrections for enthalpy calculations at 298 K. It is clear that structures **V(II)** and **V(III)** are more stable than the isomeric structure **IV**, and that structure **V(II)** is the most stable form predicted at the MP2//HF level.

Other predicted thermochemical properties deserve special attention for comparison with the experimental results. The first aspect refers to the possibility of FSi(OMe)₂(*cyc*-CH₂O)⁻

promoting either fluoride or methoxide transfer to other substrates. The dissociation energy for **V(II)** to yield either fluoride or methoxide ion is calculated to be

$$
\mathbf{V(II)} \nearrow \begin{array}{l} \text{(MeO)}_2\text{Si}(cyc\text{-OCH}_2) \ + \ \text{F}^- \qquad \Delta H_{298K} = 69.0 \ \text{kcal mol}^{-1} \\[2em] \searrow \ \text{FSi(MeO)}(cyc\text{-OCH}_2) \ + \ \text{MeO}^- \quad \Delta H_{298K} = 91.5 \ \text{kcal mol}^{-1} \end{array}
$$
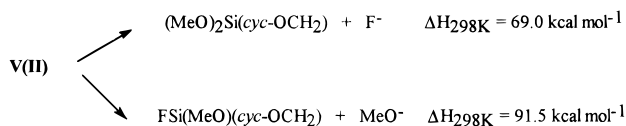
The high value calculated for the first process predicts a very high fluoride affinity for (MeO)₂Si(*cyc*-CH₂O). This number is consistent with the previously calculated value of 61.8 kcal mol⁻¹ for H₂Si(*cyc*-CH₂O) at the MP4(SDTQ)/6-31++G**// RHF/6-31++G** level including zero-point energy corrections.⁹ Such a high value for the fluoride affinity of a siloxirane system was claimed to reflect the decrease in strain energy in going from a tetrahedral-like environment in the neutral to a distorted trigonal bipyramid in the anionic species.

An analysis of the charge distribution for the different anions can provide some information regarding the expected reactivity for these systems. While several approaches can be used for this purpose, the simple Mulliken charges provide a useful qualitative guide. A high positive Mulliken charge (ranging from 1.5 to 1.78) is calculated on Si for both neutrals and anions considered here. For anion **IV**, the siloxide oxygen is calculated to have a Mulliken charge of −1.0, as might be expected for a more localized anion. For structures **V(II)** and **V(III)**, the extra Mulliken negative charge is distributed among F, the cyclic O, the O−(Me), and to a lesser extent the cyclic C.³¹

Finally, the question of relative proton affinities for the different species deserves some consideration. The occurrence of reaction 1b is indicative of a mechanism in which a nascent

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(31) The Mulliken charges on all atoms for the ionic species and neutrals are available from the authors upon request.
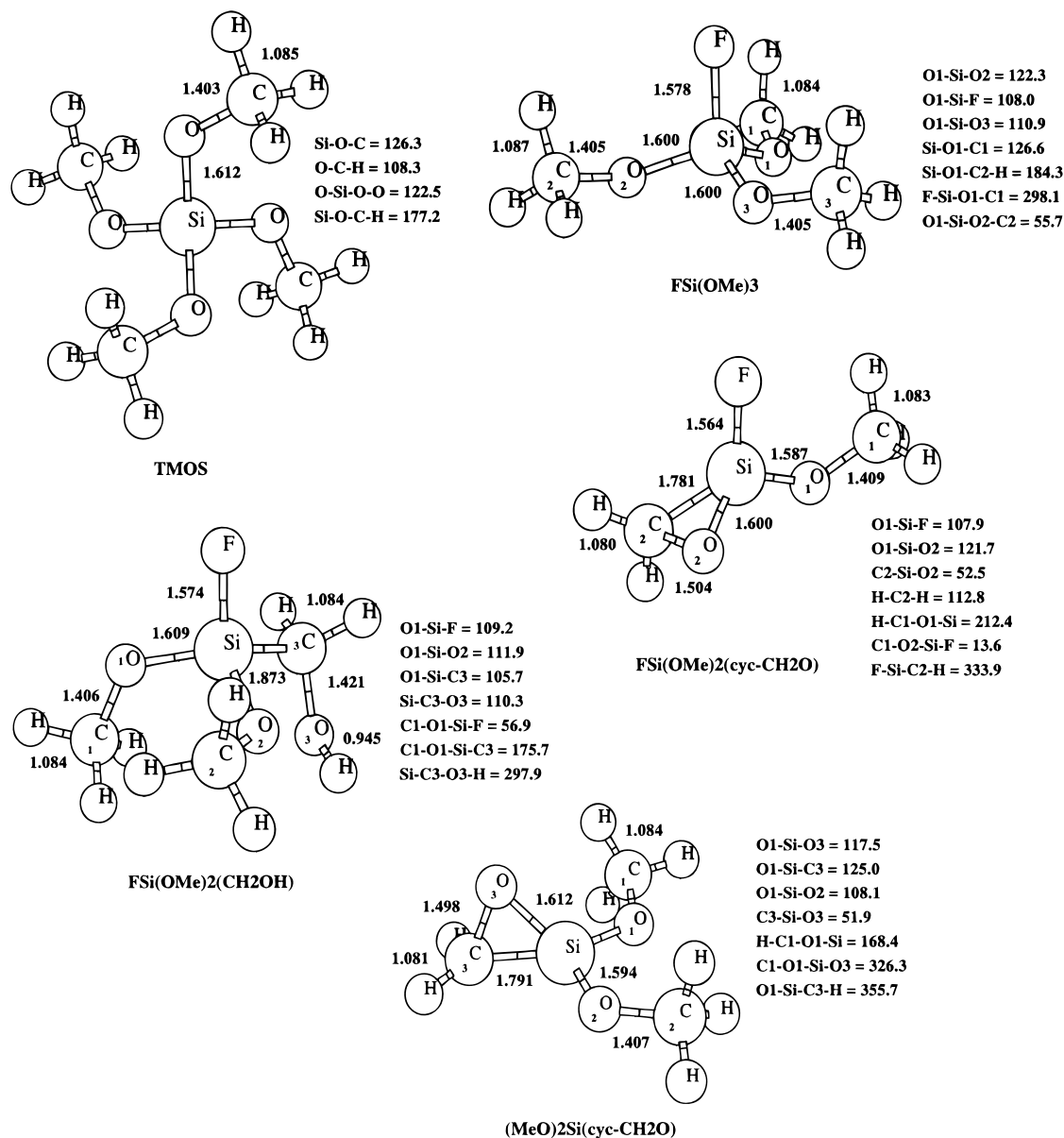
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Si-O-C = 126.3
O-C-H = 108.3
O-Si-O-O = 122.5
Si-O-C-H = 177.2

TMOS

O1-Si-O2 = 122.3
O1-Si-F = 108.0
O1-Si-O3 = 110.9
Si-O1-C1 = 126.6
Si-O1-C2-H = 184.3
F-Si-O1-C1 = 298.1
O1-Si-O2-C2 = 55.7

FSi(OMe)3

O1-Si-F = 107.9
O1-Si-O2 = 121.7
C2-Si-O2 = 52.5
H-C2-H = 112.8
H-C1-O1-Si = 212.4
C1-O2-Si-F = 13.6
F-Si-C2-H = 333.9

FSi(OMe)2(cyc-CH2O)

O1-Si-F = 109.2
O1-Si-O2 = 111.9
O1-Si-C3 = 105.7
Si-C3-O3 = 110.3
C1-O1-Si-F = 56.9
C1-O1-Si-C3 = 175.7
Si-C3-O3-H = 297.9

FSi(OMe)2(CH2OH)

O1-Si-O3 = 117.5
O1-Si-C3 = 125.0
O1-Si-O2 = 108.1
C3-Si-O3 = 51.9
H-C1-O1-Si = 168.4
C1-O1-Si-O3 = 326.3
O1-Si-C3-H = 355.7

(MeO)2Si(cyc-CH2O)

Figure 2. Optimized geometries for Si(OMe)$_4$, FSi(OMe)$_3$, FSi(OMe)$_2$(CH$_2$OH), FSi(OMe)$_2$(*cyc*-CH$_2$O), and (MeO)$_2$Si(*cyc*-CH$_2$O).

Table 1. Relative Energies Calculated at the MP2 Level for FSi(OMe)$_2$(CH$_2$O)$^-$ Ions Including ZPE and Thermal Corrections for 298 K

ionic species	ΔH(298 K)/kcal mol^{-1}
IV	17.2
V(II)	(0.0)
V(III)	7.6

methoxide ion is capable of abstracting a proton from the initial pentacoordinated adduct, [FSi(OMe)$_4$]$^-$. The proton affinity of (CH$_2$F)Si(OMe)$_2$O$^-$, **IV**, is calculated to be 350 kcal mol^{-1}, which is similar to an estimated proton affinity of 355 kcal mol^{-1} for (MeO)$_2$(Me)SiO$^-$, (MeO)$_3$SiO$^-$, F(Me)$_2$SiO$^-$, and (MeO)$_2$(H)SiO$^-$ from bracketing experiments.[32] The proton affinities of the putative **II** and **III** structures are more difficult to establish since no stable geometries could be found in the energy surface.

The theoretical calculations were then considered an appropriate background for the experimental results described below which provide a critical assessment of the theoretical predictions.

(32) Damrauer, R; Simon, R.; Krempp, M. *J. Am. Chem. Soc.* **1991**, *113*, 4431.

Experimental Section

The general experimental procedure was similar to that used in our earlier investigation of the ion/molecule reactions of Si(OMe)$_4$.[15] Ion/molecule reactions were investigated in a homemade FT-ICR spectrometer with a magnetic field set at either 1.0 or 1.25 T and interfaced to an Omega IonSpec Fourier transform data system. The cell was a standard cubic cell with sides 2.5 cm long.

Fluoride ions were generated by electron impact from NF$_3$ (Pennwalt Ozark Mahoning) at pressures around 8×10^{-8} Torr (ion gauge reading) and at electron energies of 2 eV. Tetramethoxysilane, Si(OMe)$_4$ (Aldrich, 99+%), was thoroughly degassed, dried, and purified by distilling off *in situ* any volatile methanol produced by hydrolysis of the sample. Typical partial pressures used in this work were in the range of $1-2 \times 10^{-8}$ Torr. Under these conditions, fluoride ions react completely after 400−800 ms. The subsequent ion chemistry of a given product ion generated by the F$^-$/Si(OMe)$_4$ reaction, reaction 1, was studied by selective isolation of that ion after 600 ms of reaction time. All unwanted ions were ejected with a combination of short (2 ms) on-resonance radio frequency (rf) bursts and long rf sweeps (10−15 ms) over a wide mass range. In the case of FSi(OMe)$_2$(OCH$_2$)$^-$, most experiments were carried out by reisolating the ions after 1200 ms to improve thermal equilibration of the ions.

Reagents used to test the reactivity of FSi(OMe)$_2$(OCH$_2$)$^-$ were introduced in the vacuum chamber via a pulsed valve (General Valve,

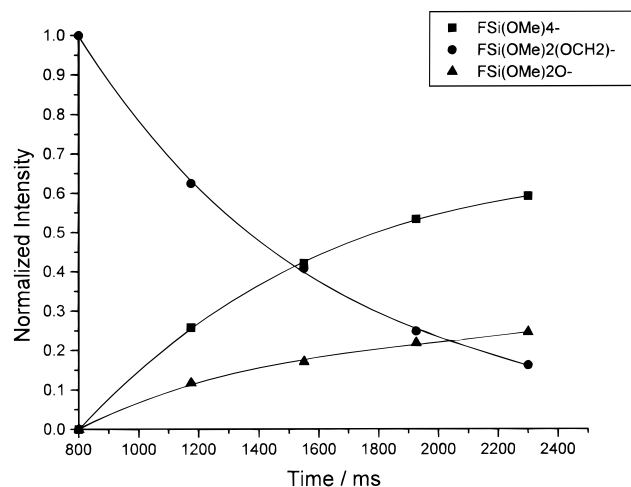**Figure 3.** The time evolution of reagent and products in the reaction of $FSi(OMe)_2(CH_2O)^-$ with $Si(OMe)_4$, reaction 2. The experimental conditions are given in the Experimental Section.

Model 9) after isolation of the reagent ions, or used under static partial pressures maintained in the neighborhood of $1-2 \times 10^{-8}$ Torr. Typical pulse widths of $2-5$ ms were used for the pulsed valve, and the maximum pressure in the ion gauge after the pulse never exceeded 5×10^{-7} Torr. A typical delay time of 5 s was used between successive pulse sequences to allow for proper pumping of the system in these experiments.

Acetylacetone, nitromethane, acetone, 2-propanol, acetic acid, ethanol, methanol and hexafluorobenzene were obtained commercially (Aldrich) and subjected to several freeze–pump–thaw cycles before sample introduction. Positive ion ICR spectra were recorded to test the purity of the samples. BF_3 (Matheson) was subjected to a triple low-temperature distillation process in order to remove impurities observed in its mass spectra.

Experimental Results

The reaction of F^- with $Si(OMe)_4$ in our FT-ICR spectrometer has been shown to yield four different ionic products (see reaction 1).[15] While our main objective was to explore the reactivity of the $[FSi(OMe)_2(CH_2O)]^-$ ion, it was necessary in several cases to compare its behavior with that of the ions formed in reactions **1a** and **1c** since presumably $FSi(OMe)_4^-$ corresponds to a pentacoordinated Si adduct, and $FSi(OMe)_2O^-$ to a siloxide type anion.

(a) Reaction of $[FSi(OMe)_2(OCH_2)]^-$ with $Si(OMe)_4$. Our ion of interest reacts with the parent $Si(OMe)_4$ by fluoride transfer to yield $FSi(OMe)_4^-$ and a neutral generically identified as $[Si(OMe)_2(OCH_2)]$, reaction 2a. Reaction 2b, which generates $FSi(OMe)_2O^-$, is observed to occur competitively as shown in Figure 3. Two neutral products are assumed to be formed in this case, $Si(OMe)_2(OCH_2)$ and Me_2O.
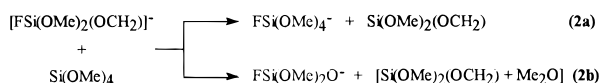
No attempt was made to determine the absolute rate constants due to the uncertainties associated with measuring the absolute pressure of $Si(OMe)_4$, but the reagent ion is observed to disappear completely through a simple exponential decay. Reaction 2a is a typical example of a fluoride transfer reaction, suggesting that $Si(OMe)_4$ has a higher fluoride affinity than $[Si(OMe)_2(OCH_2)]$. However, this observation cannot be used as a quantitative thermochemical upper limit for the fluoride affinity of $Si(OMe)_2(OCH_2)$ since that of $Si(OMe)_4$ is un-

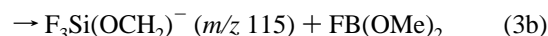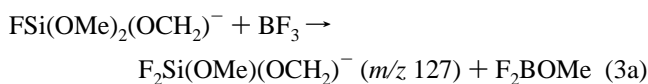known.[33] Yet, reaction 2a strongly argues in favor of a siloxirane structure for the $[FSi(OMe)_2(OCH_2)]^-$ ion. An ion with a structure similar to **IV** (or to structures **II** or **III**) would not be expected to react by F^- transfer.

The appearance of $FSi(OMe)_2O^-$ in reaction 2b suggests that reaction 2a is sufficiently exothermic to promote partial displacement of a MeO^- in the pentacoordinated adduct, $FSi(OMe)_4^-$. A nascent MeO^- ion in a $[FSi(OMe)_3\cdots^-OMe]$ type collision complex could then promote an internal nucleophilic displacement similar to that claimed for reaction 1c. While the thermochemistry of the fluoride transfer reaction is not known, the product distribution reported earlier for reaction 1 reveals that MeO^- is easily displaced from the pentacoordinated $FSi(OMe)_4^-$ ion. Nevertheless, these experiments cannot rule out the possibility that the nature of the neutral products may be different from those shown in reaction 2b. However, it should be emphasized that reasonable neutral products are difficult to suggest if the reactant ion in reaction 2b is assumed to have structure **IV** (or **II** and **III**).

While reactions 2a and 2b are reasonably conclusive regarding the nature of the $[FSi(OMe)_2(OCH_2)]^-$ anion, further experiments were considered necessary in order to establish the strength of the fluoride binding in this anion and the stability of the siloxirane ring.

(b) Reactions with BF_3. Boron trifluoride, BF_3, was considered a particularly attractive substrate because of its high fluoride affinity,[33] estimated to be in the range 72 ± 5 kcal mol^{-1}, and its capability to undergo nucleophilic attack readily.[34]

A rapid series of fluoride–methoxide exchange reactions (reaction 3) was observed to take place between $[FSi(OMe)_2(OCH_2)]^-$ and related anions with BF_3.

$$FSi(OMe)_2(OCH_2)^- + BF_3 \rightarrow$$
$$F_2Si(OMe)(OCH_2)^- \ (m/z \ 127) + F_2BOMe \quad (3a)$$
$$\rightarrow F_3Si(OCH_2)^- \ (m/z \ 115) + FB(OMe)_2 \quad (3b)$$

The kinetic scheme is complicated by the fact that $F_2Si(OMe)(OCH_2)^-$ ($m/z \ 127$) itself reacts rapidly with BF_3.

$$F_2Si(OMe)(OCH_2)^- + BF_3 \rightarrow F_3Si(OCH_2)^- + FB(OMe)_2 \quad (4)$$
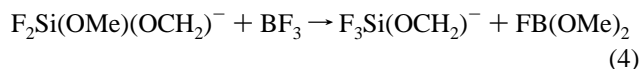
By comparison, fluoride transfer to BF_3 from the different ions occurs slowly and formation of BF_4^- is only observed to become important at long reaction times. All of the different species apparently contribute to the formation of BF_4^-, but $F_3Si(OCH_2)^-$ undergoes exclusively fluoride transfer with BF_3, and thus BF_4^- becomes the dominant ion at reaction times longer than 5 s. Fluoride transfer, reaction 5, can then be considered a slow competitive reaction in this system.
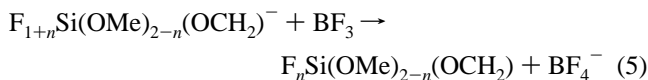
$$F_{1+n}Si(OMe)_{2-n}(OCH_2)^- + BF_3 \rightarrow$$
$$F_nSi(OMe)_{2-n}(OCH_2) + BF_4^- \quad (5)$$
$$n = 0-2$$

Figure 4 shows the time dependence of the product distribution during the first 1200 ms after isolation of the $FSi(OMe)_2(OCH_2)^-$ ion. This time dependence is clearly consistent with the set of reactions shown above, and with the fact that the fluoride transfer type reactions (reaction 5) are slow under these conditions.

(33) Larson, J. W.; McMahon, T. B. *J. Am. Chem. Soc.* **1985**, *107*, 766.
(34) For a recent example in the gas phase, see: Taylor, W. S.; Babcock, L. M. *J. Am. Chem. Soc.* **1995**, *117*, 6497.
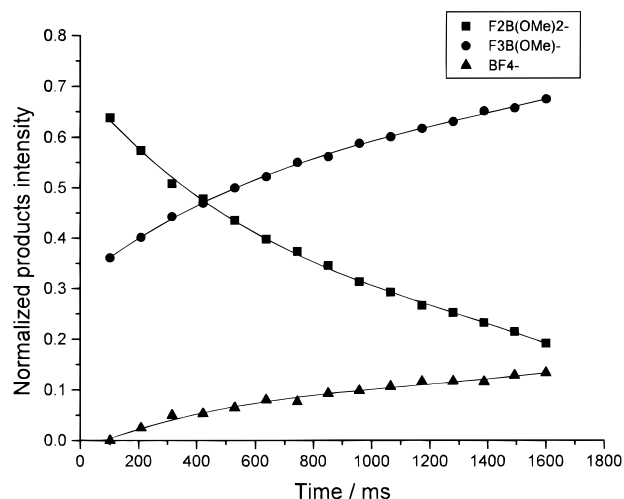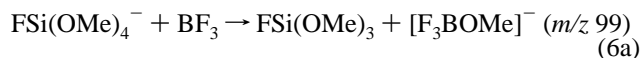
Figure 4. Product distribution as a function of time in the reaction of $FSi(OMe)_2(CH_2O)^-$ with BF_3. The time scale is characteristic of the complete disappearance of the reagent ion. Notice that BF_4^- grows with time and eventually becomes the most important species at long reaction times (5 s). (See reactions 3−5.)
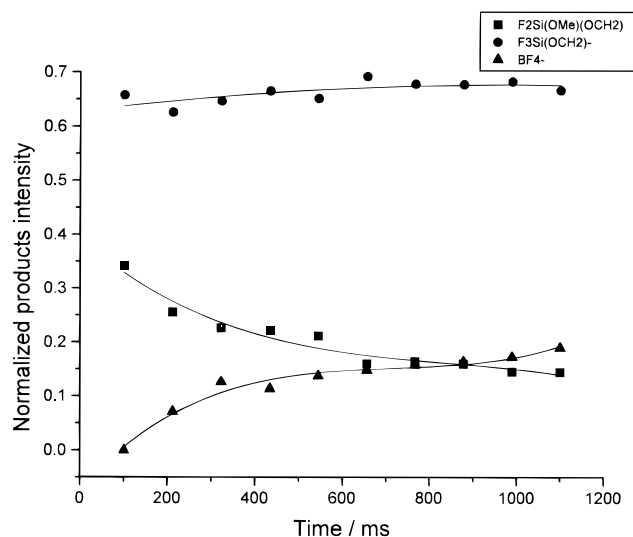

Figure 5. Product distribution as a function of time in the reaction of $FSi(OMe)_4^-$ with BF_3. The time scale is characteristic of the complete disappearance of the reagent ion. Notice that BF_4^- grows with time and eventually becomes the most important species at long reaction times (5 s). (See reactions 6−8.)
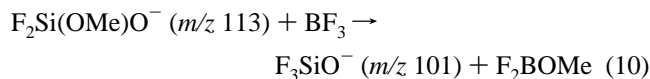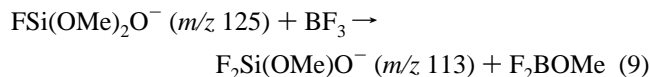
A very precise quantitative kinetic analysis of these reactions in the presence of a stationary pressure of BF_3 (as opposed to experiments where BF_3 is introduced through a pulsed valve) is complicated by the fact that $FSi(OMe)_2(OCH_2)^-$ also undergoes reaction 2 with $Si(OMe)_4$, and both product ions of reaction 2 are found to react further with BF_3 as described below.

In order to understand the significance of reactions 3−5, the reactivity patterns of $FSi(OMe)_4^-$ and $FSi(OMe)_2O^-$ in the presence of BF_3 were also studied independently. Since the structures of these two anions are less likely to be controversial, these experiments were considered to be a valuable frame of reference for the reactivity of fluoride−silane adducts and siloxide type anions with BF_3.

The pentacoordinated adduct ion, $FSi(OMe)_4^-$, was observed to react through multiple fluoride−methoxide exchange reactions as shown in reaction 6. Unlike the reactions of

$$FSi(OMe)_4^- + BF_3 \rightarrow FSi(OMe)_3 + [F_3BOMe]^- \ (m/z\ 99) \tag{6a}$$

$$\rightarrow F_2Si(OMe)_2 + F_2B(OMe)_2^- \ (m/z\ 111) \tag{6b}$$

$FSi(OMe)_2(OCH_2)^-$, the anionic product species are boron-containing ions. Isolation of either product ion of reaction 6 reveals that $F_2B(OMe)_2^-$ can react further with BF_3 to yield $[F_3BOMe]^-$ (reaction 7).

$$F_2B(OMe)_2^- \ (m/z\ 111) + BF_3 \rightarrow$$
$$F_2BOMe + [F_3BOMe]^- \ (m/z\ 99) \tag{7}$$
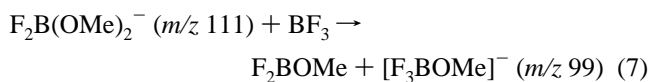
Fluoride transfer from these different species to yield BF_4^- is observed to be slow but becomes important at long reaction times. As in reaction 5, $[F_3BOMe]^-$ can only undergo fluoride transfer, reaction 8. The time evolution of the product ions is

$$F_3B(OMe)^- + BF_3 \rightarrow F_2BOMe + BF_4^- \tag{8}$$

plotted in Figure 5. The ions $F_2B(OMe)_2^-$, $F_3B(OMe)^-$, and BF_4^- display a time dependent behavior similar to that observed for the product ions of $FSi(OMe)_2(OCH_2)^-$ plotted in Figure 4. Thus, considerable similarities are observed in these reactions between $FSi(OMe)_4^-$ and $FSi(OMe)_2(OCH_2)^-$.
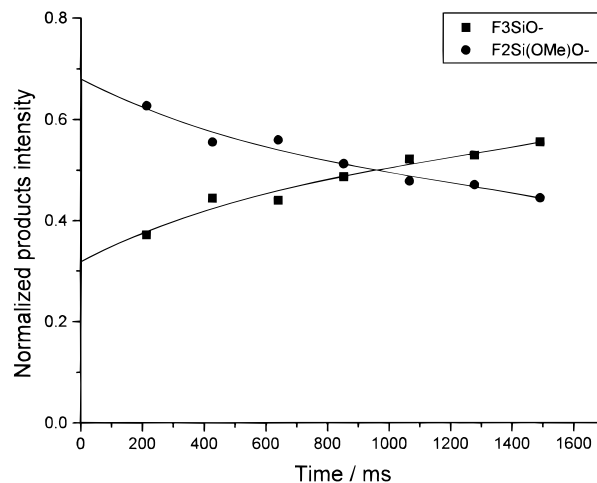
Figure 6. Product distribution as a function of time in the reaction of $FSi(OMe)_2O^-$ with BF_3 (reactions 9 and 10). Notice that BF_4^- is not formed in this case.

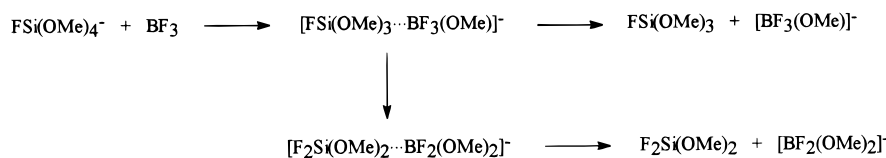On the other hand, $FSi(OMe)_2O^-$ ions generated either by 2b or 1c react with BF_3 exclusively through the fluoride-methoxide exchange reactions 9 and 10. *No BF_4^- is observed*

$$FSi(OMe)_2O^- \ (m/z\ 125) + BF_3 \rightarrow$$
$$F_2Si(OMe)O^- \ (m/z\ 113) + F_2BOMe \tag{9}$$

$$F_2Si(OMe)O^- \ (m/z\ 113) + BF_3 \rightarrow$$
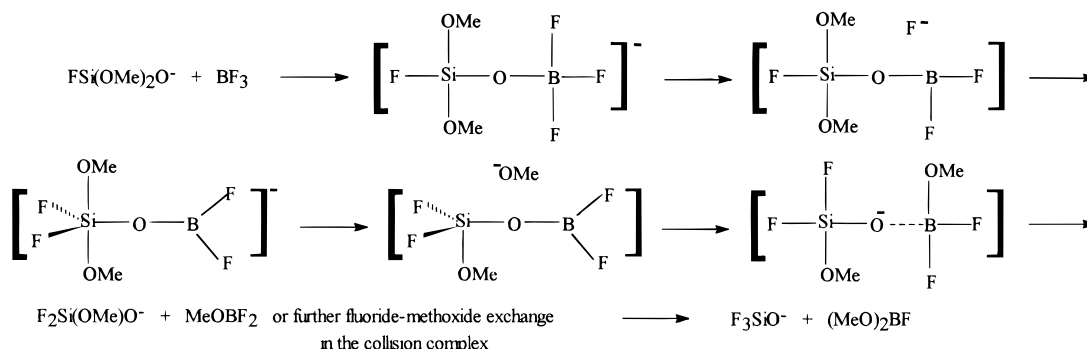$$F_3SiO^- \ (m/z\ 101) + F_2BOMe \tag{10}$$

in these reactions even at long reaction times. Figure 6 shows the time evolution of the product ions in this case.

These reactions with BF_3 allow further conclusions to be derived regarding the nature of the $FSi(OMe)_2(OCH_2)^-$ ion. For example, the reactions of $FSi(OMe)_4^-$ are consistent with the ease with which this ion can transfer MeO^- to substrates of higher methoxide affinity. Reactions 6a and 6b can then be rationalized by a scheme in which exchange of fluoride between the B and Si centers is promoted by the initial transfer of a methoxide group from the Si to the B center, Scheme 1. In

Scheme 1

$$FSi(OMe)_4^- + BF_3 \longrightarrow [FSi(OMe)_3 \cdots BF_3(OMe)]^- \longrightarrow FSi(OMe)_3 + [BF_3(OMe)]^-$$

$$\downarrow$$

$$[F_2Si(OMe)_2 \cdots BF_2(OMe)_2]^- \longrightarrow F_2Si(OMe)_2 + [BF_2(OMe)_2]^-$$

Scheme 2

$$F_2Si(OMe)O^- + MeOBF_2 \quad \text{or further fluoride-methoxide exchange} \longrightarrow F_3SiO^- + (MeO)_2BF$$
$$\text{in the collision complex}$$

this scheme, long-lived collision complexes must be present to account for the multiple fluoride−methoxide exchanges. In this situation, the final partition between neutral and anionic moieties would be determined by the relative stabilities of the corresponding Si and B species.

Reactions 9 and 10 are indicative of processes initiated by nucleophilic attack of the siloxide ion on boron as depicted in Scheme 2. Given the schemes proposed to account for the reactions of FSi(OMe)₄⁻ and FSi(OMe)₂O⁻ with BF₃, two possible alternatives can be proposed to account for reactions 3 and 4. The first alternative is to assume that reactions 3 and 4 reflect a siloxide (**IV**) or alkoxide (**III**) type behavior for the [FSi(OMe)₂(OCH₂)]⁻ ion, in which case these reactions could be explained by a sequence similar to that shown in Scheme 2. The second alternative is to consider the possibility that the ion/ neutral association of [FSi(OMe)₂(*cyc*-OCH₂)]⁻ with BF₃ activates the siloxirane ring and reaction then proceeds by ring opening and nucleophilic attack of the nascent FSi(OMe)₂CH₂O⁻ ion. This reasoning then suggests that F₂Si(OMe)(OCH₂)⁻ and F₃Si(OCH₂)⁻ ions also correspond to siloxirane species. The fact that the different F$_{n+1}$Si(OMe)$_{2-n}$(OCH₂)⁻ species can promote F⁻ transfer to BF₃, albeit slowly, as in the case of the ions derived from FSi(OMe)₄⁻, strongly argues for this second alternative and in favor of a siloxirane type structure for the FSi(OMe)₂CH₂O⁻ ion.

(c) Reactions with Gas-Phase Acids. The fact that the reaction of [FSi(OMe)₂(OCH₂)]⁻ with BF₃ can be construed as a nucleophilic attack on BF₃ mediated by activation of the siloxirane ring led us to explore the possibility of this ion reacting with gas-phase acids.

$$[FSi(OMe)_2(OCH_2)]^- + AH \xrightarrow{?} FSi(OMe)_2(CH_2OH) + A^-$$
$$\text{or}$$
$$FSi(OMe)_3$$
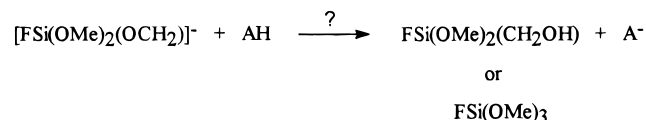
Experiments were then carried out by either pulsing the gas-phase acid into the cell or using a static pressure (1×10^{-8} Torr) of the acid. Proton abstraction was observed to occur readily from acetylacetone ($\Delta G_{acid} = 336.6$ kcal mol⁻¹), acetic acid ($\Delta G_{acid} = 341.6$ kcal mol⁻¹), nitromethane ($\Delta G_{acid} = 349.7$ kcal mol⁻¹), and acetone ($\Delta G_{acid} = 361.9$ kcal mol⁻¹), and more slowly from 2-propanol ($\Delta G_{acid} = 368.8$ kcal mol⁻¹).[35] No proton abstraction was observed from ethanol ($\Delta G_{acid} = 370.8$ kcal mol⁻¹) or methanol ($\Delta G_{acid} = 374.0$ kcal mol⁻¹).

By comparison, FSi(OMe)₄⁻ and FSi(OMe)₂O⁻ are also observed to abstract a proton from the first two substrates but not from the others. The behavior of FSi(OMe)₄⁻ can be rationalized in terms of the ease with which methoxide ion can be released to promote proton abstraction.

$$FSi(OMe)_4^- + MeCOOH \rightarrow$$
$$FSi(OMe)_3 + MeOH + MeCO_2^- \quad (11)$$
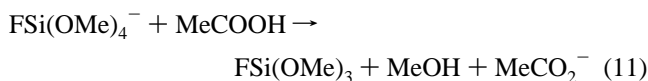
On the other hand, the reaction of FSi(OMe)₂O⁻ is consistent with the gas-phase acidity trend for silanol and substituted silanols.[32,36]

The base-like behavior of [FSi(OMe)₂(OCH₂)]⁻ resembles that of a substituted alkoxide ion. In fact, the gas-phase acidity of an RCH₂OH alcohol bearing a Si-containing substituent could well fall in the range between that of 2-propanol and ethanol. While these experiments are more consistent with an alkoxide ion type structure, like that represented by structure **III**, the results can also be accommodated by a mechanism in which proton abstraction can activate ring opening of the siloxirane structure **V** as proposed for the case of reaction with BF₃.

Few examples are known of similar type reactions in gas-phase ion chemistry. Ring opening has been observed in the gas-phase reaction of neutral ethylene oxide[37] with strong bases like OH⁻, but these reactions are better described as addition−elimination reactions.

(d) Reaction with N₂O and C₆F₆. A preliminary investigation[15] showed [FSi(OMe)₂(OCH₂)]⁻ to be unreactive toward N₂O. This observation has been used to rule out (1) a carbanion structure for our ion of interest and (2) activation of the siloxirane ring to yield a carbanion type behavior.

The behavior described above for the [FSi(OMe)₂(OCH₂)]⁻ ion suggests additional experiments with substrates which have been effective in recognizing ambidentate reactivity. While a number of reagents have been used in this respect,[39] hexafluo-

(35) *NIST Standard Reference Database 19B, NIST Negative Ion Energetics Database*, Version 3.0, compiled by J. E. Bartmess, 1993.
(36) Grimm, D. T.; Bartmess, J. E. *J. Am. Chem. Soc.* **1992**, *114*, 1227.
(37) Bierbaum, V. M.; DePuy, C. H.; Shapiro, R. H.; Stewart, J. H. *J. Am. Chem. Soc.* **1976**, *98*, 4229.
(38) DePuy, C. H.; Damrauer, R. *Organometallics* **1984**, *3*, 362.
(39) See, for example: (a) Brickhouse, M. D.; Squires, R. R. *J. Am. Chem. Soc.* **1988**, *110*, 2706. (b) Freriks, I. L.; de Koning, L. J.; Nibbering, N. M. M. *J. Am. Chem. Soc.* **1991**, *113*, 9119. (c) Zhong, M.; Brauman, J. I. *J. Am. Chem. Soc.* **1996**, *118*, 636.

robenzene was chosen in this case as an additional test for the nature of the $[FSi(OMe)_2(OCH_2)]^-$ ion. Reaction 12 was observed to occur readily and exclusively. This result confirms

$$[FSi(OMe)_2(OCH_2)]^- + C_6F_6 \rightarrow$$
$$C_6F_5O^- + [FSi(OMe)_2(CH_2F)] \quad (12)$$
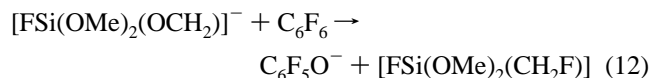
that the $[FSi(OMe)_2(OCH_2)]^-$ ion can react very efficiently in a manner similar to that of alkoxide ions, or through a reaction where the siloxirane ring is activated to yield an alkoxide-like ion in the collision complex.

Discussion

The theoretical calculations presented in the early part of the paper as well as calculations reported earlier[9] clearly establish that the most stable structure for $R_2FSi(CH_2O)^-$ ions corresponds to an anion containing a siloxirane ring. The fact that two sets of calculations with different basis sets, but including corrections for correlation energy, arrive at similar conclusions provides substantial support for the theoretical contention. While a more complete investigation was carried out in ref 9 for the energy surface of a simpler system, it is clear that a full exploration of all possible interconverting paths for $FSi(OMe)_2(OCH_2)^-$ would be a formidable task. The fact that we could not observe a stable alkoxide or carbanion structure for this anion at our level of calculation is not altogether different from the results of ref 9 where these minima for $FH_2Si(CH_2O)^-$ were claimed to be uncertain if larger basis sets or higher levels of theory were to be used.

The experimental results clearly show that $FSi(OMe)_2(OCH_2)^-$, and other related ions containing the CH_2O moiety attached to Si, can undergo fluoride transfer to substrates of high fluoride affinity. This behavior strongly supports the theoretical prediction of a stable siloxirane structure for this ion. Likewise, the fact that in all cases $FSi(OMe)_2(OCH_2)^-$ is observed to react completely with the different substrates suggests that a mixture of isomeric species is unlikely. Thus the symbiotic relationship between theory and experiment proves to be a valuable guideline in this type of problem.

Nevertheless, several of the reactions reported above reveal that $FSi(OMe)_2(OCH_2)^-$ can also promote reactions akin to those induced by anions bearing a negatively charged oxygen. The kinetic behavior of our ion of interest suggests that it is unlikely

that two structurally different $FSi(OMe)_2(OCH_2)^-$ ions are generated in this system. Thus, the idea has been advanced that the siloxirane ring can be activated by suitable substrates resulting in reactions which are typically those of an alkoxide ion. The reactions with BF_3 suggest that this ring activation is indeed more favorable than fluoride transfer, a fact that may not be surprising because of the large binding energy of F^- to these Si species. Furthermore, this ease of ring activation is in agreement with the experimental difficulty associated with isolating siloxirane derivatives and the fact that such structures become intermediates, and not stable species, in the Brook rearrangement.[5]

Finally, a word of caution needs to be introduced in comparing the experimental results for the proton abstraction and hexafluorobenzene reactions with theoretical predictions. Firstly, the actual structures of the neutral products are not known. Since rearrangements have been invoked as a likely possibility in neutral siloxirane chemistry, this possibility needs to be taken into consideration. Secondly, the calculation of the thermochemistry for ring opening involves nonisodesmic reactions. If the enthalpies for Si-containing compounds are not well described at this level of calculation unless empirical bond additivity corrections are introduced,[1,2,28] then the estimated enthalpy changes for such reactions may not be very reliable.

Supporting Information Available: Table S1 of the exponents of the primitive basis functions obtained by the GCM for C, F, O, and Si atoms using the SBK pseudopotential, Table S2 with Hartree−Fock and MP2 calculated energies for all ions and neutrals, and Figures S1 and S2 with the weight functions for the atomic orbitals of Si in atomic Si and in $Si(OCH_3)_4$ (4 pages). See any current masthead page for ordering information and Internet access instructions.

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