J. Am. Chem. Soc. **1990**, *112*, 5991-5995

The Covalent Nature of Trimethylsilyl Perchlorate and Observation of Polarized Fluorotrimethylsilane–Antimony Pentafluoride Complexes Based on ^{29}Si NMR Studies. Difficulties in Observing Long-Lived Persistent Trialkylsilicenium Ions[1]

George A. Olah,* Ludger Heiliger, Xing-Ya Li, and G. K. Surya Prakash*

Contribution from the Donald P. and Katherine B. Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, Los Angeles, California 90089-1661. *Received December 8, 1989*

Abstract: Trimethylsilyl perchlorate was studied in sulfolane solution by ^{29}Si NMR spectroscopy. The ^{29}Si NMR shift of $\delta(^{29}\mathrm{Si})$ 47 remained virtually unchanged by changing the concentrations from 0.584, to 0.29, to 0.15 M. This indicates that $(CH_3)_3SiOClO_3$ is covalent throughout this concentration range in contrast to the claims by Lambert et al. (*J. Am. Chem. Soc.* **1988**, *110*, 6364), who based on ^{35}Cl and ^{37}Cl NMR data suggested an equilibrium of the ionic and covalent forms, with 20, 29, and 35% ionic contribution, respectively, at these concentrations. If such an equilibrium would exist, the ^{29}Si NMR shifts should display significant deshieldings. Upon further dilution in the 0.1 to 0.002 M range the formation of hexamethyldisiloxane was observed, even in highly purified sulfolane, indicative of hydrolysis by residual low-level water impurity. Simultaneously formed perchloric acid which undergoes perchlorate ion exchange with the unhydrolyzed trimethylsilyl perchlorate would seem to explain the reported ^{35}Cl/^{37}Cl NMR behavior, as well as cryoscopic and conductivity data. An investigation of fluorotrialkylsilanes in SbF_5–SO_2ClF solution at −78 °C by ^{13}C and ^{29}Si NMR spectroscopy showed highly polarized, rapidly exchanging complexes, but no free silicenium ions. The reasons for the inability of observing persistent silicenium ions in the condensed state, despite claims to the contrary, are discussed.

Introduction

Trivalent sila cations, i.e. silicenium ions, are readily obtained and observed in the gas phase. They are found as high abundance fragments in the mass spectra of organosilicon compounds.[2a] However, analogous ions have remained elusive in the condensed state (solution or solid state), at least under long-lived conditions as observable species. The reasons for this are generally thought to be poor overlap between the empty 3p-orbital of silicon and π-electrons or lone pairs on carbon, nitrogen, or oxygen centers[2b] (thus the silicenium ion center cannot be stabilized by adjacent electron-donating substituents), as well as the tendency of silicon toward valence shell electron expansion rather than contraction.[3] The high affinity of silicon for oxygen, fluorine, and chlorine usually results in the reaction of solvents and/or Lewis acid halides with the developing electrophilic silicon center.[4] This is the reason why the methods developed for the preparation and study of stable carbocations[5] (using low-nucleophilicity, highly acidic systems) are not suitable for the generation of long-lived trivalent silicenium ions.[4]

Silicenium ions are involved as reaction intermediates in organosilicon reactions including solvolytic reactions,[6] but attempts directed toward the observation of stable long-lived silicenium ions have thus far been unsuccessful[7] except for claims[8-14] by Lambert and co-workers on the ionic nature of some silyl perchlorates in sulfolne and acetonitrile solvents. Recently we showed[15] by ^{29}Si and ^{35}Cl NMR spectroscopy and X-ray crystallography that triphenylsilyl perchlorate exists as a covalent ester both in solution and in the solid state. In the same study the observation of a sharp ^{35}Cl NMR resonance for triphenylsilyl perchlorate upon high dilution (<0.002 M) in CH_2Cl_2/CH_3CN was attributed to free perchloric acid formed by hydrolysis with the trace amount of water present in the solvent system.

We report now our findings on attempts to observe the persistent trimethylsilicenium ion and show based on ^{29}Si NMR studies that trimethylsilyl perchlorate, despite claims to the contrary by Lambert et al.,[13,14] is of covalent nature. Furthermore, we have found by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy trialkylfluorosilane–antimony pentafluoride systems in SO_2ClF solutions to be rapidly exchanging polarized donor–acceptor complexes. Together with considerations based on frontier orbital theory and the effect of steric bulk of substituents on the rate of exchange it is concluded that the exchange reaction proceeds in a S_Ni-Si manner. These studies also further help to estimate the ^{29}Si NMR chemical shifts of silicenium ions and show that no long-lived ions have been observed under any of the conditions used so far.

Results and Discussion

I. The Covalent Nature of Trimethylsilyl Perchlorate.

The reports of Lambert and co-workers of the ionic nature of tris(dimethylamino)silyl perchlorate, tris(isopropylthio)silyl perchlorate, triphenylsilyl perchlorate, and trimethylsilyl perchlorate[8-13] are in contrast to all previous unsuccessful attempts

---

[1] Organometallic Chemistry. 23. For part 22 see: Prakash, G. K. S.; Keyaniyan, S.; Aniszfeld, R.; Heiliger, L.; Olah, G. A.; Stevens, R. C.; Choi, H.-K.; Bau, R. *J. Am. Chem. Soc.* **1987**, *109*, 5123.

[2] (a) Weber, W. P.; Felix, R. A.; Willard, A. K. *Tetrahedron Lett.* **1970**, 907 and references therein. (b) Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 4329.

[3] Sommer, L. H. *Stereochemistry, Mechanism and Silicon*; McGraw Hill: New York, 1967.

[4] Olah, G. A.; O'Brien, D. H.; Lin, C. Y. *J. Am. Chem. Soc.* **1969**, *91*, 701.

[5] For a comprehensive review see: Olah, G. A. *Top. Curr. Chem.* **1979**, *80*, 19.

[6] (a) Flowers, M. S.; Gusel'nikov, L. E. *J. Chem. Soc. B* **1968**, 419. (b) West, R. *Int. Symp. Organosilicon Chem., Sci. Commun.* **1965**, 1. (c) Sommer, L. H.; Evans, F. *J. Am. Chem. Soc.* **1954**, *76*, 1186. (d) Sommer, L. H.; Bailey, D. L.; Coulf, J. R.; Whitmore, F. C. *Ibid.* **1954**, *76*, 801. (e) Apeloig, Y.; Stanger, A. *J. Am. Chem. Soc.* **1987**, *109*, 272.

[7] (a) Brook, A. G.; Pannel, A. K. *Can. J. Chem.* **1969**, *91*, 701. (b) Olah, G. A.; Mo, Y. K. *J. Am. Chem. Soc.* **1971**, *93*, 4942. (c) Cowley, A. H.; Cushner, M. C.; Riley, P. E. *Ibid.* **1980**, *102*, 624.

[8] McConnell, J. A. Ph.D Thesis, Northwestern University, Evanston, IL, 1986.

[9] Lambert, J. B.; Schulz, W. J., Jr. *J. Am. Chem. Soc.* **1983**, *105*, 1671.

[10] Lambert, J. B.; McConnell, J. A.; Schulz, W. J., Jr. *Ibid.* **1986**, *108*, 2482.

[11] Lambert, J. B.; Schulz, W. J., Jr.; McConnell, J. A.; Schilf W. *J. Am. Chem. Soc.* **1988**, *110*, 2201.

[12] Lambert, J. B.; McConnell, J. A.; Schilf, W.; Schultz, W. J., Jr. *J. Chem. Soc., Chem. Commun.* **1988**, 455.

[13] Lambert, J. B.; Schilf, W. *J. Am. Chem. Soc.* **1988**, *110*, 6364.

[14] Lambert, J. B.; Schultz, W. J., Jr. *The Chemistry of Organic Silicon Compounds*; The Chemistry of Functional Groups; Patai, S., Rappoport, Z., Eds.; Wiley Interscience: New York, 1989; Part II, Chapter 17.

[15] Prakash, G. K. S.; Keyaniyan, S.; Aniszfeld, R.; Heiliger, L.; Olah, G. A.; Stevens, R. C.; Choi, H. K.; Bau, R. *J. Am. Chem. Soc.* **1987**, *109*, 5123.

[16] Corey, J. Y. *J. Am. Chem. Soc.* **1975**, *97*, 3235.

0002-7863/90/1512-5991$02.50/0

to characterize long-lived, persistent silicenium ions in solution. Their claims were based on a combination of spectroscopic techniques, such as UV–vis, IR, ^{1}H, ^{13}C NMR, ^{35}Cl/^{37}Cl NMR, as well as cryoscopy and conductometry in highly dilute solutions. The technique that would provide unequivocal evidence for the ionic versus covalent structure of a prospective silicenium ion, namely ^{29}Si NMR, was, however, not found applicable under the conditions used in the studies.

Recently Lambert et al. have made extensive use of $^{35/37}$Cl NMR experiments to support the ionic character of trimethylsilyl perchlorate.[13] ^{35}Cl NMR was introduced by us[15] as a probe to differentiate ionic from covalent perchlorates in the case of the triphenylsilyl perchlorate system, which was found to be covalent. It was subsequently used by Lambert et al., who showed the presence of perchlorate anion in sulfolane solution of silyl perchlorates.[10–13] The decrease in the line width of the $^{35/37}$Cl NMR signal as well as its approach to the numerical chemical shift value of aqueous perchloric acid indeed indicates the increased ionic perchlorate nature. The data obtained at various concentrations of trimethylsilyl perchlorate in sulfolane solution revealed increased ionic perchlorate concentration upon increased dilution. It was consequently suggested that this was due to the dissociation of trimethylsilyl perchlorate to trimethylsilicenium and perchlorate ions upon high dilution.[13] The concentration dependence of the dissociation was quantified by use of a least-squares numerical analysis. An attempt was also made to account for possible hydrolysis. The results of the computational analysis remained unchanged when tripling the water content (from 5 to 15 ppm) starting at 0.001 M, which led to the conclusion that hydrolysis was not a significant factor affecting changes in line width.

The ^{29}Si NMR method should be well suited to probe for long-lived silicenium ions in solution. Consequently, we undertook study of trimethylsilyl perchlorate and its claimed concentration-dependent equilibria with trimethylsilicenium ion. If free silicenium ion is indeed involved in a fast equilibrium with its covalent perchlorate, the averaged ^{29}Si chemical shift would undergo a noticeable change upon dilution due to increased contributions of the highly deshielded ionic ^{29}Si chemical shift of the free ion. We were able to obtain ^{29}Si spectra of trimethylsilyl perchlorate in sulfolane at 0.584, 0.29, and 0.15 M concentrations, at which Lambert et al.'s ^{35}Cl NMR analysis claimed 20%, 29%, and 35% free ions.[13] Assuming Olah and Field's prediction of the trimethylsilyl cation ^{29}Si chemical shift of $\delta(^{29}\mathrm{Si})$ 225[17] to be the low-field limit (IGLO calculations by Schindler actually indicate a far more deshielded theoretical ^{29}Si chemical shift of $\delta(^{29}\mathrm{Si})$ 324[18]) and having determined the ^{29}Si resonance of neat trimethylsilyl perchlorate (acetone-d_6 capillary external lock) as $\delta(^{29}\mathrm{Si})$ 47, the following averaged ^{29}Si NMR shifts are calculated for the equilibria: the 20% ionic system should have an average chemical shift of $\delta(^{29}\mathrm{Si})$ 82, and the 29% at $\delta(^{29}\mathrm{Si})$ 99 and 35% ionic contribution should move the signal to $\delta(^{29}\mathrm{Si})$ 109. The actually observed chemical shifts, however, remain constant throughout all three concentrations at $\delta(^{29}\mathrm{Si})$ 47. These results clearly negate the claim by Lambert et al. of equilibria containing free trimethylsilicenium ion in the concentrations studied and would seem to necessitate a different explanation for the observed ^{35}Cl NMR data (vide infra). At the same time it has not been possible to obtain satisfactory ^{29}Si NMR spectra below 0.1 M concentration (due to lack of sensitivity and negative NOE associated with the ^{29}Si nucleus) and directly probe the nature of the system in extremely dilute solutions. Such studies must await use of ^{29}Si-enriched systems.

When monitoring the single ^{1}H NMR peak of trimethylsilyl perchlorate in acetonitrile or sulfolane upon dilution from 0.1 to 0.002 M concentration, we noticed the appearance of a second resonance at 0.01 M concentration, which was identified as hexamethyldisiloxane (inter alia by adding an authentic sample to the solution and observing the increase in the intensity of only this peak). Identification of the product by GC-MS was also carried out. Upon further dilution the trimethylsilyl perchlorate peak totally disappeared, with only the hexamethyldisiloxane signal remaining. The ^{1}H NMR chemical shift of the trimethylsilyl perchlorate upon dilution from 0.1 to 0.01 M remains at $\delta(^1\mathrm{H})$ 0.186, indicating no ionization or onset of it (small solvent effects on changing concentrations of solute are of course possible). In concentrations below 0.01 M hydrolysis products such as hexamethyldisiloxane and perchloric acid are observed.

We can reconcile these observations and account for the constancy of the ^{29}Si NMR chemical shift as well as the ^{35}Cl NMR data of Lambert et al.[13] by the effect of residual water impurity in the system. Water impurity in sulfolane and acetonitrile is extremely difficult to remove.[19,20] It readily hydrolyzes trimethylsilyl perchlorate at the studied low concentrations to yield the corresponding trimethylsilanol or hexamethyldisiloxane and perchloric acid. At higher solute concentrations the remaining silyl perchlorate exchanges perchlorate anion with perchloric acid via well-precedented pentacoordinated siliconium species[3] resulting in an averaged $^{35/37}$Cl NMR signal proportional to the concentrations of the two species, respectively (eq 1).

$$\rightarrow\mathrm{Si{-}OClO_3} + \mathrm{H^{+}\overset{*}{Cl}O_4^{-}} \rightleftharpoons \rightarrow\mathrm{Si{-}O\overset{*}{Cl}O_3} + \mathrm{H^{+}ClO_4^{-}} \quad (1)$$

As the solutions are further diluted the amount of water relative to solute increases. Consequently, the amount of perchlorate anion and its contribution to the average $^{35/37}$Cl NMR signal increases until finally at comparable water and silyl perchlorate concentrations the latter is completely hydrolyzed to give the spectral characteristics of perchloric acid. This exchange leaves the ^{29}Si NMR signal of the covalent trimethylsilyl perchlorate unaffected since the substrate having undergone exchange is indistinguishable from the one prior to it. The requirement that this exchange be fast on the NMR time scale was shown to be so by Lambert et al.[13] The ratio of line widths for the two Cl isotopes was found to be equal to the square of the ratio of the two quadrupole moments supporting that the line shape is controlled by fast quadrupolar relaxation[21] and that the exchange reaction is even faster than the nuclear spin relaxation.

Sulfolane used preferentially by Lambert for cryoscopy and conductivity measurements is, as mentioned, extremely difficult to properly purify and handle under dry conditions. Commercial sulfolane contains up to 2% 2,5-dihydrothiophene 1,1-dioxide, sulfolene (determined and isolated by gas chromatography), which cannot be separated from sulfolane by simple distillation. Strong acids such as concentrated sulfuric acid as well as nitronium salts gave colorations with sulfolane containing sulfolene impurity. To purify sulfolane triple distillation from NaOH pellets is required with subsequent distillation from calcium hydride to remove traces of water.[22] Even with this method, however, removal of traces of water is not assured. The method of purifying sulfolane as noted by Lambert[8] consisted of a single distillation from NaOH pellets. This treatment cannot have afforded the purity needed for any meaningful studies (spectroscopic or cryoscopic) for detection of free silicenium ion in highly dilute solutions. Only in their latest publication did Lambert et al. indicate that sulfolane was doubly distilled, first from BaO, then from $\mathrm{CaH_2}$, but without any observed difference in the residual water concentration, as determined by the Karl Fischer method.[13] Olah and Overchuck, however, have previously found the Karl Fischer water determination unreliable and irreproducible on carefully dried sulfolane when checked on samples to which known amounts of water were added.[22] These observations showed the unreliability of the Karl Fischer method to establish the purity of sulfolane. The claimed water concentration of 0.001–0.003 M thus may be an inaccurate measurement of the actual water content of the sulfolane used.

---

(17) Olah, G. A.; Field, L. D. *Organometallics* **1982**, *1*, 1485.

(18) Schindler, M. Personal communication.

(19) Brueggeller, P.; Mayer, E. *Z. Naturforsch.* **1979**, *343*, 891.

(20) Brendel, D. Dissertation, Universitaet Erlangen-Nuernberg, 1985.

(21) (a) Harris, R. K. *Nuclear Magnetic Resonance Spectroscopy*; Pitman: London, 1983. (b) Brevard, C.; Granger, P. *Handbook of High Resolution Multinuclear NMR*; Wiley-Interscience: New York, 1981.

(22) Olah, G. A.; Overchuck, N. A. *Can. J. Chem.* **1965**, *43*, 3279.

(23) Atkins, P. W. *Physical Chemistry*, 2nd ed.; Oxford University Press: London, U.K., 1982.

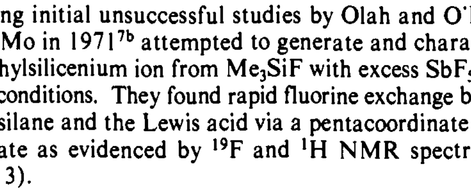
In any event, it is evident that the concentrations of solute "silyl cation" and the water content of the solvent are at least comparable, even at the low levels of the latter stated by authors.[8-13] The method of cryoscopy, it should be remembered, does not permit distinction of particles but only numbers of species involved. Conductivity studies per se also cannot identify conducting species. As we ourselves have not carried out either conductivity or cryoscopic measurements we do not intend to further comment on Lambert's results. However, we would like to point out that over the years many investigators were misled by studies in highly dilute solutions where impurities comparable to solute concentrations were present.

Thomas and Rochow for example in 1956 carried out conductometric studies on various triarylsilyl chlorides in stringently dried acetonitrile, but they still found traces of water responsible for the conductance observed in the solutions.[24] Their data covered a concentration range from 1 × 10^{-4} to 2 × 10^{-3} M, including that used by Lambert et al. (approximate 1 × 10^{-3} M). If anything, trimethylsilyl perchlorate can be expected to be even more susceptible to hydrolysis, compounding the difficulty encountered by Rochow and Thomas. Conductance and cryoscopic measurements in highly dilute solutions thus can hardly be considered as conclusive evidence for long-lived, persistent trimethylsilicenium ion or for this season any other silicenium ions.

II. Study of Exchanging Polarized Trialkylfluorosilane–Antimony Pentafluoride Complexes. The major reason for the failure to observe long-lived trivalent silicon ions is the lack of sufficiently nonnucleophilic counterions and solvents. All systems used in so-called stable carbocation chemistry, i.e. based on antimony pentafluoride and other superacids, were found to be unsuitable. Silicon is known to bind most strongly to fluorine and oxygen, and this explains why complex fluorides and perchlorates form covalent silicon species.[25] As the Si–Br bond is much weaker than the Si–Cl and S–F bonds, Olah and Field employed $AlBr_3$ as the Lewis acid in CH_2Br_2 as solvent in an attempt to ionize organosilyl bromides.[17] This system, although it could be successfully used to generate persistent *tert*-butyl cation,[19] gave with Me_3SiBr only a modestly deshielded ^{29}Si NMR signal accompanied by a diminished line width of the quadrupolar ^{27}Al NMR resonance indicating only polarization of the Si–Br bond via strong complexation by $AlBr_3$. $AlBr_3$ thereby acquires pseudotetrahedral environment decreasing the quadrupolar field gradient around the aluminum nucleus which results in a narrower line width of the ^{27}Al NMR peak. The limited magnitude of deshielding of the ^{29}Si NMR signal and narrowing of the line width of the ^{27}Al resonance, however, preclude persistent ionization to the trimethylsilicenium and tetrabromoaluminate ions (eq 2).

$$\mathrm{Me_3SiBr + AlBr_3 \rightarrow Me_3\overset{\delta+}{Si}\overset{\delta-}{Br} \rightarrow AlBr_3 \not\rightarrow Me_3Si^+\,AlBr_4^-} \qquad (2)$$

Following initial unsuccessful studies by Olah and O'Brien,[4] Olah and Mo in 1971[7b] attempted to generate and characterize the trimethylsilicenium ion from Me_3SiF with excess SbF_5 under stable ion conditions. They found rapid fluorine exchange between the fluorosilane and the Lewis acid via a pentacoordinate silicon intermediate as evidenced by ^{19}F and ^{1}H NMR spectroscopy (equation 3).



(3)

In continuation of these studies, since Olah and Mo[7b] at the time had not carried out ^{13}C or ^{29}Si NMR investigations, we have now extended the work. After slowly introducing Me_3SiF into a solution of excess SbF_5 in SO_2ClF at −78 °C and recording the ^{13}C and ^{29}Si NMR spectra at −100 °C we observed a broad singlet at −1.9 ppm for methyl carbon and a significantly deshielded broad singlet at +102 ppm for the silicon nucleus deshielded by 70 ppm from its progenitor. The peaks sharpen up considerably upon warming the solution to −60 °C consistent with an increased rate of fluorine exchange at more elevated temperatures. When an excess of Me_3SiF was used under the reaction conditions the NMR spectra at −60 °C showed an only slightly deshielded methyl resonance (<1 ppm) in the ^{1}H and ^{13}C NMR spectra as well as a very broad more shielded ^{29}Si signal at 50 ppm due to an increased contribution of uncomplexed Me_3SiF to the averaged NMR signal. The ^{29}Si chemical shift of $\delta(^{29}Si)$ 102 represents the most highly dehsielded Si resonance reported for a polarized and rapidly exchanging trimethylsilyl system, but not that of the trimethylsilicenium ion (for which $\delta(^{29}Si)$ would be expected to be more deshielded by at least 120 ppm).

Table I. ^{1}H, ^{13}C, and ^{29}Si NMR Data of Exchanging R_3SiF–SbF_5 Systems in SO_2ClF Solution

silyl fluoride	SbF_5 (equiv)	temp, °C	$\delta(^{1}H)$	$\delta(^{13}C)$	$\delta(^{29}Si)$
Me_3SiF	4	−100	−0.288	−1.9	102
Et_3SiF	4	−60	0.056 (CH_3)	3.58 (CH_3)	
			0.041 (CH_2)	3.62 (CH_2)	98
i-Pr_3SiF	5	−40	0.3 (CH)	1.9 (CH)	
			−0.092 (CH_3)	13.9 (CH_3)	93
t-Bu_3SiF	4	−40	1.76[a]	22.5 (C, J_{C-F} = 12.2 Hz)	not obsd
				26.7 (CH_3)	

[a] Taken from ref 27a,b.

In order to further investigate the exchanging fluorosilane systems we subsequently increased the bulk of the alkyl substituents to examine the effect of crowding on the silicon center. By subjecting Et_3SiF to reaction with 2 equiv of SbF_5 at −78 °C in SO_2ClF broad singlet absorptions are obtained in the ^{1}H and ^{13}C NMR spectra at $\delta(^{1}H)$ 0.1 (line width = 10 Hz) and $\delta(^{13}C)$ 3.6, respectively. The ^{29}Si NMR signal at $\delta(^{29}Si)$ 95, however, is fairly narrow even at this temperature, indicating that exchange is still fast on the NMR time scale. Adding another 2 equiv of SbF_5 to the solution and raising the temperature to −60 °C resolves both the proton and carbon resonances into two peaks, respectively, at $\delta(^{1}H)$ 0.056 and 0.041 was a 3:2 intensity ratio in the ^{1}H spectrum and $\delta(^{13}C)$ 3.58 and 3.62 for the methyl and methylene carbons in the ^{13}C spectrum (multiplicities determined by spin–echo techniques). The ^{29}Si peak was found deshielded to $\delta(^{29}Si)$ 98, consistent with a concentration-dependent exchange process rather than free silicenium ion formation. It is apparent that the ethyl ligands do not introduce sufficient steric congestion for the exchange to be slowed down noticeably. Isopropyl groups, however, were expected to cause more severe steric interaction. Thus when reacting *i*-Pr_3SiF with 2-fold excess of SbF_5 in SO_2ClF at −78 °C a doublet at $\delta(^{29}Si)$ 75 ($^{1}J_{Si-F}$ = 310 Hz) in the ^{29}Si NMR is observed proving that if exchange still occurs it has to be now slower than the NMR time scale. Warming the solution to −60 °C and adding another equivalent of SbF_5 results in broadening of the doublet and the appearance of another broad peak at $\delta(^{29}Si)$ 93. As anticipated the isopropyl groups provide significant steric hindrance which decreases the rate of fluorine exchange reflected in coupling between Si and F and generally broader lines. When a fifth equivalent of SbF_5 was added and the temperature was raised to −40 °C, the doublet disappeared in the ^{29}Si NMR spectrum and the peak at $\delta(^{29}Si)$ 93 sharpened up considerably. Table I summarizes the ^{29}Si, ^{13}C, and ^{1}H NMR data of the trialkylsilyl fluorides investigated under stable ion conditions.

Evidently, the exchange is affected as the activation barrier increases with increasing steric crowding around the silicon center. Crowding can be better accommodated by a trigonal-bipyramidal intermediate state (S_N2 like) than a pentagonal-pyramidal one (S_Ni like) since the angle between the alkyl groups can assume 120° in the former but would be considerably smaller in the latter (Chart I).[3]

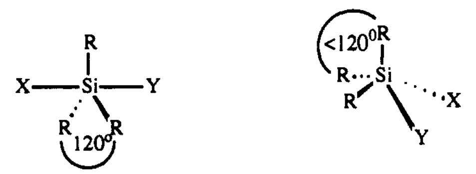
A potential S_N2-Si intermediate (transition state) could involve an associated arrangement of the silyl fluoride and antimony pentafluoride units implying a large positive entropy of activation

---

[24] Rochow, E. G.; Thomas, A. B. *J. Inorg. Nucl. Chem.* **1957**, *4*, 205.

[25] For review see: Corriu, R. J. P.; Henner, M. *J. Organomet. Chem.* **1974**, *74*, 1.

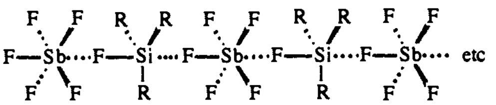
Chart I



S_N2 - Si

S_Ni - Si

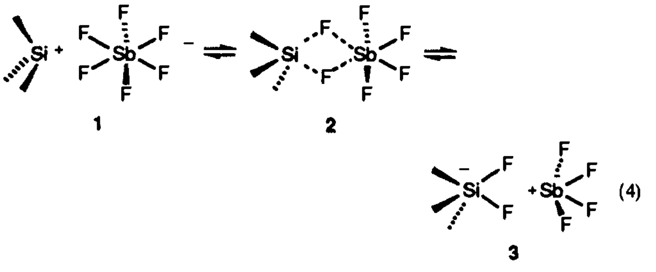
Chart II



owing to a highly ordered structure (Chart II).

If frontier orbital theory, restricted to HOMO–LUMO interactions, is applied to discern the favored structure, the energetically more favorable one is the S_Ni-Si intermediate. It has been pointed out by perturbation arguments that high electronegativity leaving groups with contracted valence orbitals attached to silicon and hard nucleophiles in aprotic solvents provide preferable conditions for S_Ni-Si reaction mechanisms.[26] Considering the exchange reaction of SbF_5 in SO_2ClF (aprotic solvent) with trialkylsilyl fluorides, R_3SiF, the arguments for an S_Ni-Si over the S_N2-Si mechanism are augmented. SbF_5 by complexing R_3SiF effectively increases the electronegativity of fluorine and thus the ionic character of the Si–F bond (valence orbital contraction on fluorine and bond elongation) thereby enhancing the contribution of silicon to the σ^* molecular orbital (LUMO) resulting in a substantial lowering of the energy level. As for the incoming nucleophile, fluoride in an aprotic solvent has a high-lying HOMO (n-electrons), which now has a compatible energy level to mix with the σ^* of the silane (Chart III).

There is no free fluoride ion involved, but as SbF_5 complexes the silyl fluoride the fluorines attached to the antimony become more labile. There is no need for involvement of the empty d-orbitals on silicon which woiuld be destabilizing since empty orbitals cannot delocalize developing positive charge. Due to these perturbation arguments and the entropically disfavored arrangement in an S_N2-Si intermediate, it is suggested that fluorine exchange between trialkylsilyl fluorides and SbF_5 proceeds by a S_Ni-Si intermediate at very fast rates even at low temperatures. As increased bulkiness of the substituents around silicon retards the rate of this reaction this corroborates the rationale for an S_Ni-Si type exchanging system. Certainly, the highly deshielded silicon atom of three of the studied substrates indicates significant positive charge on silicon and therefore a noticeable silicenium ion contribution. Indeed, if one envisions fast equilibrium between silicenium ion **1** and siliconium ion **3** and then approximates the expected ^{29}Si chemical shift value of the exchanging system by averaging the projected chemical shifts of **1** and **3** (the average of $\delta(^{29}Si)$ 250 for Me_3Si^+ and $\delta(^{29}Si)$ −50 for $Me_3SiF_2^-$), the overall ^{29}Si resonance would be $\delta^{29}Si$ 100 (eq 4).



The actually observed value of $\delta(^{29}Si)$ 102 for the Me_3SiF/SbF_5 system may be coincidental but could be taken as indicative of the proposed involvement of exchanging ionic structures. The SbF_4^+ ion is not unprecedented, and it has been involved as electrophile in the reaction of di-*tert*-butylacetylene with SbF_5.[20] It is, however, not possible for NMR techniques to ascertain whether **1** and **3** could be actual intermediates and local minima on the potential energy surface or whether these ions represent only resonance forms in the valence bond description of the system. The activation barrier for the interconversion equilibrium depicted in eq 4 would necessarily be smaller than the barrier of the transition from Lewis acid–base adduct to **1** or **3**, since on lowering the temperature quenching of the exchange and not interchange between **1** and **3** is observed. It is therefore reasonable to suggest **2** as the exchanging system with a finite lifetime since the ^{29}Si NMR deshielding is clearly too large for a typical only slightly polarized silyl fluoride–Lewis acid complex. Structures **1** and **3** can be considered limiting resonance structures for **2**.

In our studies we were only interested in finding the actual limit of steric crowding to prevent the exchange from occurring. A static R_3SiF/SbF_5 system would most likely be still only a polarized Lewis acid–base adduct, although it would offer the possibility of ionization to the highly crowded silicenium ion.

Not wanting to leave this possibility unexplored we proceeded to investigate the t-Bu_3SiF system since the screening of the silicon atom by the three bulky *tert*-butyl groups was reported to be responsible for a variety of unusual properties of this and other t-Bu_3SiX compounds.[27] The Si–H stretching frequency of 2078 cm^{-1} for X = H is the lowest value for organosilanes recorded so far indicative of an extraordinarily electron rich Si–H bond.[27a] More importantly, the preferred mode of substitution reaction on the silicon center is electrophilic rather than the generally observed facile nucleophilic displacement via pentacoordinated silicon intermediates.[27a–c] We treated t-Bu_3SiF with various amounts of excess SbF_5 in SO_2ClF. Weidenbruch et al.[27b] indeed first reported in 1977 the ^1H and ^{19}F NMR data on this system and concluded Lewis acid–base complex formation because of a failure to observe t-Bu_3Si-Nu derivatives when quenching the reaction mixture with NuH[27b] (AcOH, H_2O, PhH). Even if the silicenium ion had formed, the nucleophilic quenching products could not necessarily have been observed due to the highly favorable protolytic cleavage reaction that would regenerate the Si–F bond (eq 5). The reported ^1H and ^{19}F NMR data in 5-fold excess of SbF_5 were inconclusive concerning generation of any fast exchanging strongly polarized complex, since only a slightly deshielded ^1H NMR signal was observed with disappearance of the ^{19}F resonance. We reinvestigated the system and found the ^1H methyl singlet as well as the ^{19}F resonance to be broad at concentrations of 3- to 5-fold excess of SbF_5 from −30 to −60 °C in contrast to the less hindered silyl fluorides, Me_3SiF and Et_3SiF. We were not able to reproduce the total disappearance of the ^{19}F signal but did observe a decrease of its intensity paralleled by extensive line broadening at higher SbF_5 concentrations. The ^{13}C NMR study, however, unequivocally proved that the system is that of a polarized Lewis acid–base adduct at concentrations up to 4-fold excess of SbF_5 even at −40 °C as evidenced by a well-resolved doublet for the quaternary carbon at $\delta(^{13}C)$ 22.5 ($^2J_{C-F}$ = 12.2 Hz) along with the methyl singlet at $\delta(^{13}C)$ 26.7. If fluorine exchange were still operative at this stage it would have to be slow on the NMR time scale. At still higher excess of SbF_5 as well as at higher temperature both the methyl and the quaternary carbon peaks broaden even further and the coupling of the latter to fluorine could no longer be resolved, again suggesting the onset or an increased rate of fluorine exchange. At somewhat elevated temperature of −30 °C we noticed protolytic cleavage of the *tert*-butyl groups to occur generating Me_3C^+ cation in a competing reaction, due to inevitable protic impurities in the SbF_5 used. We were unsuccessful in

$$t\text{-Bu}_3\text{SiNu} + \text{HF/SbF}_5 \rightarrow t\text{-Bu}_3\text{SiF/SbF}_5 + \text{NuH} \qquad (5)$$

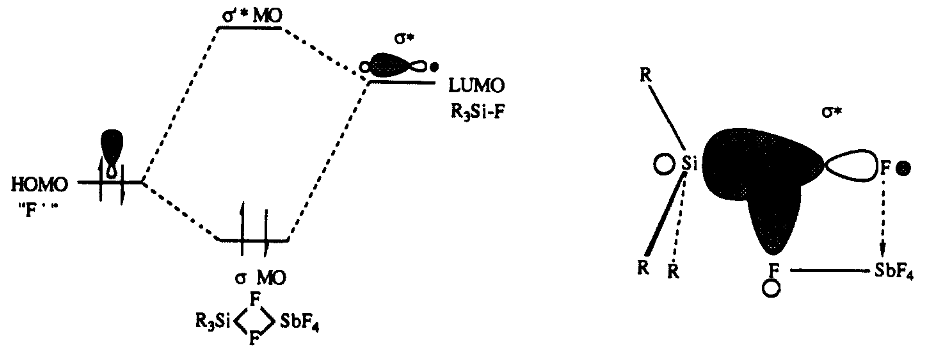
---

[26] Anh, N. T.; Minot, C. *J. Am. Chem. Soc.* **1980**, *102*, 103. For related discussion see: Chojnowski, J.; Fortuniak, W.; Stańczyk, W. *J. Am. Chem. Soc.* **1987**, *109*, 7776.

[27] (a) Weidenbruch, N.; Peter, W. *Angew. Chem.* **1975**, *87*, 670. (b) Weidenbruch, M.; Pesel, H.; Peter, W.; Streichen, R. *J. Organomet. Chem.* **1977**, *141*, 9. (c) Eaborn, C.; Saxena, A. K. *J. Organomet. Chem.* **1984**, *271*, 33.

[28] Dauben, H. J., Jr.; Honnen, L. R.; Harmon, K. M. *J. Org. Chem.* **1960**, *25*, 1442.

Chart III



obtaining ^{29}Si NMR spectra at any temperature or concentration examined, possibly due to lack of protons β to the silicon center entailing long relaxation times for the relatively insensitive ^{29}Si nucleus. The three bulky *tert*-butyl substituents seem to introduce a sufficient steric barrier to preclude the fluorine exchange reaction to the limit where protic cleavage starts to take over as a competing reaction. Steric crowding around silicon, however, still does not lead to a persistent silicenium ion.

Conclusions

The ^{29}Si NMR spectroscopic study of trimethylsilyl perchlorate in sulfolane solution showed that no persistent, long-lived ionic silicenium ion and no equilibrium with covalent perchlorate was observed up to 0.15 M concentration. In highly dilute solutions hydrolysis by water impurity in the solvent gives perchloric acid and siloxanes (silanols).

Studies directed to find conditions for observable persistent trialkylsilicenium ions indicate that the strongest of Lewis acids, SbF_5, brings abount a fast exchange reaction with fluorotrialkylsilanes rendering the silicon atom electron deficient as shown by ^{29}Si NMR spectroscopy to an heretofore unprecedented degree. The exchange reaction proceeds by a S_Ni-Si intermediate as shown by the steric effect of increasingly bulkier alkyl groups around silicon as well as considerations of frontier orbital perturbation theory. From these studies one can also estimate the ^{29}Si NMR chemical shifts of the yet unobserved free trialkylsilicenium ions.

We would like to emphasize that transient formation of trivalent silyl cation intermediates readily takes place in silicon chemistry not only in hydride-transfer reactions with carbocations but also in S_N1-type reactions and rearrangements of organosilanes. There is also no difficulty in assuming in principle that in highly dilute solutions of polarized trialkylsilyl esters (including perchlorates) or trialkylsilyl halide–Lewis acid complexes some ionic equilibria may be present. However, so far no silicenium ions could be observed by spectroscopic means in these systems. Extreme care is needed in interpreting the results of conductivity and cryoscopic experiments due to problems associated with maintaining dilute solutions free of impurities. Silyl cations are further well-studied in the gas phase. It is not the lack of thermodynamic stability but kinetic instability that renders their observation as long-lived, persistent species so far unsuccessful in solution.

Experimental Section

Me_3SiF, Me_3SiH (PCR), *i*-Pr_3SiH, and Ph_3SiH (Aldrich) were commercially available and checked for sufficient purity prior to use (GC/MS). Et_3SiH (Petrarch) was distilled before use due to major $(Et_3Si)_2O$ contamination. All the solvents used in this study such as SO_2ClF, CH_3CN, and CH_2Cl_2 were rigorously purified and dried following literature procedures. Sulfolane was rigorously purified by initial heating with KOH at 100 °C for 2 days followed by double distillation over CaH_2 in an argon atmosphere.

NMR Spectra. ^{13}C spectra were recorded on either a Varian Associates Model FT 80 (external lock) or Varian Associates Model VXR 200 (data system VXR 4000) NMR spectrometer equipped with a 10-mm and a 5-mm broadband variable-temperature probe, respectively. All ^1H, ^{29}Si, and ^{19}F spectra were obtained on the latter, operating with an internal lock provided by an acetone-d_6 capillary. ^1H, ^{13}C, and ^{29}Si resonances were referenced to external (capillary) tetramethylsilane and ^{19}F signals to external $CFCl_3$ at $\delta = 0.00$ ppm, respectively. The following specific conditions were used to obtain 39.742 MHz ^{29}Si NMR spectra of trimethylsilyl perchlorate samples. Each sample was run over a period of 24 h with a pulse delay of 10 s and a pulse width of 45°.

Mass Spectra. Mass spectra were obtained on a Finnigan MAT INCOS 50 mass spectrometer operating at an ionization voltage of 70 eV, coupled with a Varian 3400 gas chromatograph (silicon glass capillary column DB5-30N, 0.25-μm film).

Preparation of Et_3SiF, *i*-Pr_3SiF, and *t*-Bu_3SiF. R_3SiH (10 mmol) was reacted with 5 mL of pure HF/pyridine (60:40) in a capped Teflon flask for 24 h at room temperature with vigorous stirring (magnetic bar). The resulting mixture is poured into 50 mL of water and extracted three times with 20-mL portions of CH_2Cl_2. The combined extracts are washed with 5 *m* HCl and water again and dried over $NaHCO_3$ and $MgSO_4$. After evaporation of the CH_2Cl_2 the pure (GC/MS) R_3SiF was isolated by distillation. *tert*-Butyl fluoride was prepared following the procedure of Weidenbruch et al.[27b] Trityl perchlorate was freshly prepared[28] and used under a blanket of dry argon.

Preparation of $Me_3SiOClO_3$ in Sulfolane and Acetonitrile. Into an oven-dried tube charged with dry argon gas was placed 68.5 mg of trityl perchlorate, and 2 mL of acetonitrile was added via a syringe to give a homogeneous orange 0.1 M solution. Me_3SiH was then introduced into the solution until the original color of the trityl salt completely disappeared. An aliquot of the resulting solution was transferred into an oven-dried 5-mm NMR tube and the ^1H NMR spectrum recorded. Solutions of other concentrations were prepared by dilution of aliquots of the original solution in acetonitrile. The sulfolane solutions of $Me_3SiOClO_3$ were prepared in an analogous manner (solidified sulfolane had to be gently heated for transfer).

Preparation of $R_3SiF{:}xSbF_5$ Complexes. Freshly triply distilled SbF_5 was used. A preweighed amount of SbF_5 dissolved in 1 mL of dry SO_2ClF is treated with the appropriate amount of trialkylsilyl fluoride at −95 °C (using ethanol/liquid N_2 slush).

Acknowledgment. Support of our work by the National Science Foundation is gratefully acknowledged.