Angewandte
International Edition Chemie

DOI: 10.1002/anie.201203970

Gas-Phase Reactions

Sequential Methyl–Fluorine Exchange Reactions of Siloxide Ions in the Gas Phase**

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Organosilanols have received increasing attention as useful reagents in organic synthesis,[1] as precursor compounds for materials,[2] and as intermediates in sol-gel processes that involve the hydrolysis and polycondensation of alkoxysilanes, thus leading to hybrid nanomaterials, siloxane-type oligomers, and zeolite-type compounds.[3] Silanols are more acidic than alcohols both in solution and in the gas phase,[4] and their conjugate bases, $\equiv$Si$-$O$^-$ species, play a crucial role in the initial steps of polymerization reactions of alkoxysilanes in basic media. As a result, a number of theoretical studies have addressed the role of silanols and siloxide species to better understand the mechanism of the initial steps of sol-gel processes.[5] Likewise, several aspects of the fundamental reactivity of alkoxysilanes in these processes have been probed by gas-phase ion-chemistry techniques in an attempt to characterize the intrinsic properties of these substrates.[6]

During our studies of the gas-phase reactivity of simple R_3MO^- (M = Si, Ge, and Ti) ions we discovered an unusual gas-phase metathesis-type reaction for some of these anions that is promoted by NF_3 and other fluorinated species and results in the exchange of the alkyl groups by fluorine. This is a remarkable reaction and should attract much interest because the presence of a fluorine atom directly bonded to the silicon center of a $\equiv SiO^-$ species can dramatically influence the reactivity of this moiety.[7]

The kinetics data for the gas-phase reaction of Me_3SiO^- ions in the presence of NF_3 is presented in graphical form in Figure 1. In these experiments, Me_3SiO^- ions were generated and trapped in an FT-ICR spectrometer[8] from the reaction of F^- (generated from NF_3 at nominal pressures of approximately 2.1×10^{-8} Torr)[9] and Me_3SiOEt (maintained at nominal pressures of approximately 7.8×10^{-9} Torr). The primary fluoride ion reactants were obtained by dissociative electron attachment inside the cell of the FT-ICR spectrometer. Because the gas-phase reaction of F^- and Me_3SiOEt yields predominantly EtO^- by direct displacement, isolation of the Me_3SiO^- ions was achieved by continuous ejection of the EtO^- ions and removal of other primary products by a series of short radiofrequency pulses tuned to the cyclotron frequencies of the unwanted ions. This method prevented reactions involving EtO^- ions, thus proving effective for our purposes.

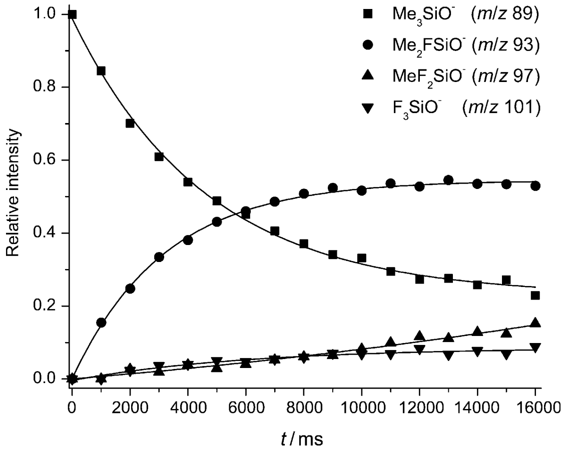

Figure 1. Reaction kinetics of NF_3 (2.12×10^{-8} Torr) reacting with Me_3SiO^- (*m*/*z* 89), which is generated from the reaction of F^- and Me_3SiOEt (7.8×10^{-9} Torr). The partial pressures are nominal values measured with an ionization gauge.

The kinetics data (Figure 1) are consistent with a set of reactions in which methyl groups are sequentially exchanged with fluorine [Eq. (1)].

$$Me_{3-n}F_nSiO^- + NF_3 \rightarrow Me_{2-n}F_{n+1}SiO^- + MeNF_2\ (n = 0-2) \qquad (1)$$

These sequential exchange reactions were calculated at the DFT/B3LYP/6-311+G(3df,2p) level of theory as being highly exothermic: ΔH° at 298 K for the exchange reaction of $Me_{3-n}F_nSiO^-$ where $n = 0$, 1, and 2 was calculated as being -358.0, -353.4, and $-338.2\ \mathrm{kJ\,mol^{-1}}$, respectively. The rate constant for the $n = 0$ reaction was estimated using the calibrated pressure for NF_3 and the general procedure outlined in a previous publication[8] and was found to be approximately $7\times10^{-11}\ \mathrm{cm^3\,molecule\,s^{-1}}$.[8] The fact that methyl groups are replaced sequentially in this transformation was further confirmed by studying the dependence of the

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[**] This project was supported by funding from the Air Force Office of Scientific Research (AFOSR), the Brazilian Research Council (CNPq), the São Paulo Research Foundation (FAPESP), and the National Institute of Science, Technology and Innovation of Complex Functional Materials (INOMAT). We thank Mathias Bickelhaupt for suggesting the halogen-attack pathway and Veronica Bierbaum for discussions regarding our experimental results. T.C.C. acknowledges CNPq for a graduate fellowship and J.M.R. acknowledges the support of the Office for Higher Education of Brazil (CAPES) through its National Senior Visiting Professorship Program.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201203970.

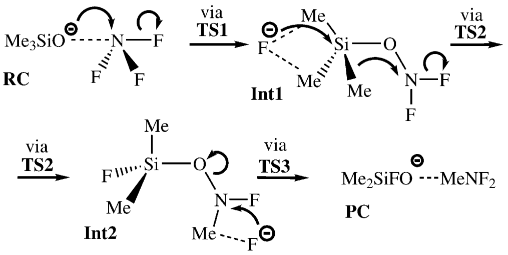
kinetics on the partial pressure of NF_3. In addition, the second Me/F exchange reaction was independently characterized through experiments in which Me_2FSiO^- was generated directly from a different precursor.

Considering that NF_3 as a neutral substrate is relatively inert in gas-phase negative-ion chemistry,[10] we explored other neutral substrates to better understand these reactions. For example, the use of SO_2F_2, both as a precursor of F^- ions and as a neutral substrate to react with Me_3SiO^-, also resulted in the same type of sequential reactions together with the observation of other reaction products that are presently under investigation.

The apparent simplicity and the novelty of the Me_3SiO^-/NF_3 reaction [Eq. (1)] motivated us to carefully consider possible mechanisms. Previously, when the gas-phase reaction between Me_3SiO^- and SiF_4 was studied using flowing-afterglow techniques, it was revealed that F_3SiO^- presumably forms through a mechanism that involves nucleophilic attack on SiF_4 followed by nucleophilic internal return of the nascent fluoride ion,[11] a mechanism, which is analogous to that of the reaction promoted by alkoxide ions.[12] The outcome of reaction between Me_3SiO^- and NF_3 is different from what would be predicted based on these previous examples. Therefore, the reaction was investigated using model chemistry calculations, which is a valuable means for studying reactions involving siloxide-type anions.[13] Calculations were carried out at the DFT/B3LYP/6-311+G(3df,2p) level of theory, after a preoptimization at the DFT/B3LYP/6-31+G(d) level of theory, with the Gaussian 03 suite of programs.[14a] Stationary points were characterized by vibrational-frequency analyses using the same basis set. Connectivity along the reaction coordinate was confirmed by IRC calculations,[15] which were carried out with the Gaussian 09 suite of programs.[14b] A scale factor of 0.964 was used for the zero-point-energy (ZPE) corrections.[16]

Three possibilities for the first step of the reaction were considered: a) nucleophilic attack of the siloxide ion at the nitrogen center; b) nucleophilic attack of the siloxide ion at a fluorine atom of the neutral NF_3; and c) activation of Me_3SiO^- to release an incipient Me^- anion and silanone, that is, induced dissociation of Me_3SiO^- ions.[17] Only the first mechanism was predicted to proceed through a nearly barrierless process, which would be compatible with our experimental rate constant ($k_{exp} > 10^{-2}\, k_{collision}$). The other two mechanisms were predicted to involve sizable activation energies (in the range of 125 $kJ\,mol^{-1}$ above the energy of the reactants) and thus would not be expected to occur within the time scale of our FT-ICR experiment in the absence of some form of ion activation.

Nucleophilic attack at a nitrogen center is not a very common process and only a few facile gas-phase displacement reactions at a nitrogen center have been experimentally observed[18] and are supported by theoretical calculations.[19] In our case, backside attack of the siloxide ion on the nitrogen center is predicted to proceed initially through the formation of a weakly bound reactant complex (**RC**), which then proceeds further through a transition state (**TS1**; Scheme 1) that is isoenergetic with the reactants at our level of theory (Figure 2). The reaction is then calculated to proceed further through internal nucleophilic return of the nascent fluoride ion, which becomes loosely attached to Me_3SiONF_2 to yield an intermediate identified as **Int1** [$F^-\cdots Me_3SiONF_2$], which is predicted to be considerably more stable than the reactants. **Int1** then evolves further, via **TS2**, through a concerted attack of the loosely attached fluoride ion on the silicon center and displacement of a Me^- ion, which attacks the nitrogen center.



Scheme 1. Proposed reaction mechanism for the Me/F exchange reaction of Me_3SiO^- mediated by NF_3. Dashed line represents loose bonds between fragments.

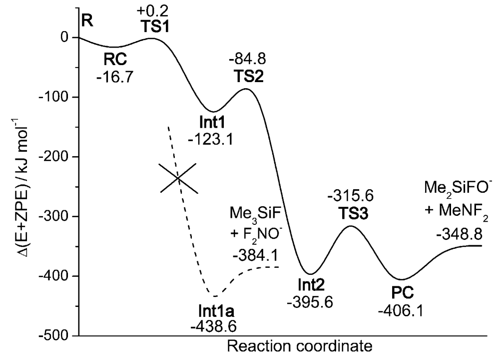


Figure 2. Energy diagram for the Me_3SiO^-/NF_3 reaction calculated at the B3LYP/6-311+G(3df,2p) level of theory. The dashed line represents the hypothetical (and unobserved) pathway that would lead to the formation of Me_3SiF and F_2NO^- via adduct **Int1 a**.

This concerted transformation, which proceeds via **TS2**, leads to the loosely bound intermediate **Int2** [$F^-\cdots N(F)(Me)OSi(F)Me_2$]. **Int2** can then further proceed by an F^- attack on the nitrogen center via **TS3** resulting in the breakage of the O–N bond and formation of the product complex (**PC**) [$Me_2SiFO^-\cdots MeNF_2$]. This complex can then dissociate into the final products of reaction (1; $n = 0$)

The calculated geometries for the intermediates and transition states of Scheme 1 are given in Figure 3 (the coordinates and energy data for all species can be found in the Supporting Information). Several points related to the structural data deserve highlighting:

a) the geometry of **TS1** resembles the transition states calculated for S_N2 reactions of halide ions at the nitrogen center of haloamines (NH_2X, X = F, Cl, Br, I);[20]
b) comparison of the geometries of **Int1** and **TS2** reveals that while the approach of F^- to the silicon center results in the elongation of the Si–Me bond (from 1.878 to 2.610 Å), the approach of the Me group to the nitrogen center causes the synchronous elongation of the N–F bond (from approximately 1.5 to 1.944 Å);

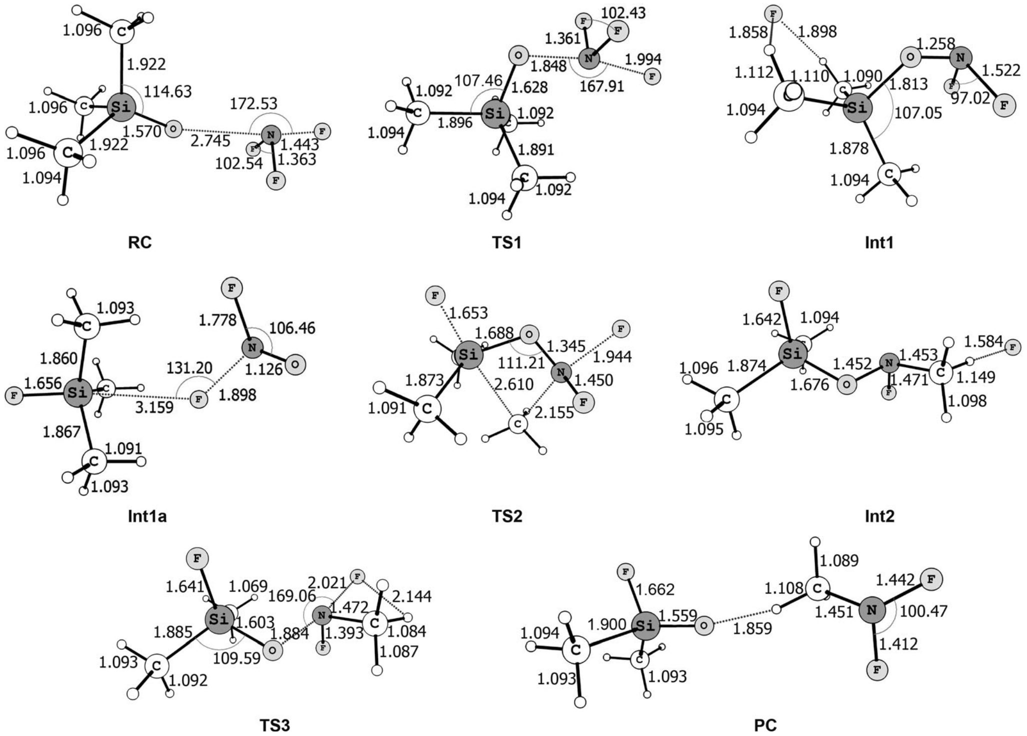


Figure 3. Calculated geometries for reaction intermediates and transition states at the B3LYP/6-311+G(3df,2p) level of theory. Distances are given in Å and angles are given in degrees.

c) the Me_2FSiO moiety is essentially formed in **Int2** and plays a secondary role in **TS3** other than the contraction of the Si–O bond that leads to the formation of the product complex (**PC**).

There are other interesting features in this mechanism that deserve further discussion. The internal nucleophilic return of F^- does not yield directly a pentacoordinated-siliconate species, $[F(Me)_3SiONF_2]^-$, which, by analogy with the reaction of Me_3SiO^- and SiF_4 reported by Damrauer et al., would be predicted to give NF_2O^- as the final ionic product.[11] Interestingly enough, attempts to optimize the pentacoordinated structure of the siliconate species result in **Int1a** (Figure 2), an intermediate that consists of Me_3SiF and FN=O bridged by F^- (The coordinates for **Int1a** can be found in the Supporting Information). The failure to characterize the pentacoordinated-siliconate species suggests that this species is not stable as a stationary point along the reaction coordinate, and if formed, would proceed directly to **Int1a**, yielding NF_2O^- and Me_3SiF as final products. The formation of the pentacoordinated species is believed not to occur for this system because NF_2O^- was not observed in our experiments. By comparison, the concerted attack of the fluoride ion on the silicon atom with the subsequent displacement of an incipient Me^- is consistent with previous gas-phase experiments on reactions of simple anions with silanes.[21]

Whereas previous experiments have shown the ability of gas-phase siliconate motifs to undergo exchange of alkoxy groups for fluorine,[22] reaction (1) is unique in its ability to undergo exchange of an alkyl moiety for fluorine. The gas-phase reactivity of a variety of other siloxide ions, within the context of the transformation described herein, is currently being explored.

Received: May 22, 2012

Keywords: exchange interactions · FT-ICR mass spectrometry · gas-phase reactions · reaction mechanisms · siloxides

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Communications

Gas-Phase Reactions

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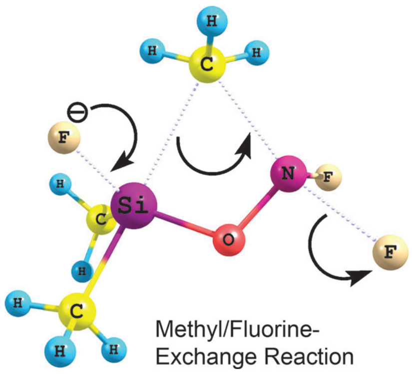
Sequential Methyl–Fluorine Exchange Reactions of Siloxide Ions in the Gas Phase



Exchange Me for a fluorine: Trimethylsiloxide ions in the presence of NF_3 in the gas phase undergo an unusual and sequential metathesis-type reaction wherein methyl groups are exchanged for fluorine. Theoretical calculations suggest that the reaction proceeds by a three-step internal-nucleophilic-displacement mechanism which features a pentacoordinated siliconate species (see picture) as a transition state rather than as an intermediate.