Experimental and theoretical studies of gas-phase reactions of SiF_x^+ ($x = 1$–3) with ammonia: intramolecular H-atom transfer reactions with SiF_3^+ and $F_2Si(NH_2)^+$

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Abstract

Gas-phase ion-molecule reactions between the Lewis acids SiF_x^+ ($x = 1$–3) and ammonia have been investigated both experimentally and theoretically. Experimental studies were performed with a selected ion flow tube (SIFT) apparatus with helium buffer gas at 294 ± 3 K and at 0.35 ± 0.01 Torr. The monofluorosilicon cation SiF^+ was found to be unreactive toward ammonia, while SiF_2^+ was observed to undergo electron transfer with NH_3. The trifluorosilyl cation SiF_3^+ reacted consecutively with two ammonia molecules by HF elimination to produce $FSi(NH_2)_2^+$ which subsequently reacted with three NH_3 molecules in succession to form adduct ions, with no further HF eliminations. Molecular orbital calculations were performed on all ionic and neutral molecular species associated with the chemistry of SiF_3^+. Gradient optimizations were performed on reactants, on transition structures, and on products, both at the Hartree-Fock (HF)/3-21G level of theory, and at the density functional Becke-Lee-Yang-Parr (B-LYP)/6-31$G(d,p)$ level. Harmonic frequency calculations were performed on all optimized structures at critical points at the latter level, from which, also, zero-point vibrational energies (ZPE) were obtained. The results of molecular orbital investigations revealed mechanistic insight into the experimentally-observed HF elimination reactions; in particular, the occurrence of H-atom transfer on a double-minimum potential-energy hypersurface. Theory also confirmed the thermodynamic legitimacy of the observed reactions and the validity of the nonobservation of a HF elimination reaction between $FSi(NH_2)_2^+$ and ammonia under SIFT conditions, a process that was reported to have occurred in a previous Fourier transform ion cyclotron resonance (FTICR) study. Molecular orbital calculations also have shown that the lowest-energy isomer associated with the empirical formula of the second adduct ion, $FSi(NH_2)_2(NH_3)_2^+$, is one which has a nearly tetrahedral geometry in the heavy atoms, and solvates an ammonia molecule by hydrogen bonding. Comparisons also were made between the results of the present study and those of an earlier SIFT investigation of the reactions of Lewis acids SiF_x^+ ($x = 1$–3) with H_2O. (Int J Mass Spectrom 185/186/187 (1999) 381–392) © 1999 Elsevier Science B.V.

Keywords: Gas-phase ion chemistry; Silicon fluoride cations; Ammonia; Intramolecular H-atom transfer; Selected-ion flow tube; Molecular orbital calculations; Structures and stabilities

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1. Introduction

Recent experimental investigations in our laboratory have shown that the silicon–fluoride cations SiF^+, SiF_2^+ and SiF_3^+ all react with H_2O by HF elimination of type (1).

$$F_xSi(OH)_y^+ + H_2O \rightarrow F_{x-1}(SiOH)_{y+1} + HF \qquad (1)$$
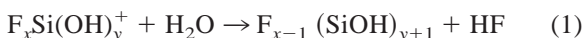
Concomitant theoretical investigations indicated that these reactions involve an *intramolecular H-atom transfer* on a double-minimum potential energy surface [1]. In the case of SiF_2^+ and SiF_3^+ sequential HF elimination reactions ultimately lead to the exchange of all Si–F bonds for Si–OH bonds in this manner [1]. Our experiments were performed with a selected ion flow tube (SIFT) apparatus at 293 ± 4 K and a helium pressure of 0.35 ± 0.01 Torr. An earlier FTICR study had indicated a similar behaviour for SiF_3^+ (at total pressures in the range 3×10^{-7} to 2×10^{-6} Torr) not only with water, but also with ammonia according to reaction (2) with x, y =

$$F_xSi(NH_2)_y^+ + NH_3 \rightarrow F_{x-1}Si(NH_2)_{y+1} + HF \qquad (2)$$
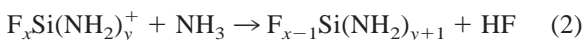
3, 0, 2, 1 and 1, 2 [2]. We report here the results of a SIFT study of reaction (2) and of studies extended to reactions of SiF^+ and SiF_2^+. It shall be seen that significant differences in reactivity are observable with ammonia both among the three fluorinated siliconium ions and in comparison with the water chemistry. However, HF elimination did again prevail with x, y = 3, 0 and 2, 1 but not 1, 2. Molecular orbital calculations are used to complement the experimental work and to provide insight into ion structures and thermodynamics. The calculations again establish a double-minimum potential energy surface for H-atom transfer and they can account for the differences between the water and ammonia chemistry in terms of differences in the thermodynamics of Si–O and Si–N bonding.

We have previously investigated the chemistry of other silicon-containing cations with ammonia in studies directed primarily toward the role of such reactions in the synthesis of Si–N containing neutral molecules as it might proceed in interstellar clouds [3]. Also, we have investigated ion chemistry with cyanides that leads to Si–N bonding [4].

2. Experimental methods

The gas-phase ion-molecule reactions reported in this study were investigated with the SIFT technique in the Ion Chemistry Laboratory at York University [5, 6]. The SiF_n^+ ions were produced by electron impact upon neutral SiF_4 (Matheson, >99.6 mol%) in a low-pressure ion source from a 3% mixture of SiF_4 in helium at various electron energies: 50 eV for SiF_3^+, 70 eV for SiF_2^+, and 80 eV for SiF^+. They were then mass selected with a quadrupole mass filter and introduced via a Venturi inlet into a flow of helium buffer gas at a pressure of 0.35 Torr. Ammonia (Matheson, anhydrous grade) was added into the reaction region downstream. Reactant and product ions were followed as a function of the amount of added ammonia. Rate coefficients were determined in the usual manner [5, 6]. The rate coefficients for primary reactions reported here are estimated to have an uncertainty of at most ±30%. Higher-order rate coefficients were obtained by fitting the experimental data to the solutions of the system of differential equations for successive reactions. Reverse reactions were not included. The one branching reaction observed was included explicitly in the reaction mechanism. The accuracy for this fitting procedure depends on several parameters and is reported separately for every calculated high-order rate coefficient.

3. Computational methods

Theoretical calculations were performed using the GAUSSIAN suite of programs [7]. Geometry optimizations of all critical points of closed-shell potential energy surfaces have been performed with the restricted Hartree-Fock (RHF) formalism with a split-valence 3-21G basis set [8]. Subsequently, geometry optimizations were performed on the same molecules with the density functional [9] Becke technique which includes the Slater (local spin density) exchange functional [9(a), (b), 10] with nonlocal gradient-corrected terms included [11], and the Lee-Yang-Parr method which includes local and nonlocal gradient-corrected correlation functionals [12]. Geometry op-

timizations and subsequent harmonic frequency calculations at this level [henceforth denoted Becke-Lee-Yang-Parr (B-LYP)] were performed using the standard Gaussian split-valence 6-31$G(d,p)$ basis set [12, 13]. Transition structures were located either by an initial point-by-point profile analysis, followed by refinement with the eigenvector-following (EF) algorithm [14], or directly from the geometries of the two associated local minima by the synchronous transit-guided quasi-Newton (STQN) method [15]. Intrinsic reaction coordinate (IRC) [16] analyses were performed to verify the identities of the two ions at local minima that are interconnected through each transition structure. All critical points were subjected to harmonic frequency calculations at the same level of theory as that used in the optimizations. These calculations provided zero-point vibrational energies.

Geometry optimizations of all the critical points on the open-shell potential energy surfaces were performed with the restricted open-shell Hartree-Fock (ROHF) [17] formalism, first with the 3-21G basis set, then with the 6-31$G(d,p)$ basis set. Harmonic frequency calculations were performed at ROHF/6-31$G(d,p)$ on all critical points optimized at this level of theory.

4. Experimental results

The rate coefficients for the three primary reactions obtained from the semilogarithmic decay of the primary ions and the higher-order rate coefficient obtained by fitting the observed ion–signal profile for the higher-order ion are summarized in Table 1.

SiF^+ + NH_3: SiF^+ cations were observed not to react with ammonia, $k < 1 \times 10^{-13}$ cm^3 mol^{-1} s^{-1}, under our SIFT conditions. This result is not surprising. Electron transfer with ammonia is endothermic by 66 kcal mol^{-1} (ionization energy IE(SiF$^.$) = 7.28 eV and IE(NH$_3$) = 10.16 ± 0.01 eV [18]) and our calculations at the B-LYP/6-31$G(d,p)$ level of theory indicate that the HF-elimination reaction (3) is endothermic by 4.5 kcal mol^{-1}.
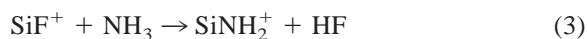
$$SiF^+ + NH_3 \rightarrow SiNH_2^+ + HF \tag{3}$$

Table 1
Rate coefficients and reaction probabilities for reactions with ammonia

Reactant ion	Products	k_{exp}^a	k_c^b	k_{exp}/k_c^c
SiF^+	none	<0.001	22	$<5 \times 10^{-5}$
$SiF_2^{.+}$	$NH_3^{.+}$ + SiF_2	8.0	21	0.38
SiF_3^+	$F_2SiNH_2^+$ + HF	4.9	21	0.23
$F_2SiNH_2^+$	$FSi(NH_2)_2^+$ + HF	5.3	21	0.25
	$F_2Si(NH_2)NH_3^+$			
	NH_4^+ + F_2SiNH			

[a] The k_{exp} values are the measured effective bimolecular reaction rate constants at a temperature of (294 ± 3) K and at a helium buffer gas pressure of (0.35 ± 0.01) Torr, and are reported in units of 10^{-10} cm^3 mol^{-1} s^{-1}. The absolute accuracies of these rate constants are ±30%; relative accuracies are smaller than ±10%.
[b] The collision rate constants, k_c, are derived from a transition-state treatment [T. Su, W.J. Chesnavich, J. Chem. Phys. 76 (1982) 5183].
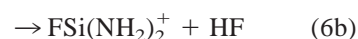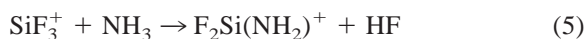[c] k_{exp}/k_c ratios are measures of reaction efficiencies.

$SiF_2^{.+}$ + NH_3: The experimental results obtained for this reaction are shown in Fig. 1 and are consistent with the occurrence of an electron transfer as indicated in reaction (4). Electron transfer is exothermic by 0.62 eV (14 kcal mol^{-1}) because IE(SiF$_2$) = 10.78 ± 0.05 eV [18].

$$SiF_2^{.+} + NH_3 \rightarrow SiF_2 + NH_3^{.+} \tag{4}$$

HF elimination to produce $FSiNH_2^+$ was not observed, <1%. The rapid secondary reaction observed in Fig. 1 between $NH_3^{.+}$ and ammonia to yield NH_4^+ is well known in the literature [19].

SiF_3^+ + NH_3: Fig. 2 displays the chemistry initiated by SiF_3^+ in ammonia. The observed ion profiles are consistent with the occurrence of two sequential HF elimination reactions, reactions (5) and (6a), followed by three sequential ammonia "solvation" reactions, reactions (7a)–(9).

$$SiF_3^+ + NH_3 \rightarrow F_2Si(NH_2)^+ + HF \tag{5}$$

$$F_2Si(NH_2)^+ + NH_3 \rightarrow F_2Si(NH_2)NH_3^+ \tag{6a}$$

$$\rightarrow FSi(NH_2)_2^+ + HF \tag{6b}$$
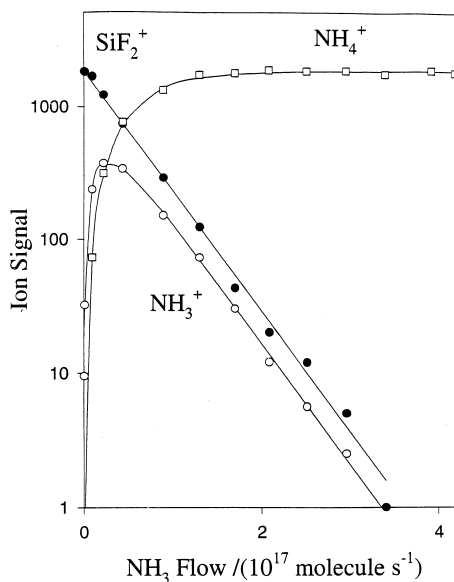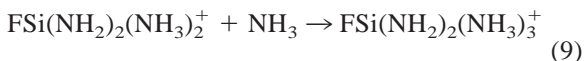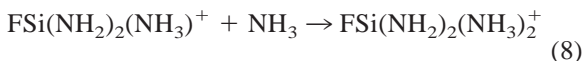
$$\rightarrow NH_4^+ + F_2SiNH \tag{6c}$$

Fig. 1. Variations in ion signals recorded as a function of the flow of ammonia added to a helium buffer gas in which SiF_2^+ has been established as a predominant ion.
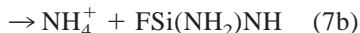

Fig. 2. Variations in ion signals recorded as a function of the flow of ammonia added to a helium buffer gas in which SiF_3^+ has been established as a predominant ion. SiF_2^+ and F_2SiOH^+ were also initially present due to the collisional dissociation of SiF_3^+ upon injection and the reaction of SiF_3^+ with water impurities in the helium, respectively. Both of these ions were present in amounts less than 15% of the initial SiF_3^+ signal. The known contributions of the chemistry initiated by these two ions with ammonia to the formation of NH_4^+ have been subtracted from the NH_4^+ profile.

$$FSi(NH_2)_2^+ + NH_3 \rightarrow FSi(NH_2)_2(NH_3)^+ \qquad (7a)$$

$$\rightarrow NH_4^+ + FSi(NH_2)NH \quad (7b)$$

$$FSi(NH_2)_2(NH_3)^+ + NH_3 \rightarrow FSi(NH_2)_2(NH_3)_2^+ \qquad (8)$$

$$FSi(NH_2)_2(NH_3)_2^+ + NH_3 \rightarrow FSi(NH_2)_2(NH_3)_3^+ \qquad (9)$$

The effective bimolecular rate constant k for the initial HF elimination is 4.9×10^{-10} cm^3 mol^{-1} s^{-1}. Electron transfer does not compete as a primary reaction because of the low ionization energy of SiF_3 which has been reported to be 9.3 eV [18]. Reaction (6) also proceeds rapidly, $k = 5.3 \times 10^{-10}$ cm^3 mol^{-1} s^{-1}, as does reaction (7) for which we can report only a lower limit, $k > 1 \times 10^{-10}$ cm^3 mol^{-1} s^{-1}, because of the complexity introduced into the fitting procedure by the occurrence of three product channels in the precursor reaction (6). We estimate product fractions of 0.4/0.35/0.25 for reactions (6a)/(6b)/(6c) and 0.6/0.4 for reactions (7a)/(7b). They were obtained from an ion-signal ratio plot in the usual manner. The thermodynamics of the proton-transfer channels (6c) and (7b) could not be estimated
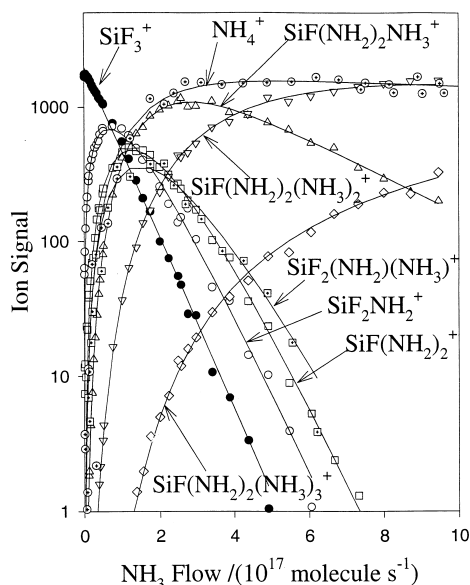
because of the unknown proton affinities of the molecules F_2SiNH and $FSi(NH_2)NH$.

Not all fluorine atoms of SiF_3^+ are eliminated by sequential HF elimination; the HF elimination reaction of $FSi(NH_2)_2^+$ with ammonia was not observed under our experimental operating conditions. This result is different from that found in an earlier Fourier transform ion cyclotron resonance (FTICR) study at much lower pressures that has reported the observation of *three* successive HF eliminations ultimately to form $Si(NH_2)_3^+$ which then undergoes NH_3 additions [2]. It is possible that HF elimination is preempted in our higher-pressure experiments by collisional stabilization to form the adduct ion. But, as will be shown later, the results of our calculations indicate that the third HF elimination is actually endothermic by 7.0 kcal mol^{-1}. This would imply that the reacting ions in the FTICR apparatus had some suprathermal kinetic or internal energy.

Table 2
Total energies (in Hartrees) and zero-point energies (in kcal mol^{-1}) for molecular species associated with the ammonia chemistry of SiF$_3^+$

Molecule	HF/3-21G	B-LYP/6-31$G(d, p)$	ZPE[a]
NH$_3$, **1**	$-55.872\,20$	$-56.528\,21$	21.0
HF, **2**	$-99.460\,22$	$-100.411\,48$	5.6
SiF$_3^+$, **3**	$-583.895\,98$	$-588.773\,09$	5.8
F$_3$SiNH$_3^+$, **4**	$-639.969\,78$	$-645.452\,77$	30.6
TS **4 → 6**, **5**	$-639.880\,77$	$-645.370\,59$	27.4
F$_2$Si(NH$_2$)$^+$ . . . FH, **6**	$-639.903\,30$	$-645.375\,87$	27.5
F$_2$SiNH$_2^+$, **7**	$-540.357\,39$	$-544.908\,69$	20.3
F$_2$Si(NH$_2$)(NH$_3$)$^+$, **8**	$-596.388\,70$	$-601.552\,00$	44.8
TS **8 → 10**, **9**	$-596.302\,53$	$-601.473\,99$	41.7
FSi(NH$_2$)$_2^+$ . . FH, **10**	$-596.316\,15$	$-601.475\,14$	41.6
SiF(NH$_2$)$_2^+$, **11**	$-496.792\,76$	$-501.025\,69$	34.5
FSi(NH$_2$)$_2$(NH$_3$)$^+$, **12**	$-552.789\,24$	$-557.641\,62$	59.2
Si(NH$_2$)$_3^+$, **13**	$-453.206\,93$	$-457.130\,12$	49.2
Si(NH$_2$)$_2$(NH$_3$)$_2^+$, **14**	$-608.709\,24$	$-614.210\,03$	81.7

[a]From B-LYP/6-31$G(d, p)$ harmonic frequency calculations; unscaled.

Not shown in Fig. 2 are the chemistries initiated by the presence of SiF$_2^+$ ions formed by the collisional dissociation of the injected SiF$_3^+$ and the presence of F$_2$SiOH$^+$ formed by the reaction of SiF$_3^+$ with water impurities in the helium. Details of the water chemistry proceeding under SIFT conditions have been reported elsewhere [1].

5. Theoretical results

Given that SiF$^+$ is nonreactive with ammonia and that SiF$_2^+$ reacts only by electron transfer, we restricted our calculations to the chemistry initiated by SiF$_3^+$. Results of the calculations are presented in Table 2 which provides total energies for individual molecular species at both HF/3-21G and B-LYP/6-31$G(d,p)$ levels of theory along with (unscaled) zero-point energies obtained with B-LYP/6-31$G(d,p)$ harmonic frequency calculations. The resulting optimized geometries are displayed in Fig. 3.

Fig. 3 contains a wealth of structural information and a few of the more interesting features will be discussed here. Comparison of structures **11**, **7** and **3** show the Si–F distance in ions SiF$_n$(NH$_2$)$_m^+$, where

$m + n = 3$, to decrease as n increases. These changes are comparable to those in fluorosilanes where the contraction in the Si–F distances with increased substitution by fluorine has been attributed to negative hyperconjugation [20–22]. In ions **7**, **11** and **13** the opposite behaviour is observed, with the Si–N distance increasing with the number of NH$_2$ groups. These geometric changes can be attributed, in part, to the greater ability of the NH$_2$ group (relative to F) to delocalize charge through π conjugation. Thus, in ion **7**, the amino group carries a large fraction of the positive charge and has the largest amount of Si–N double bond character. This is reflected in the Si–N distance of 1.645 Å which is considerably shorter than the distance in H$_3$SiNH$_2$ (1.724 Å at HF/6-31$G(d,p)$ [23]). Ion **11** has two NH$_2$ groups and, although individually these each carry less positive charge than the single NH$_2$ group in **7**, there is also less charge on the fluorine and consequently the Si–N and Si–F distances are all longer than in **7**. Delocalization of the charge onto NH$_2$ groups is maximized in Si(NH$_2$)$_3^+$, ion **13**, and here the Si–N distances are even longer. However, in **13** steric interactions between hydrogen atoms on adjacent nitrogen atoms force the amino groups to be twisted out of plane and into a conformation that is not optimum for π conjugation.

Ions **4**, **8** and **12** all contain a NH$_3^+$ group attached to silicon and the long Si–N distances (all >1.89 Å) indicate that these ions are best described as being SiF$_n$(NH$_2$)$_m^+$ silyl cations strongly "solvated" by an ammonia molecule. The Si–N distance is shortest in ion **4**, SiF$_3^+$. . .NH$_3$, and longest in ion **13**, Si(NH$_2$)$_3^+$. . .NH$_3$, consistent with Si(NH$_2$)$_3^+$ being more stabilized by π conjugation and therefore having less need for stabilization from "solvation". In each "solvated" ion the Si–F and Si–N bond distances are all 0.02–0.03 Å longer than in the unsolvated ion, showing that "solvation" has a major effect on the geometries of these ions.

Ions **6** and **10**, both formally fluorosilanes protonated on silicon, have long Si–FH$^+$ bonds and are silyl cations SiF$_n$(NH$_2$)$_m^+$ "solvated" by HF. Finally, ion **14** is essentially ion **12** with an ammonia molecule attached to the "solvating" ammonia molecule. This
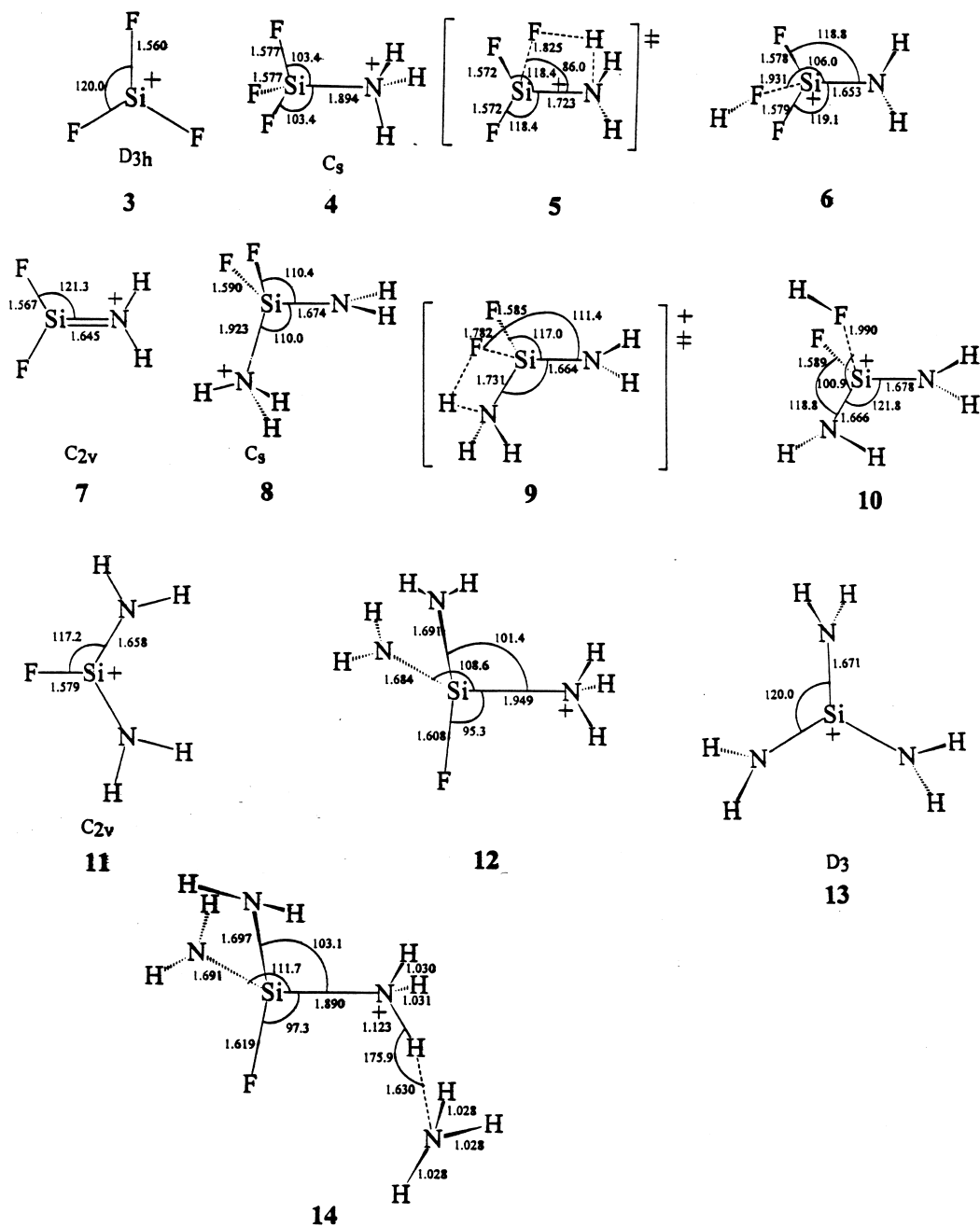
Fig. 3. Geometric parameters for ionic reactants, transition structures, intermediates, and products associated with the chemistry initiated by the reaction of SiF_3^+ with ammonia. The number beneath each structure corresponds to that assigned in Table 2 which provides total and zero-point energies. Bond lengths and bond angles are provided only for heavy (nonhydrogen) atom bonds except in the case of ion **14**.
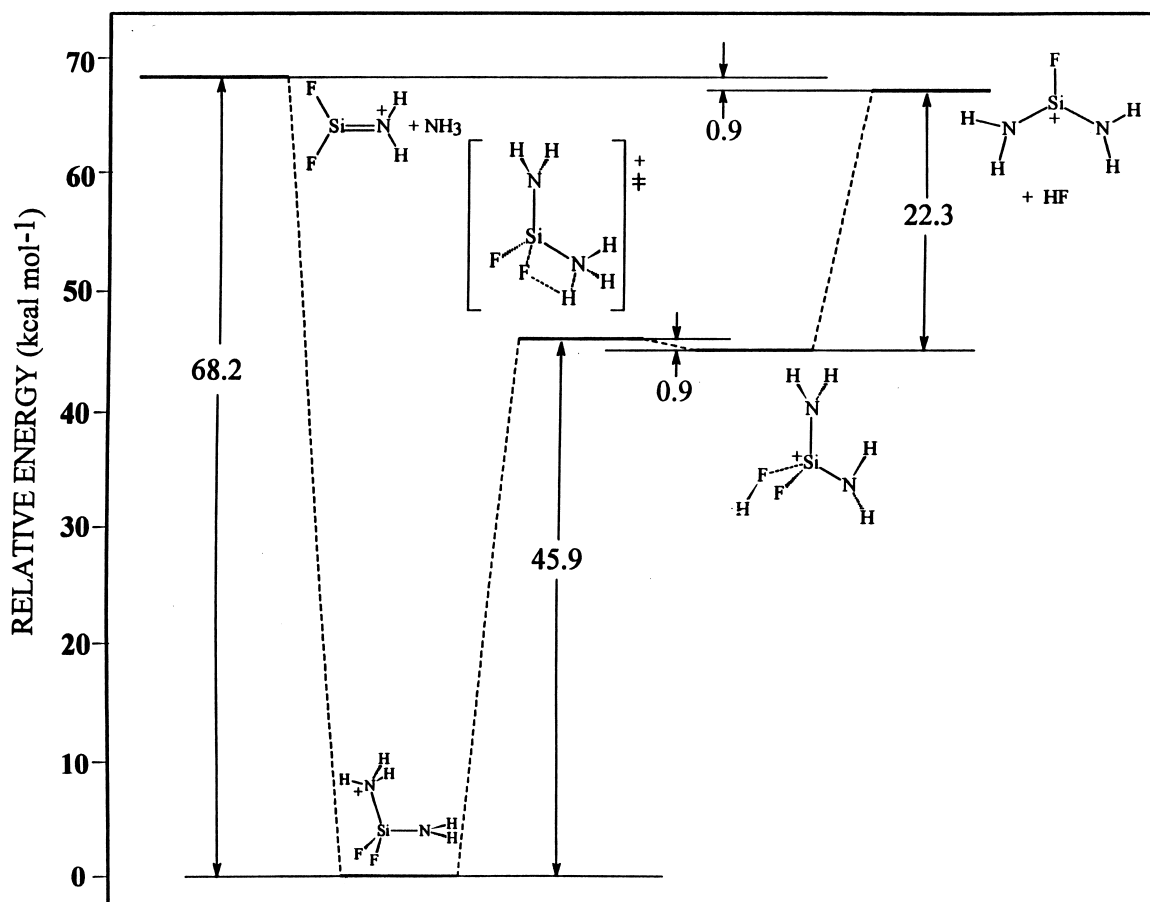
Fig. 4. Potential energy hypersurface associated with the reaction of $F_2Si(NH_2)^+$ with ammonia.

produces a shortening of the $F(NH_2)_2Si^+$...NH_3 distance to 1.890 Å from 1.949 Å, but **14** is still best described as being a silyl cation "solvated" by NH_3...NH_3.

Fig. 4 shows the topology of the potential energy hypersurface associated with the gas-phase HF-elimination reaction of $F_2Si(NH_2)^+$ with NH_3, reaction (4). Similar topological features exist on the potential energy surface associated with the primary HF-elimination reaction between SiF_3^+ with NH_3, reaction (3). The relative energies of all critical points associated with these two reactions are provided in Table 3. Both reactions (3) and (4) are characterized by double minima and may be viewed to proceed sequentially via formation of a solvated complex, intramolecular

H-atom transfer (*a* 1, 3-H-atom shift) and dissociation of the resulting solvated complex into products. In Fig. 4 the first well depth along the reaction coordinate corresponds to the stabilization energy of the first solvated complex, $F_2SiNH_2^+$ ··· NH_3 (structure **8**), relative to the reactants, while the second well depth corresponds to the stabilization energy of the second solvated complex, $FSi(NH_2)_2^+$ ··· HF (structure **10**), relative to the energy of the products. The latter complex is only marginally lower in energy than the transition structure at the B-LYP/6-31$G(d,p)$ level of theory. Formation of a solvated complex, $F_2Si(NH_2)NH_3^+$, was observed experimentally, presumably because the occurrence of some collisional stabilization.
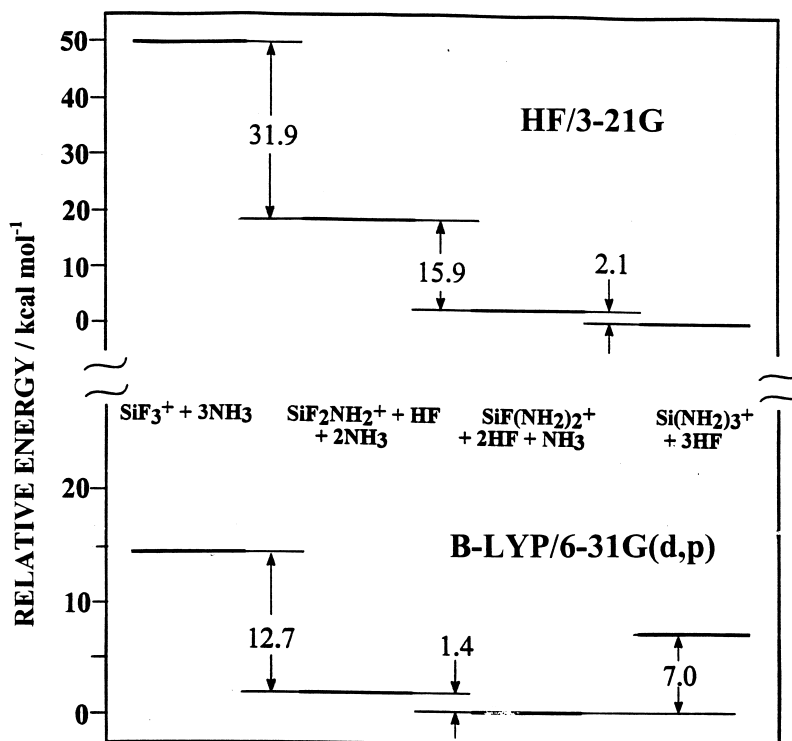
Fig. 5. Enthalpies of successive HF eliminations associated with the gas-phase ammonia chemistry of SiF_3^+, as calculated at HF/3-21G (top) and at B-LYP/6-31$G(d,p)$ (bottom). Unscaled zero-point vibrational energies (ZPE), calculated at B-LYP/6-31$G(d,p)$, are included.

The occurrence of a third HF elimination, viz. reaction (10), is calculated to be endothermic by 7.0 kcal mol^{-1} at the B-LYP/6-31$G(d,p)$ level of theory.

$$FSi(NH_2)_2^+ + NH_3 \rightarrow Si(NH_2)_3^+ + HF \qquad (10)$$

This result is consistent with our failure to observe the occurrence of reaction (10) at room temperature but is not consistent with the earlier FTICR study. It may be that reaction (10) is driven under the low-pressure ICR conditions by some kinetic and/or internal excitation. On the other hand, perhaps theory overestimates the enthalpy change. Under SIFT conditions reaction (10) could be preempted by collisional stabilization to form the adduct $FSi(NH_2)_2NH_3^+$ which was observed, particularly in view of the observation of some formation of adduct by reaction (6a). But Fig. 5 clearly shows that reaction (10) is endothermic at the higher level of theory.

The structure of the adduct $FSi(NH_2)_2NH_3^+$ and that of next ammonia adduct observed experimentally were also investigated theoretically at B-LYP/6-31$G(d,p)$. Table 3 shows that the two ammonia molecules are bound by 34.4 and 23.7 kcal mol^{-1}, respectively. The computations indicate that the addition reaction (7a) can be viewed to proceed by nucleophilic attack of the nitrogen lone electron pair of NH_3 upon the (formal) positive charge on the silicon atom of $FSi(NH_2)_2^+$ (structure **11**). The resulting adduct ion, structure **12**, contains silicon in a nearly tetrahedral bonding arrangement. By contrast, the computed lowest-energy arrangement of the product of the subsequent addition of NH_3 to **12**, structure **14**, reveals the existence of a hydrogen bond with the added ammonia molecule. An examination of the N–H bond lengths in **14** shows the existence of two elongated N–H interactions (1.123 Å and 1.630 Å) at the site of the hydrogen bond. The lengths of the neighbouring N–H bonds

Table 3
Relative energies[a] of critical points on the potential-energy surfaces associated with the ammonia chemistry of SiF_3^+

Reaction	Reactants	Adduct	TS between adduct and solvated ion	Product ion solvated by HF	Separated products
$SiF_3^+ + NH_3 \rightarrow F_2Si(NH_2)^+ + HF$	+91.2	0.0	+48.4	+45.2	+78.5
$F_2Si(NH_2)^+ + NH_3 \rightarrow FSi(NH_2)_2^+ + HF$	+68.2	0.0	+45.9	+45.0	+67.3
$FSi(NH_2)_2^+ + NH_3 \rightarrow FSi(NH_2)_2(NH_3)^+$	+34.4	0.0	—	—	—
$FSi(NH_2)_2(NH_3)^+ + NH_3 \rightarrow FSi(NH_2)_2(NH_3)_2^+$	+23.7	0.0	—	—	—

[a] In kcal mol^{-1}, from B-LYP/6-31$G(d,p)$ optimizations; unscaled ZPE included.

(1.028–1.031 Å) are more representative of "normal" N–H single bonds.

6. Comparisons with the chemistry initiated by SiF_3^+ in H_2O

The chemistry that we have observed with ammonia is very similar to that we have recently reported for HF-elimination reactions of $F_xSi(OH)_y^+$ with H_2O ($x = 1$–3, $y = 0$–2) [1]. Also, there are analogies in the calculated topological features of the potential energy surfaces. There is however one important difference: While only two sequential HF eliminations were observed with ammonia, all three HF eliminations were observed in the sequential chemistry with water. We attribute this difference in chemical behaviour to a difference in the thermochemistry of HF elimination, viz. to the prediction that the third HF elimination is *endothermic* in the case of ammonia.

This difference in the thermochemistry of HF elimination can be understood in terms of the stabilizations of the secondary and tertiary product ions of the water reactions, $FSi(OH)_2^+$ and $Si(OH)_3^+$, vis-à-vis those of the ammonia reactions, $FSi(NH_2)_2^+$ and $Si(NH_2)_3^+$. Both $FSiX_2^+$ ions (X = OH or NH_2) have planar geometries with the positive charge formally on silicon. However, the formally empty p orbital on this silicon atom is the recipient of π-electron density from its neighbouring substituent groups (one F and two OH groups in the former species; one F and two NH_2 groups in the latter ion) and this delocalizes the charge on to the substituents. The SiX_3^+ ions, how-

ever, have rather different geometric characteristics. The $Si(OH)_3^+$ ion is planar; thus, the formal positive charge on silicon still can be delocalized through the π system. However, $Si(NH_2)_3^+$ does not have a planar geometry (the hydrogen atoms of the amino groups are rotated approximately 23° out of the plane of the heavy atoms in the B-LYP/6-31$G(d,p)$ optimized geometry; the resulting ion has D_3 symmetry). Thus, the empty p orbital on silicon cannot receive π-electron density from the nitrogen p orbitals as extensively as in a planar geometric arrangement. Thus, the formal positive charge on silicon is delocalized to a lesser extent in $Si(NH_2)_3^+$ than in $Si(OH)_3^+$, with the result that the triaminosilicon cation is less stabilized than is its trihydroxy analogue. As the reaction which corresponds to the third HF elimination in the water chemistry has been calculated to be only slightly exothermic [by 1.5 kcal mol^{-1} at B-LYP/6-31$G(d,p)$], it is not surprising then that the analogous reaction in the ammonia chemistry is endothermic.

A closer inspection of the calculated energetics associated with the HF eliminations of the ammonia and water chemistries reveals that the first such elimination is more exothermic in the ammonia chemistry, but that subsequent eliminations are less exothermic or are endothermic (see Fig. 6). The ΔE values for the three HF eliminations in which NH_3 is the nucleophile are -12.7, -1.4, and $+7.0$ kcal mol^{-1} at B-LYP/6-31$G(d,p)$; they are -7.0, -3.9, and -1.5 kcal mol^{-1} with water as the nucleophile (see Fig. 6). The different results associated with the first HF eliminations can be explained in terms of the product ions of the respective reactions. In the SiF_3^+ +
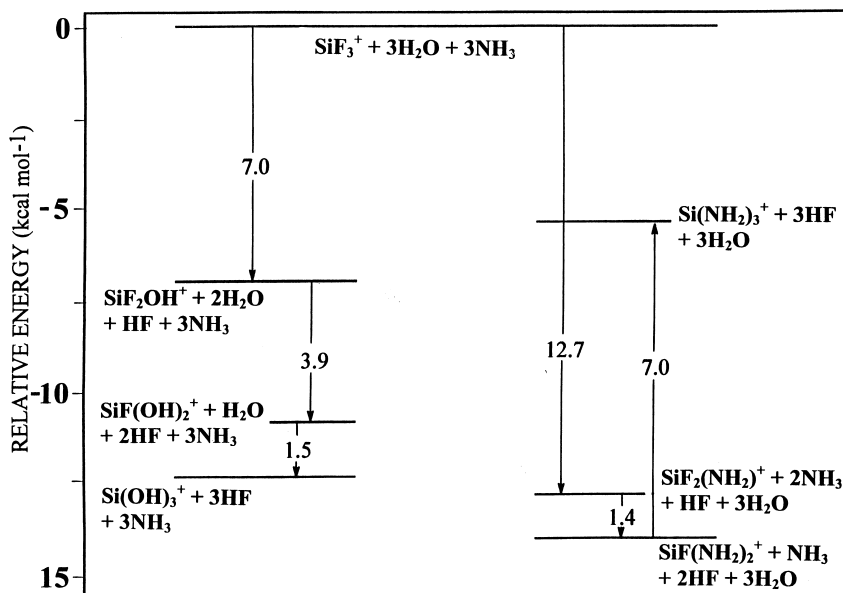
Fig. 6. A comparison of the energetics of successive HF eliminations associated with the gas-phase water chemistry of SiF_3^+ (left) vis-à-vis the ammonia chemistry (right), as calculated at B-LYP/6-31$G(d,p)$. Unscaled zero-point vibrational energies (ZPE), calculated at B-LYP/6-31$G(d,p)$, are included.

NH$_3$ reaction, the product ion **7** has a planar structure with C_{2v} symmetry; the silicon–nitrogen interaction is best described, at least formally, by a double bond. By contrast, the analogous product ion of the SiF_3^+ + H$_2$O reaction, F$_2$SiOH$^+$, has only a plane of symmetry coincident with the plane of the constituent atoms (C_S point group); the Si–O–H bond angle is 126.4° at B-LYP/6-31$G(d,p)$. This structural feature suggests the presence of a σ-electron lone pair on the oxygen atom in the symmetry plane of the molecule. The Si–O distance in F$_2$SiOH$^+$ (1.583 Å) suggests that the bonding is intermediate between a single and a double bond. In addition, Mayer bond order calculations [24] performed on structures **15** and **16** at HF/6-31$G(d,p)$//B-LYP/6-31$G(d,p)$, show that the Si–N interaction in **7**, while not equivalent to a double bond, still is stronger than the Si–O bond of its oxygen analogue. It is, therefore, not surprising that the first HF elimination associated with the SiF_3^+ + NH$_3$ reaction is the more exothermic reaction.

   In contrast to the large difference in ΔE values between the respective first and third HF eliminations, the magnitudes of the energy differences for the
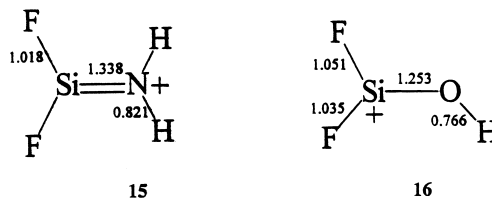
second HF eliminations are similar (-3.9 kcal mol^{-1} for the water chemistry; -1.4 kcal mol^{-1} for the ammonia chemistry). This (small) difference can be attributed, at least in part, to the presence of conformational differences which exist between the analogous dihydroxyfluoro- and diaminofluorosilicon secondary product ions. In the case of FSi(NH$_2$)$_2^+$, there is only one planar (C_{2v}) structural isomer (structure **11**); the FSi(OH)$_2^+$ molecular formula has three planar (C_S) isomers. Whereas the conformer depicted as ion **17** has the lowest energy of these three isomers, it is ion **18**, the highest-energy isomer, with which the most meaningful comparison to the diamino-analogue **11** can be made, because of the presence of similar destabilizing H/H interactive. These interactions result in **18** being 2.0 kcal mol^{-1} higher in energy than

17

18   11
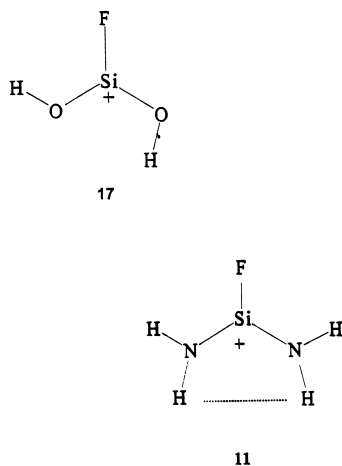
is **17**; thus, an HF elimination reaction to form **18** (instead of **17**) would be exothermic only by $3.9 - 2.0 = 1.9$ kcal mol^{-1}. This value is very similar to the exothermicity associated with the HF elimination to produce **11** from **7** (1.4 kcal mol^{-1}). Thus, the second HF eliminations of the water and ammonia chemistries are the most similar energetically, but would possess an even greater thermodynamic similarity on formation of conformationally analogous products.

7. Conclusions

A great variability has been observed for the gas-phase reactions of the fluorinated silicon ions SiF_x^+ with ammonia for $x = 1, 2$ and 3 proceeding under SIFT conditions in helium buffer gas at 0.35 ± 0.01 Torr and 294 ± 3 K: the monofluorosilicon cation is unreactive, ammonia rapidly transfers an electron to SiF_2^+, while SiF_3^+ reacts with ammonia to eliminate HF. Higher-order reactions with ammonia in the chemistry initiated by SiF_3^+ lead to the elimination of one additional HF molecule followed by sequential solvation. Aside from the occurrence of HF elimination with SiF_3^+, this chemistry differs markedly from that observed previously with water under similar operating conditions.

Calculations at the B-LYP/6-31$G(d,p)$ level of theory suggest that the HF elimination reactions observed experimentally proceed on the potential energy hypersurfaces with double minima. Some formation of the stabilized intermediate in the first minimum on the surface for the reaction of $F_2Si(NH_2)^+$ with ammonia was observed. In sharp contrast to the water chemistry, the substitution of the third Si–F bond in SiF_3^+ with NH_2 by HF elimination was computed to be endothermic and was not observed under SIFT conditions. This observation and computation is at odds with recent FTICR measurements. Higher-order adduct ions were also observed and computed. The double-adduct ion $FSi(NH_2)_2(NH_3)_2^+$ was found by theory to have an interesting, nearly-tetrahedral structure solvated by ammonia via hydrogen bonding.

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