should be 0.036 for this vibration. An isotope shift of 0.044 is calculated for the bending vibration in O–Fe–O with a 120° bond angle. Thus the isotope shift for the 517-cm^{-1} band is compatible with our assignment of 946 cm^{-1} to bent O–Fe–O. The isotope shift for a linear O–Fe–O molecule should be 0.037 which rules out a linear O–Fe–O structure for the molecule giving the 946-cm^{-1} band and leaves as still reasonable our assignment of the 969-cm^{-1} band to linear O–Fe–O.

Some spectral features which we observe were not observed in ref 18a apparently because their spectra are much less intense than ours. In ref 18a it is noted that with annealing the 956- and 969-cm^{-1} bands increase relative to the 946-cm^{-1} band which decreases with annealing but, their spectra were too weak to get isotope shifts for these more stable species as we did. Some differences in relative intensity among these bands between the two works are probably due to the different methods of producing Fe atoms. In ref 18a the Fe atoms are produced by evaporation at 1950 K which suggests the O–Fe–O linear and metastable bent molecules are formed by energetic Fe atoms colliding with O_2 molecules at the matrix surface. In this work the Fe atoms are sputtered into Ar gas not over several hundred degrees (°C). Under these conditions with Ar* and O atoms present the O–Fe–O species are believed formed by the mechanisms given previously.

The verification of the existence of a stable FeO_2 complex which still contains an O–O bond lends credence to the proposal of a molecularly adsorbed O_2 precursor state in iron oxidation. Although previously reported[18a] the present results indicate that the infrared band previously assigned to FeO_2 is for a species that does not contain an O–O bond. The stability of the FeO_2 complex in the 15–25 K range indicates that in the interaction of O_2 with a single Fe atom there is at least a small activation energy for the dissociation of the O–O bond. The disappearance of the band for the O–O stretch at 35–40 K could be FeO_2 acquiring sufficient energy to break the O–O bond or to Fe cluster formation furnishing multiple Fe sites upon which O–O bond rupture occurs with very little or no activation energy. In the many annealing experiments performed no tendency for the 969-cm^{-1} band to grow at the expense of the 956-cm^{-1} band was observed as would be the case if O–O bond breaking were occurring in FeO_2. Also experiments were performed in which a 20-mA current was used in the hollow-cathode discharge rather than the usual 50 mA current so that the Fe atom concentration was considerably reduced. In these runs the 956-cm^{-1} band for FeO_2 was not reduced in intensity after 10 min at 40 K. This indicates that O–O bond rupture occurs more readily on iron sites involving several iron atoms than on single Fe atoms.

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Registry No. O–Fe–O, 12411-15-3; FeO_2, 58220-66-9; FeO, 1345-25-1; ^{18}O, 14797-71-8.

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Matrix-Isolation Studies of Lewis Acid/Base Interactions: Infrared Spectra of the 1:1 Adduct $SiF_4{\cdot}NH_3$

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The codeposition of NH_3 and SiF_4 into inert matrices at dilutions as high as 1/1/4000 gives rise to an extremely sharp set of product bands, at 409, 456, 706, 854, 952, and 1253 cm^{-1}. Consideration of the isotopic shifts of these bands and comparison to spectra of the known 1:2 adduct indicate that these bands can be assigned to a 1:1 adduct, $SiF_4{\cdot}NH_3$. The spectra also suggest a trigonal-bipyramidal arrangement about the central silicon, with the NH_3 group in an axial position. The codeposition of $SiCl_4$ with NH_3 gave rise to product bands as well, but only when relatively high concentrations were employed. These bands are ascribed to a 1:1 adduct as well, which is considerably less strongly bound than the SiF_4 analogue. The matrix codeposition of SiF_4 with dimethyl ether did not give rise to any product bands, indicating that a stable adduct is not formed.

Introduction

Complexes between strong Lewis acids and bases have been known for a number of years,[1-3] especially for such Lewis acids as BF_3 and PF_5. Similar complexes for relatively strong Lewis acids such as SiF_4 are not as well characterized, although a number have been discovered. With very strong bases such as trimethylamine, SiF_4 forms 1:1 and 1:2 complexes, both of which can be isolated at room temperature.[4-6] For the strongest base known (using a gas-phase proton affinity scale), the fluoride anion F^-, both 1:1 adducts (SiF_5^-)[7] and 1:2 adducts (SiF_6^{2-})[8] are known as well. However, with somewhat weaker bases such as NH_3, hydrazine,[9] or dimethylformamide[10] only 1:2 adducts have been observed. The complex $SiF_4{\cdot}2NH_3$ has been isolated in the solid phase, where it is the oldest known compound containing a Si–N bond;[11] in the gas phase, virial coefficients and dissociation data for the reaction $SiF_4{\cdot}2NH_3(s) \rightleftarrows SiF_4(g) + 2NH_3(g)$ have been obtained.[12,13]

At the same time, studies of the Lewis acid/base chemistry of the silicon tetrahalides from SiF_4 to SiI_4 demonstrate a large difference in reactivity. Several studies have shown that $SiCl_4$ will react with a number of bases to form distinct products,[14,15] while SiF_4 forms adducts with these bases. At the same time, workers have shown that the order of stability of the silicon tetrahalides toward a standard base depends on the base chosen (hard vs. soft), and these results show that $SiCl_4$ and $SiBr_4$ are softer acids than SiF_4, as might be anticipated.[16] Also,

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in certain acid/base complexes of SiF_4, dehydrofluorination is possible to yield a stable aminofluorosilane.[17]

It is surprising that a 1:1 adduct of SiF_4 with moderate-strength bases has not been detected; there is no clear reason why such a complex should not be stable. Rather, the equilibrium between SiF_4 and NH_3 may lie far to the side of the 1:2 adduct. If a 1:1 complex could be isolated under appropriate conditions, the structure would be of interest: Would the overall geometry around the silicon center be trigonal bipyramidal, and if so, would the NH_3 group be in an axial or equatorial position? Also, such a study might provide more evidence and insight as to the similarities and differences in the chemistries of SiF_4 and $SiCl_4$.

The matrix-isolation technique has proven to be an excellent means of investigating chemical species that are thermodynamically stable but too reactive or short-lived for detection at room temperature.[18,19] In addition, matrix isolation has been applied in a number of cases to the study of protic acid/base complexes,[20-22] as well as recently to the study of weak acid/base interactions such as between hydrohalic acids and olefins and acetylene.[23] The application of matrix isolation to the study of Lewis acid/base complexes should be likewise feasible and might provide a route to such adducts as the 1:1 complex between SiF_4 and NH_3. Consequently, a systematic study was undertaken to identify and characterize complexes formed between SiF_4 and NH_3 and between $SiCl_4$ and NH_3 after isolation in an inert matrix.

Experimental Section

The experiments conducted in this study were all carried out on a conventional matrix-isolation apparatus, which has been described previously.[24] So that equilibration and formation of the known stable 1:2 complex between SiF_4 and NH_3 might be avoided, the two reactants were each diluted with argon or nitrogen in separate vacuum lines and codeposited from different deposition lines onto the cold window. Mixing took place immediately in front of the 15 K cold window, with rapid condensation, so that isolation of the initial reaction product might be possible. SiF_4 (Matheson) and NH_3 (Matheson) were used after purification by one or more freeze/thaw cycles at 77 K, and the stainless-steel line used for NH_3 was conditioned thoroughly with gaseous NH_3, which adsorbs strongly. ND_3 (Merck, 99% D) was also purified by freeze/thaw cycles, after deuterating the vacuum line thoroughly with D_2O and flaming. Mixed NH_3/ND_3 experiments were conducted by introducing equal amounts of NH_3 and ND_3 into a vacuum line that was thoroughly deuterated. $^{15}NH_3$ was treated in a similar fashion. $SiCl_4$ was introduced into the system via a glass finger and distilled from an appropriate slush bath to remove impurity HCl. Argon and nitrogen were used as matrix gases; argon was used without further purification, while nitrogen was passed through a copper coil cooled to 77 K.

Samples were generally deposited for 15–20 h at 2 mmol/h from each vacuum line, before final survey and high-resolution scans were recorded on a Beckman IR-12 infrared spectrophotometer. Normal-coordinate calculations were conducted with use of a program from the Research Council of Canada at the University of Cincinnati Computing Center.

Results

Blank or background spectra of the various reactants used in this study have been recorded in past studies from this laboratory; additional blank experiments at different dilutions were conducted when needed. All of the blank spectra were in good agreement with literature spectra.

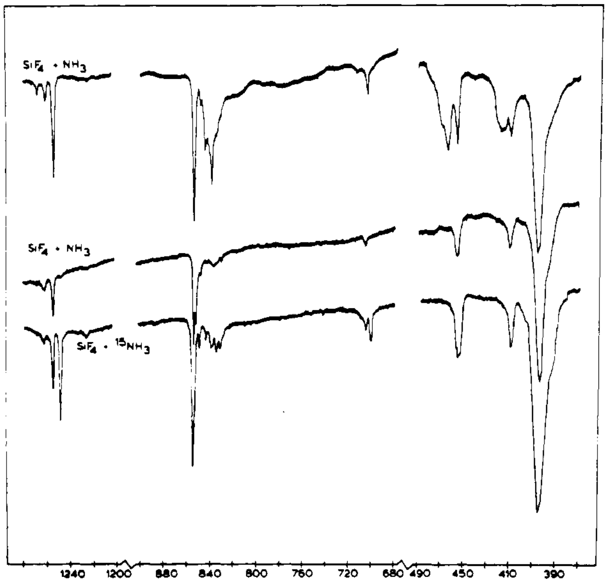

Figure 1. Infrared spectra of the reaction products of the codeposition of NH_3 and SiF_4 in argon matrices. The top trace was taken from an experiment using samples of $Ar/SiF_4 = 1000$ and $Ar/NH_3 = 1000$; the whole middle trace involved samples of $Ar/SiF_4 = 1500$ and $Ar/NH_3 = 1500$. The lower trace shows the analogous experiment using $^{15}NH_3$.

Table I. Band Positions and Assignments for the Argon Matrix Isolated $SiF_4 \cdot NH_3$ Adduct[a]

$SiF_4 \cdot NH_3$	$SiF_4 \cdot {}^{15}NH_3$	$SiF_4 \cdot ND_3$	assignt
1253	1247	953[c]	A_1, sym def NH_3
952[b]	952[b]	952[b]	E, eq Si–F str
854	854	854	A_1, ax Si–F str
706	701		E, NH_3 rock
456	456	456	E, Si–F def
409	409	409	E, Si–F def

[a] Assignments and symmetries assuming C_{3v} symmetry; band positions in cm^{-1}. [b] Nitrogen matrix; average of site-split doublet. [c] Tentative assignment; see text.

$SiF_4 + NH_3$. These two reactants were codeposited from two different vacuum lines in a number of experiments over a wide concentration range. Most experiments were conducted at the dilution $Ar/SiF_4 = 1000$ and $Ar/NH_3 = 1000$, and since equal flow rates were employed, the overall dilution $Ar/SiF_4/NH_3$ was about 2000/1/1. Under these conditions, the spectrum showed a number of product bands, which could not be assigned to either parent species, at 409, 416, 456, 463, 706, 839, 854, 1253, and 1266 cm^{-1}. These fell into two groups: a very sharp intense set and a set that was somewhat broader and less intense, near each of the bands in the first set. So that it could be determined which of these bands were due to an isolated reaction product and which to aggregate or perturbed species, more dilute experiments were conducted. At 1/1/3000, the second set of bands was greatly diminished, and the first set remained sharp and intense; the two most intense bands, at 854 and 1253 cm^{-1}, had bandwidths of about 1 cm^{-1}. At this greater dilution, two weak satellite bands were observed on the low-energy side of the 854 cm^{-1} band, at about 849 and 844 cm^{-1}.

More concentrated experiments were conducted as well, with concentrations as high as 1/1/250, in an attempt to identify weak bands of the product species. The major effect, however, was to intensify all of the previously observed bands and to enhance the bands of the second set relative to the first set of bands. Argon-matrix spectra are displayed in the traces

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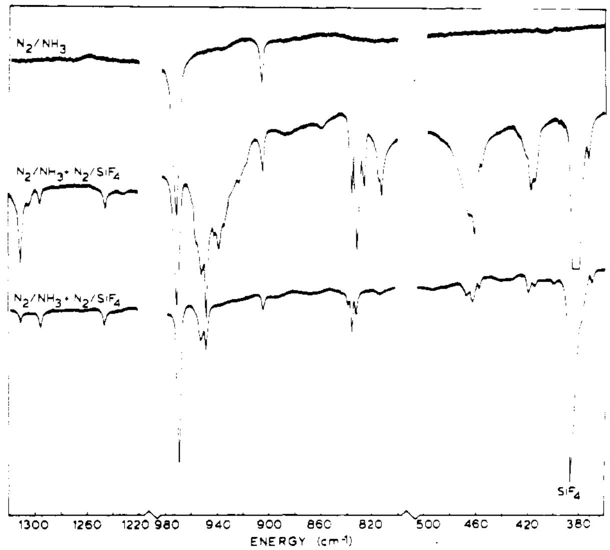

Figure 2. Nitrogen-matrix spectra of the reaction products of the codeposition of SiF_4 and NH_3 at the concentration $N_2/SiF_4/NH_3$ = 2000/1/1 in the middle trace and 4000/1/1 in the lower trace.

of Figure 1, while band positions are listed in Table I.

The spectral region between 950 and 1050 cm^{-1} was very cluttered in these experiments, due to rotation, inversion, and dimerization of NH_3 in argon matrices. However, it has been shown that in nitrogen matrices, inversion and rotation are minimized, which can simplify this spectral region considerably.[25,26] To look for product bands above 950 cm^{-1}, a series of nitrogen-matrix experiments were conducted, including blank experiments with NH_3 and SiF_4. When a sample of N_2/NH_3 = 1000 was codeposited with a sample of N_2/SiF_4 = 1000, numerous product bands were detected, generally in spectral regions near the bands observed in argon matrices. Band locations were 415, 418, 458, 463, 466, 710, 722, 764, 814, 832, 835, 838, 939, 950, 954, 1248, 1296, and 1310 cm^{-1}, with the bands at 814 and 939 cm^{-1} appearing somewhat broader than the remaining bands, which in all cases appeared as multiplets in the different spectral regions. When a sample of N_2/NH_3 = 2000 was codeposited with a sample of N_2/SiF_4 = 2000 so that the overall dilution was 1/1/4000, all of the bands remained, except those at 814 and 939 cm^{-1}, marking these as analogues of the second set of bands described above in the argon-matrix experiments. The remaining bands appeared as either distinct doublets or triplets near the position of the bands in the argon-matrix experiments, except for the 950, 954, 957 cm^{-1} triplet, which does not have an argon-matrix counterpart. The argon-matrix counterpart would have been thoroughly hidden under the rotation/inversion structure of parent NH_3. Figure 2 shows the spectra obtained in these nitrogen-matrix experiments.

As a test of the behavior of this system in the limit of no matrix material, pure SiF_4 was deposited from one vacuum line concurrently with pure NH_3 from a second vacuum line onto the CsI cold window. The resulting spectrum showed dominant features at 730 and 1390 cm^{-1}, along with features of intermediate intensity between 400 and 500 cm^{-1} and a broad band centered near 930 cm^{-1} with a shoulder at 850 cm^{-1}.

For comparison, a sample of the known, room-temperature solid $SiF_4 \cdot 2NH_3$ was prepared by cocondensing SiF_4 and NH_3 into a glass finger at 77 K and allowing the mixture to warm. A Nujol mull spectrum of this solid showed the same dominant features at 730 and 1390 cm^{-1}, but the remaining features observed above between 400 and 500 cm^{-1} and 850 and 950 cm^{-1} were not present.

SiF_4 + $^{15}NH_3$. This pair of reactants was investigated in three experiments, each at a dilution of 1/1/2000 in argon. The spectrum in each case showed primarily the first, sharp set of bands, either being in the same location or shifted slightly to lower energy. The band at 409 cm^{-1} was not affected by ^{15}N substitution, while the band at 456 cm^{-1} appeared to be broadened slightly, but no distinct ^{15}N peak was resolved. The band at 706 cm^{-1} shifted to 701 cm^{-1}, while the band at 854 cm^{-1} did not show any ^{15}N shift within the resolution of the instrument, and the band at 1253 cm^{-1} did show a considerable ^{15}N shift, to 1247 cm^{-1}. It should also be noted that the $^{15}NH_3$ sample was initially about 95% ^{15}N, and with some exchange in the vacuum line with residual $^{14}NH_3$ from previous experiments, the final $^{15}N/^{14}N$ ratio was about 3/2 so that the ^{14}N bands were also observed in the ^{15}N experiments.

$^{15}NH_3$ and SiF_4 were also codeposited and reacted in nitrogen matrices, primarily to observe the dependence on the 950-cm^{-1} band system on ^{15}N substitution. The triplet near 950 cm^{-1} did not show a measurable isotopic shift, while the shifts for the remaining product bands were identical with those obtained in argon matrices.

SiF_4 + ND_3. These two reactants were investigated in a number of experiments as well; the spectra obtained were considerably more complex as a consequence of the rapid exchange of ND_3 with any hydrogen-containing impurities in the vacuum line. Consequently, all ND_3 experiments contained at least some NHD_2, NH_2D, and NH_3. However, by repeated deuteration of the deposition line, samples with a D/H ratio of nearly 10 could be obtained. In such an experiment, a new set of bands were obtained, corresponding to the first, sharp set of bands in the analogous NH_3 experiments. These were located at 409, 456, 854, and 953 cm^{-1}, while a deuterium counterpart for the 706-cm^{-1} band could not be located, presumably due to low intensity. However, it was clear that the 706-cm^{-1} band did have a deuterium shift, as no band was observed near 706 cm^{-1}. In addition, a relatively weak band was observed near 1054 cm^{-1}, on the high side of the intense 1025-cm^{-1} absorption of parent SiF_4. So that reaction products of NHD_2 and NH_2D could be detected, a sample containing NH_3 and ND_3 in a deuterated vacuum line was prepared; the resulting spectra indicated a D/H ratio of about 3/1. When this sample was codeposited with Ar/SiF_4 = 1000, the results were quite similar to those of the best ND_3 experiment, except for the band system between 953 and 1253 cm^{-1}. Here, both the 953- and 1253-cm^{-1} bands were observed, although the 953-cm^{-1} band was quite strong and the 1253-cm^{-1} one was quite weak. In addition, the 1054-cm^{-1} band was present with moderate intensity, and an additional intermediate band was observed near 1170 cm^{-1}. The spectra of the reaction products of SiF_4 with partially and thoroughly deuterated ND_3 samples are shown in the traces of Figure 3, while band positions are listed in Table I.

SiF_4 + $(CH_3)_2O$. For comparison, SiF_4 was codeposited with a weaker base, dimethyl ether, in several experiments over concentration ranges from 2000/1/1 to 400/1/1 in argon. In none of these experiments were any distinct product bands observed; in the most concentrated experiments several very broad diffuse features were detected, which served to indicate that a distinct adduct was not formed.

$SiCl_4$ + NH_3. Samples of $Ar/SiCl_4$ = 1000 were codeposited with samples of Ar/NH_3 = 1000 in several experiments, and in each case no new product bands were observed. However, when sample concentrations were increased to 1/250 from each deposition line, product bands were observed at 412, 504, 544, and 1289 cm^{-1}. These bands were somewhat broader

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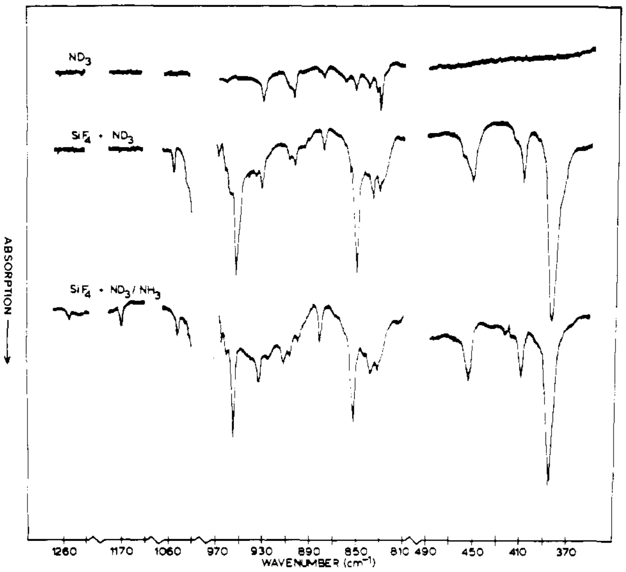

Figure 3. Infrared spectra of the reaction products of SiF_4 and ND_3 in argon matrices for two levels of deuteration. The top traces show a blank experiment of Ar/ND_3, for comparison.

and less well-defined than in the SiF_4 studies and were relatively weak, except for the 544-cm^{-1} band, which was moderately intense.

$SiCl_4$ + ND_3. A sample of $Ar/SiCl_4$ = 250 was codeposited with a sample of Ar/ND_3 = 250 in one experiment, and three product bands were observed, near 410, 500, and 544 cm^{-1}, very near the three lower bands in the NH_3 experiment, and with the observed bandwidth, it is not certain that any deuterium shift occurred. However, the upper band at 1289 cm^{-1} in the NH_3 experiment was not present, and no deuterium counterpart for this product band was observed.

Discussion

As anticipated for the codeposition of a Lewis acid with a Lewis base into an inert matrix, a distinct reaction did occur when SiF_4 and NH_3 were codeposited. A series of product bands were detected, in addition to the bands that can be assigned to the parent species. The product bands can be divided into two sets; the first was a set of very sharp bands that persisted at high dilution (1/1/3000), and the second was a set that was predominant at high concentrations (1/1/500). The first set of bands consist of the bands at 409, 456, 706, 854, and 1253 cm^{-1} for the normal isotopes of all atoms, while the second set consists of broader bands, at 416, 463, 839, and 12600 cm^{-1}. The concentration dependence and breadth of the bands indicate that the second set is due to either aggregate or perturbed species, while the first set is due to an isolated, distinct reaction product. The interest in the present study is in the isolated or pseudo-gas-phase reaction product, and consequently the focus of this study will be on the first set of bands.

The nitrogen-matrix experiments provided similar results: a primary set of bands that persisted at dilutions as high as 1/1/4000 and a second set of bands that was distinct at 1/1/2000 and disappeared at higher dilution. Two major differences were noticeable in the nitrogen experiments, however. First, multiplet structure was observed for each band such as the 832, 835, 838 cm^{-1} triplet, while only singlets were observed in argon. This multiplet structure can be ascribed to site splitting, and for most band systems, triplets were observed, indicative of three primary sites. Apparently, the tight packing of the nitrogen matrix, which prevents the rotation and inversion of NH_3, also gives rise to the multiple isolation sites. The site splitting of the 415-, 460-, and 835-cm^{-1} band systems was small, only a few cm^{-1} between components, while the splitting of the 710- and 1250-cm^{-1} band systems was large, roughly 50 cm^{-1}. As discussed below, these modes can be assigned to NH_3 vibrations in the product, and these are much more sensitive to the local environment than the skeletal motions of the SiF_4 framework.

The second major difference is the observation in nitrogen matrices of a triplet at 950, 954, 957 cm^{-1}, which has no argon-matrix counterpart. This is presumably due to the fact that in argon matrices the region above 950 cm^{-1} is totally obscured by NH_3 features and is probably lost in this background. However, in the argon-matrix reaction of SiF_4 with ND_3, the 950–1000-cm^{-1} region is much less cluttered. An intense band was observed at 953 cm^{-1}; this may be the argon-matrix counterpart of the 950-cm^{-1} nitrogen-matrix band. This band represents one additional vibrational mode of the complex; due to sharpness and clarity, argon-matrix band positions will be used for assignments, except for this 950-cm^{-1} nitrogen-matrix band.

Several different types of distinct reaction products might be envisioned for this system; the most likely three are the 1:1 adduct, the 2:1 adduct, and a dehydrofluorination reaction product. The 1:2 reaction product is quite well-known in the crystalline phase, which suggests that dehydrofluorination does not occur. The choice between a 1:1 and 1:2 reaction product is more difficult, but comparison to known spectra can provide some information. The spectra of the 1:2 adduct, $SiF_4{\cdot}2NH_3$, has a very intense Si–F absorption near 730 cm^{-1}, with the NH_3 ligands in a cis-octahedral geometry.[9,10] This agrees very well with the Si–F stretches of the octahedral anion SiF_6^{2-} but does not agree at all with the spectrum obtained here. The most intense spectral features occur at 853 and 950 cm^{-1} and can be assigned (see below) to Si–F stretching modes. No intense feature is observed near 730 cm^{-1}, suggesting that the species produced here is not the 1:2 adduct. Moreover, the 853- and 950-cm^{-1} bands come near the intense Si–F stretching modes of the SiF_5^- anion, in a trigonal-bipyramidal geometry,[7] which suggests that the product observed here is a 1:1 adduct. Moreover, it would be hard to envision formation of a 1:2 adduct without an intermediate 1:1 adduct, which should also be isolated in these studies. Indeed, at a dilution of 1/1/4000, one would anticipate that only the 1:1 complex would have time to form before condensation into a rigid inert-gas crystal.

The codeposition of pure NH_3 with pure SiF_4 and rapid condensation of the mixture gave rise to the intense bands anticipated for the 1:2 adduct, at 730 and 1390 cm^{-1}. Several additional bands were observed, between 400 and 500 cm^{-1} and near 900 cm^{-1}, which were reminiscent of the product bands observed in an argon matrix. These bands are apparently not due to the 1:2 adduct as the room-temperature spectrum of the solid 1:2 compound does not have these features. This further supports the assignment of the argon-matrix bands to the 1:1 adduct, suggesting that even in the absence of a matrix material, rapid quenching at 15 K of a gaseous mixture of SiF_4 and NH_3 gives rise to both the 1:1 and 1:2 adduct.

The ^{15}N isotopic data shed some light on the composition as well. For several bands that were observed, such as the 706-cm^{-1} band system, a distinct ^{14}N–^{15}N doublet was observed due to the presence of both isotopes in the $^{15}NH_3$ experiment. If the product species contained two NH_3 groups, an intermediate band would be expected for the mixed-product species containing one ^{14}N and one ^{15}N, unless the two nitrogen atoms were totally vibrationally decoupled. For a relatively small species, this is quite unlikely, and the ^{15}N isotopic data also support assignment to a 1:1 complex. Finally, it is well-known that SiF_4 forms 1:1 complexes with other, stronger bases such as trimethylamine so that a 1:1 complex with NH_3 is chemically reasonable. On the basis of the above arguments, assignment of the product bands observed here to the 1:1 adduct between SiF_4 and NH_3, $SiF_4 \cdot NH_3$, is made. The previous lack of observation of this species probably reflects the fact that the equilibrium lies far to the side of the 1:2 adduct, but the present matrix conditions do not allow equilibrium to be established.

Band Assignments

Band assignments for the observed bands are relatively straightforward. The intense band at 854 cm^{-1} showed no shift with either ^{15}N or deuterium substitution, marking this as a vibration of the SiF_4 skeleton. Weak bands were observed on the low-energy side of this band at 849 and 844 cm^{-1}, suggestive of silicon isotope splitting in natural abundance. Silicon exists primarily as ^{28}Si (93%) with two less abundant isotopes, ^{29}Si (3%) and ^{30}Si (4%), so that two less intense low-energy satellites are anticipated for a Si–F stretching mode, and these are assigned as the bands at 849 and 844 cm^{-1}. The 950-cm^{-1} band likewise falls in the Si–F stretching region and shows no ^{15}N isotopic shift. Consequently, this band is assigned to a second Si–F stretching vibration. Site splitting in the nitrogen matrices precluded observation of ^{29}Si and ^{30}Si isotopic counterparts.

The bands detected at 409 and 456 cm^{-1} are in a region generally assigned to Si–F deformation modes, particularly for the SiF_5^- anion. These two bands showed very little, if any, shift with either deuterium or ^{15}N and hence are assigned to two Si–F deformation modes in the 1:1 reaction complex.

By comparison, the band at 1253 cm^{-1} disappeared when ND_3 was employed; the only candidate for a deuterium counterpart is the 953-cm^{-1} band. However, this band may also be due to a Si–F stretching mode, observed at 950 cm^{-1} in N_2. It is possible that both bands are contained within the band envelope, with accidental geometry, since they are of different symmetry types and will not split in a Fermi-resonance interaction. While a definite assignment of the 953-cm^{-1} band is not possible, it is clear that the 1253-cm^{-1} band does shift upon deuteration. Moreover, the 1253-cm^{-1} band shows a distinct ^{15}N shift to 1247 cm^{-1}, marking this as a vibration of the NH_3 ligand. Coordinated ammine groups generally show a very strong band in the region 1000–1400 cm^{-1} due to the symmetric deformation or umbrella mode of the pyramidal NH_3 group. This band has also been shown[8] to be very sensitive to the strength of interaction with the metal center or Lewis acid. On the other hand, the antisymmetric deformation mode that occurs near 1630 cm^{-1} for free NH_3 shows very little shift with complexation. Hence, the intense band at 1253 cm^{-1} is readily assigned to the symmetric deformation of the coordinated NH_3 group. In the experiment employing a mixture of ND_3 and NH_3, so that the intermediate species NHD_2 and NH_2D were present, this mode should show two intermediate bands, due to the complex of SiF_4 with either mixed H/D species. Such bands were observed near 1054 and 1170 cm^{-1}, further supporting this assignment as well as demonstrating that the product complex contains three equivalent hydrogen atoms, as would be expected for the 1:1 adduct.

The 706-cm^{-1} band was much weaker than the other bands and falls into a region that can be assigned either to an additional Si–F stretching mode or to an NH_3 rocking mode. However, this band showed a strong ^{15}N shift, to 701 cm^{-1}, as well as apparently a strong deuterium shift. This band vanished upon deuteration, and while a deuterium counterpart was not observed, it is nonetheless clear that there is a strong deuterium shift. The lack of observation of the deuterium counterpart of the 706-cm^{-1} band is probably due to low intensity, as deuterium vibrations are roughly a factor of 2 weaker than the corresponding hydrogenic vibrations. Moreover, the rocking mode of coordinated NH_3 groups fall in the region 600–800 cm^{-1}, so this assignment is appropriate. In particular, a number of transition-metal ammine complexes that show a symmetric NH_3 deformation near 1240 cm^{-1} have the corresponding rocking mode near 695 cm^{-1}, which matches nicely the band positions here.[8]

Another possible assignment for the 706-cm^{-1} band is to the Si–N stretching mode, which some authors[9,28,29] report as high as 900 cm^{-1}, while others[27] place this mode below 300 cm^{-1}. this mode should be relatively weak and should show a large ^{15}N shift. The 706-cm^{-1} band does show a 5-cm^{-1} ^{15}N shift, but the simple normal-coordinate calculations discussed below indicate that a shift of 10–15 cm^{-1} would be more appropriate for this vibration. Moreover, these calculations suggest that the mode is likely to lie below 300 cm^{-1} and does not appear to be the best assignment for the band, although it cannot be ruled out.

Structure of the Adduct

Observation of the bands discussed above can provide some information concerning the overall structure of the complex. The Si–F stretching modes are in a region indicative of a trigonal-bipyramidal configuration, as might be anticipated from simple valence-bond theory. Two possibilities then exist, a C_{3v} axial interaction or a C_{2v} equatorial interaction. The former possibility was favored for the 1:1 adduct between SiF_4 and trimethylamine,[27] while the latter would be favored on the grounds of steric and electronegativity arguments. On the basis of allowed bands, the C_{3v} geometry would give rise to three Si–F stretching modes, while the C_{2v} model would give rise to four.[8] However, not all of these would be expected to be particularly intense and might escape detection.

To provide at least some delineation between these models, very simple normal-coordinate calculations were carried out. However, only a few of the numerous possible fundamental vibrations were observed, so two major simplifications were used. First, only vibrations of the SiF_4 skeleton were calculated, by treating the NH_3 ligand as a point mass, with the appropriate mass for the isotope under consideration. Second, only diagonal force constants were employed to fit the observed bands; four force constants were employed, two of which were taken from previous work[28] and held constant. Thus, only two were varied, the Si–F stretching force constant F_R and the F–Si–F bending force constant F_α, to obtain a reasonable fit to the observed stretching and bending modes.

With the NH_3 group in the axial position, the best fit, $F_R = 3.93$ mdyn/Å and F_α 1.34 mdyn/Å, predicts the doubly degenerate equatorial Si–F stretching mode to fall at 950 cm^{-1}, with the axial Si–F stretching mode at 835 cm^{-1}, which match two observed bands in nitrogen matrices. This fit predicts the symmetric A_1 equatorial stretch to fall at 593 cm^{-1}. However, this mode should be very weak in the infrared as it is totally symmetric; in the analogous D_{3h} species SiF_5^-, this mode is infrared inactive. This fit also predicts SiF_4 bending modes at 463 and 405 cm^{-1}, not far from the observed bands at 456 and 409 cm^{-1}.

The calculations for the C_{2v} model were optimized by fitting the highest energy calculated band to the highest observed fundamental at 950 cm^{-1}. With this fit, $F_R = 3.76$ mdyn/Å, stretching bands were predicted at 950, 913, 788, and 580 cm^{-1}, while only two were observed at 950 and 835 cm^{-1}. The lowest energy stretch at 592 cm^{-1} would be expected to be quite weak, as it is the symmetric axial Si–F stretch, but the remaining three should all have reasonable intensities. On this basis, the C_{3v} model must be favored slightly. In addition, this

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model predicts more than two bending modes in the 400–500-cm^{-1} region, which also points to the C_{3v} structure. However, the use of lack of observation of bands in structure assignments is risky, and while the C_{3v} structure is preferred for this complex, the spectra are insufficient to definitively rule a C_{2v} interaction.

$SiCl_4 \cdot NH_3$

An adduct between $SiCl_4$ and NH_3 is not known; to date only distinct reactions have been reported.[14,15] However, under matrix-isolation conditions stabilization of an adduct would appear feasible. Moreover, $SiCl_4$ adducts are known with stronger bases such as trimethylamine.[16,30] When $SiCl_4$ was codeposited with NH_3 in argon matrices, product bands were observed when relatively high concentrations were employed. Even so, these product bands were quite weak, indicating immediately that product formation does not occur nearly as readily with $SiCl_4$ as with SiF_4. Three of these bands, at 412, 504, and 544 cm^{-1}, showed no deuterium shift, within the bandwidth of the bands, and are in the Si–Cl stretching region. Hence, these bands are assigned to Si–Cl stretching motions in the product species. The upper band, at 1289 cm^{-1}, did show a large deuterium shift inasmuch as this band disappeared when ND_3 was employed, although a deuterium counterpart was not observed. A strong deuterium shift would put this band in the 970-cm^{-1} region, which is obscured by residual NH_3. This band is probably the symmetric deformation mode of the NH_3 group in the product adduct, analogous to the 1253-cm^{-1} band in the SiF_4 experiments.

A possible alternative product would be $Si(NH_2)Cl_3$, formed through reaction and elimination of HCl. However, no HCl was detected in the final spectrum. Also, the aminochlorosilane would be expected to have three essentially equivalent chlorines, and only two distinct Si–Cl stretching modes would be anticipated, one singly and one doubly degenerate. Instead, three such modes were observed, as would be anticipated for either a C_{3v} or C_{2v} adduct. Hence, the product species is very likely the 1:1 adduct, although the dehydrochlorination product cannot be completely ruled out.

Acid/Base Chemistry

The extreme ease of formation of the 1:1 adduct between SiF_4 and NH_3 and the relative difficulty of formation of the adduct between $SiCl_4$ and NH_3 suggest either that $SiCl_4$ is a considerably weaker Lewis acid than SiF_4 or that a larger barrier to complex formation is present. There is no particular reason to anticipate a larger barrier for $SiCl_4$; indeed one might have expected a larger barrier for SiF_4 on the basis of reorganizational energies. Rather, these results seem to indicate that $SiCl_4$ is a weaker Lewis acid than SiF_4; this is consistent with the chloride compound being weaker than the fluoride compound for a number of second-row compounds, including PX_3 and PX_5.[31,32]

It is also interesting to note that no Lewis acid/base adducts have been reported between SiF_4 and oxygen-containing bases. In the present study, SiF_4 was codeposited with $(CH_3)_2O$ in several experiments, and no product was detected. Dimethyl ether is a somewhat weaker base than NH_3,[33] and hence there appears to be some minimum acidity/basicity difference needed to effect adduct formation under these conditions; BF_3, which is a stronger Lewis acid[35] than SiF_4, will form a 1:1 adduct with $(CH_3)_2O$.[34] In addition, the codeposition of Ar/SiF_4 samples with Ar/PH_3 samples at dilutions of 1/250 + 1/250 gave little, if any, product.[36] PH_3 has a proton affinity[33] nearly exactly that of $(CH_3)_2O$, supporting the notion of a minimum basicity necessary for complex formation under these conditions.

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Registry No. $SiF_4 \cdot NH_3$, 71562-57-7; $SiCl_4 \cdot NH_3$, 77924-85-7; SiF_4, 7783-61-1; $SiCl_4$, 10026-04-7; deuterium, 7782-39-0; ^{15}N, 14390-96-6.

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Reaction of Dimethylsilylene with Allylic Methyl Sulfides

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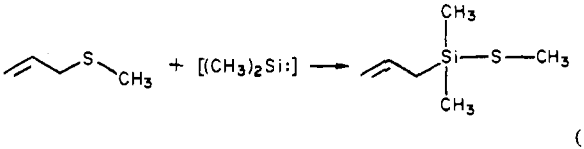
Photochemically generated dimethylsilylene reacts regiospecifically with allylic methyl sulfides to yield allylic dimethyl(methylthio)silanes.

We should like to report a novel insertion reaction of dimethylsilylene into allylic carbon–sulfur single bonds of allylic methyl sulfides.[1] For example, dimethylsilylene generated by photolysis of dodecamethylcyclohexasilane[2] in the presence of allyl methyl sulfide in cyclohexane solvent yields allyldimethyl(methylthio)silane (36%). It should be noted that in control experiments no reaction of dimethylsilylene with dialkyl sulfides such as diethyl sulfide was observed (eq 1).



(1)

The fact that dichlorocarbene and carbethoxycarbene both react with allylic methyl sulfides via initial electrophilic attack of the carbene on a lone pair of electrons of the sulfur to yield a zwitterionic intermediate which reacts further via a 2,3-

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