Electronic and Geometric Structures of $^{+}\text{ScNH}_2$ and $^{+}\text{ScNH}_3$

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The electronic and geometric structures of $^{+}\text{ScNH}_2$ and three isomers of $^{+}\text{ScNH}_3$ have been studied by ab initio MCSCF and CI techniques. All three isomers of $^{+}\text{ScNH}_3$ are calculated to be exothermic products relative to $\text{Sc}^+$ and $\text{NH}_3$, and the ion–dipole complex $^{+}\text{ScNH}_4$ is the most exothermic. The $^{+}\text{ScNH}_2$ bond energy is calculated to be 79 kcal/mol, in agreement with a recent experimental result of 85 kcal/mol. The nature of the bonding in $^{+}\text{ScNH}_2$ is analyzed, and the structure and energetics of various insertion products of $\text{Sc}^+$ and $\text{NH}_3$ are discussed.

Introduction

The rich gas-phase chemistry of transition metal ions with amines and ammonia is being explored by several groups.1–6 These studies have produced accurate bond strengths for several intermediates and considerable insight into the mechanism of the various observed reactions. We believe that a detailed understanding of the electronic and geometric structures of these intermediates is central to an understanding of these reactions, and direct reaction have also been examined and compared with the chain reaction. It has been found that a chain reaction should be considered a favorable pathway in pyrolytic SiC formation. A reaction path for the formation of silyl radical from silylene has also been proposed.

It has been verified theoretically that a Si–Si bond is more likely to form than a Si–C bond. This suggests that the Si rather than the SiC phase is preferentially formed during pyrolytic SiC CVD, which is consistent with the experimental result. Since the surface of the Si phase may have many dangling bonds, molecules containing carbon such as $\text{CH}_4$ can readily react to form a Si–C bond.

Moreover, $\text{CH}_4$ can react even with saturated Si atoms to form a Si–C bond: see Figure 6. This is because the orbital pattern for a saturated Si atom is different from that for a saturated C atom, which has been shown in Figure 2: the LUMO of $\text{SiH}_4$ is extended much more than that of $\text{CH}_4$.

Our model reaction systems are so small that a further extended approach should be performed in order to get a comprehensive picture of the complex reaction systems. Our approach is considered a preliminary step for a real understanding of the SiC formation mechanism.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan, for which we express our gratitude. The numerical calculations were carried out at the Data Processing Center of Kyoto University and the Computer Center of the Institute for Molecular Science (IMS). We are grateful for their generous permission to use FACOM M-780 and VP-400, and HITAC M-680H and S-820 computer systems, respectively.

Registry No. $\text{SiH}_4$, 7803-62-5; $\text{CH}_4$, 74-82-8; SiC, 409-21-2.

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The lowest state of the 3d configuration is of $^2\text{F}$ symmetry and is 14 kcal/mol above the $^2\text{D}$. $\text{NH}_3$ has a $^2\text{B}_1$ ground state and an excited $^2\text{A}_1$ state which is 32 kcal/mol higher in energy.11

These energy levels are shown in Figure 1. The doublet states of $\text{NH}_3$ can combine with the triplet states of $\text{Sc}^+$ to form doublets and quartets and with the singlet states

\[ \text{Sc}^+ \text{NH}_2 \]

\[ \text{Sc}^+ \text{NH}_3 \]

Preliminaries. The 4s3d electronic configuration of $\text{Sc}^+$ gives rise to a $^2\text{D}$ ground state and a $^4\text{A}_1$ state 6.9 kcal/mol higher.16

\[ \text{H} \]

\[ \text{H} \]

\[ \text{H} \]

\[ \text{H} \]


These states would not be distinguishable from the covalently bound configuration of \( \text{Sc}^+ \). Formally, we form a dative bond as

\[
\text{Sc}^+ + \text{NH}_2 \rightarrow \text{Sc}^+ \text{NH}_2^-
\]

or ‘\( \text{F} \) states to form a quartet in which we have the same symmetry.

Alternatively, we may form this state from the excited 2\( \text{AI} \) state of \( \text{NH}_2 \) with a formal covalent bond in the \( \sigma \) system. The remaining 3d electron could interact with an excited \( 1\text{S} \) orbital on \( \text{Sc}^+ \) to form an electrostatic complex with \( \text{NH}_2 \) (4).

Table II: Energies of the Lowest 2\( \text{A}_2 \) State of \( \text{ScNH}_2 \)

<table>
<thead>
<tr>
<th>calculation</th>
<th>( R = 3.75 \text{ au} )</th>
<th>( R = 20.00 \text{ au} )</th>
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<tr>
<td>GVB(4/8)</td>
<td>-815.236756</td>
<td>-815.091136</td>
</tr>
<tr>
<td>GVB(4/8)+1+2</td>
<td>-815.405876</td>
<td>-815.240213</td>
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</tbody>
</table>

carried out for this 2\( \text{A}_2 \) symmetry. These (GVB(4/8)) calculations predict the geometry

\[
\text{Sc}^+ + \text{NH}_2 \rightarrow \text{Sc}^+ \text{NH}_2^-
\]

GVB(4/8) calculations were also carried out for the nonplanar structure (2) as a function of the angle between \( \text{Sc}^+ \) and the \( \text{NH}_2 \) plane. The molecule is planar but requires only 0.3 kcal/mol to move the \( \text{Sc}^+ \) 10\( \text{E} \) out of plane and 0.9 kcal/mol to move it 20\( \text{E} \). The electron distribution is shown in Table I and is compared with the asymptotic fragments \( \text{Sc}^+ + \text{NH}_2 \) and \( \text{NH}_2 \) (2\( \text{B}_2 \)). Note that the \( \sigma \) orbital on \( \text{N} \) gains 0.69 e while the \( \pi \) orbital on \( \text{Sc}^+ \) loses 0.71 e. Simultaneously, the \( \sigma \) orbitals on \( \text{Sc}^+ \) gain 0.22 e while the 2s, 2p\( \text{p} \), and 2p\( \text{p} \) orbitals on \( \text{N} \) lose 0.33 e. This picture of a large charge transfer in the \( \sigma \) system is supported by the electron density contours shown in Figure 2, where we subtract the density of the noninteracting fragments from the molecular density. Figure 2 shows a cut in both the molecular plane and perpendicular to the molecular plane. The solid lines represent an increase in electron density, and the dashed, a decrease in density. Clearly, there has been a large electron shift from the \( \text{Sc}^+ \) \( 3\text{d}_\sigma \) to the \( \text{N} \) \( 2\text{p} \) orbital.

To estimate the \( \text{Sc}^+ - \text{NH}_2 \) bond energy in the 2\( \text{A}_2 \) state, we carried out a GVB(4/8)+1+2 configuration interaction calculation at \( \text{Sc}^+ - \text{NH}_2 \) separations of 3.75 and 20 au. This calculation consisted of 190000 configuration state functions (CSFs), separated to the 3\( \text{F} \) state of \( \text{Sc}^+ \) and the 2\( \text{B}_2 \) state of \( \text{NH}_2 \), and gave the energies shown in Table II. The difference between these two energies is 166 millihartrees (1 millihartree = 0.62751 kcal/mol) and corresponds to a bond energy of 106 kcal/mol. Our calculated 3\( \text{D} \)-3\( \text{F} \) separation in \( \text{Sc}^+ \) is 18.6 kcal/mol, relative to ground state fragments, we calculate a bond energy of 87 kcal/mol. To estimate the size consistency error, we calculated the SCF+1+2 energy of \( \text{Sc}^+ \) (3\( \text{F} \)) and the GVB(3/6)+1+2 energy of \( \text{NH}_2 \) (2\( \text{B}_2 \)). These energies sum to -815.25597 au, which is 15 millihartrees lower than the CI energy at 20 au, shown in Table II. This 15 millihartrees represents a rather conservative estimate for the size consistency error, which reduces the calculated bond energy by 9.6 kcal/mol to -77 kcal/mol. Additional calculations in which an STO-3G representation of an \( \text{f} \) orbital (\( \alpha = 2.6 \) for...
Mavridis et al. ~ScNH$_2^+$ 2A$_2$ in the Molecular Plane

Density of the Fragments Sc$^+$ & NH$_2$

Density Difference for ScNH$_2^+ 2A_2$

Mavridis et al. ~ScNH$_2^+$ 2A$_2$ \perp to the Molecular Plane

Density of the Fragments Sc$^+$ & NH$_2$

Density Difference for ScNH$_2^+ 2A_2$

**Figure 2.** Electron density contours of 2A$_2$($\text{ScNH}_2$) in the molecular plane and perpendicular to the molecular plane. Also presented are the density contours of the superimposed fragments and the corresponding density difference.

Each component was added to the Sc$^+$ basis predicts a differential lowering of the molecule relative to the separated fragments of 2 kcal/mol, bringing our calculated bond energy to $\sim$79 kcal/mol.

GVB(4/8) calculations on the 2A$_1$ (d$_{x^2}$), 2B$_1$ (d$_{xy}$), and 2B$_2$ (d$_{xy}$) states predict the order $^2$A$_2 < ^2$A$_1 (\sim 0) < ^2$B$_2 (7.8 \text{ kcal/mol}) < ^2$B$_1 (21.3 \text{ kcal/mol})$

with the energy separation from the $^2$A$_3$ in parentheses. All states have similar geometries, with an Sc-N separation of $\sim$2.00 \AA{} and an NH$_2$ angle of $\sim$107°.

While the bonding electron distribution in the $^2$A$_3$ and $^2$B$_3$ states is very similar to that in the $^2$A$_2$ state, the $^2$B$_1$ differs significantly. By symmetry the $^2$B$_1$ state should have three $\pi_e$ electrons and therefore a significantly decreased opportunity for charge transfer via the $\sigma$ system. In addition, the in situ, asymptotic state of NH$_2$ should be the $^2$A$_1$.

The equilibrium atomic orbital population in $^2$B$_1$ is

$$4s^{0.07}d_e^{1.07}d_{xx}^{1.04}p_z^{0.17} \text{ on Sc}$$

and

$$2s^{1.46}2p_{1/2}^{1.39}2p_{3/2}^{1.13}2p_x^{1.73} \text{ on N}$$

Clearly, the 4s electron has been transferred to the N($\sigma$) orbital (a mixture of 2s, 2p$_x$, and 2p$_z$). If we compare this with the electron distribution in the $^2$A$_2$ state

$$4s^{0.05}d_e^{0.16}d_{xx}^{0.23}d_{xy}^{1.00} \text{ on Sc}$$

and

$$2s^{1.46}2p_{1/2}^{1.41}2p_{3/2}^{1.14}2p_x^{1.66} \text{ on N}$$

we see very little change on N and essentially the same number of electrons on Sc in the two states. We suspect that the 22 kcal/mol bond energy difference between the $^2$A$_3$ and $^2$B$_3$ is an artifact of referring both to the ground state of Sc$^+$ and NH$_2$. For example, when the $^2$A$_3$ is referred to the fragments Sc$^+$(d$^2$) + NH$_2$, the $^2$B$_3$ state should be augmented by the energy required to excite the $^2$B$_3$(NH$_2$) to $^2$A$_3$(NH$_2$) or 32 kcal/mol and the 13 kcal/mol required to close the NH$_2$ angle in the $^2$A$_3$ state from 144° to 104°. This results in a bond energy of 100 kcal/mol, in substantial agreement with the $^2$A$_3$ number of 99 kcal/mol. These energies are shown in Figure 3.

**Figure 3.** Comparison of +Sc–NH$_2$ bond energies in the $^2$A$_3$ and $^2$B$_1$ states.

NH$_2$(B$_1$), we must augment the calculated bond energy of 79 kcal/mol of the Sc$^+$(d$^2$)–Sc$^+$(d$^2$) excitation energy of 20 kcal/mol. This results in a bond energy of 99 kcal/mol relative to the "natural" asymptote. The calculated bond energy of 55 kcal/mol for the $^2$B$_3$ state should be augmented by the energy required to excite the $^2$B$_3$(NH$_2$) to $^2$A$_3$(NH$_2$) or 32 kcal/mol and the 13 kcal/mol required to close the NH$_2$ angle in the $^2$A$_3$ state from 144° to 104°. This results in a bond energy of 100 kcal/mol, in substantial agreement with the $^2$A$_3$ number of 99 kcal/mol. These energies are shown in Figure 3.

Quartet States. Quartet states obtain when the two valence electrons on Sc$^+$ and the one unpaired electron on NH$_2$ are all kept high spin. For Sc$^+$ in the d$^3$ state we have high-spin electrons in a 4s and a 3d orbital while for NH$_2$ in the $^2$B$_1$ the high-spin

Structures of $^{+}\text{ScNH}_2$ and $^{+}\text{ScNH}_3$

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of $^{+}\text{ScNH}_2$ and the separated fragments placed at the equilibrium separation. The solid contours represent an increase in density in the molecule relative to the separated fragments. The increase on Sc$^+$ is a consequence of $4s \rightarrow 3d$ promotion, required to compact the density on Sc$^+$. The increase on NH$_2$ is a result of the polarization of the electrons due to the positive charge on Sc$^+$. Note that the difference maps are very similar regardless of whether the cut contains the molecular plane or is perpendicular to it. Note that the singly occupied 3d$_{xy}$ electron does not contribute in either plane.

The electrostatic interaction of Sc$^+$ in the 3d$_{6z^2}$, 3d$_{r}$ configuration with NH$_2$($^{1}\text{B}_1$) was evaluated and found to be very similar to the interaction with Sc$^+$(4s3d). This is somewhat surprising in that we expected the lone pair on NH$_2$ to bond by forming a dative bond with the empty Sc(4s$\sigma$) system.

However, for this to happen the Sc$^+$ would have to receive some electron density, and with the d electrons high spin coupled, there was no mechanism available to Sc$^+$ to keep its +1 charge. Apparently, the Coulombic energy the molecule would lose was not to be made up by the dative bond.

These results are summarized in Figure 6. Note that the quartet states shown arise from the interaction of the two ground-state fragments, $^{3}\text{D}$(Sc$^+$) and $^{2}\text{B}_1$(NH$_2$). A set of doublet electrostatic states will of course result from the $^{1}\text{D}$(Sc$^+$) and $^{2}\text{B}_1$(NH$_2$). Since the $^{3}\text{D}$$-^{1}\text{D}$ separation is only 7 kcal/mol and the $^{2}\text{D}$ and $^{2}\text{D}$ states of Sc$^+$ should have the same electrostatic interaction with NH$_2$, we expect the lowest electrostatically bound $^{2}\text{B}_2$ state to be $\sim$27 kcal/mol below the ground-state asymptotes. This means that the electrostatic doublets and quartets will be interleaved. Obviously, a similar argument holds for the quartets arising from the $^{3}\text{F}$ and $^{2}\text{B}_1$ asymptotes. This congestion of electronic potential surfaces with their associated vibrational levels produces a virtual continuum of states, which is in contrast to the

Figure 4. Potential energy curves of various quartet states of $^{+}\text{ScNH}_2$ calculated at the GVB(3/6) level.

electron is in the $\pi$ or $b_1$ orbital. The symmetry of the resulting molecular state, in $C_{4v}$, is determined by the symmetry of the singly occupied 3d orbital. Specifically, we have $^4\text{B}_1$ (3d, or 3d$_{xy}$), $^4\text{A}_1$ (3d$_{x^2-y^2}$), $^4\text{A}_2$ (3d$_{yz}$, or 3d$_{xy}$), or $^4\text{B}_2$ (3d$_{x^2-y^2}$). The potential energy of these four states at the GVB(3/6) level are shown in Figure 4. Examination of the population analysis confirms that there is no electron transfer in these states. The electron density plot shown in Figure 5 suggests however that there has been considerable mutual polarization of the NH$_2$ and Sc$^+$. Figure 5 shows a contour map of the difference between the electron density of the $^4\text{B}_2$ state

![Figure 4](image-url)  
Figure 4. Potential energy curves of various quartet states of $^{+}\text{ScNH}_2$ calculated at the GVB(3/6) level.

![Figure 5](image-url)  
Figure 5. Electron density contours of the $^4\text{B}_2$ state of $^{+}\text{ScNH}_2$ in the molecular plane and perpendicular to the molecular plane. Also presented are the density contours of the superimposed fragments and the corresponding density difference.
ScNH₃⁺ is the electrostatic or charge-dipole complex in which NH₃ is bound to Sc⁺. The interaction energy of Sc⁺ in the 4s3d configuration with NH₃ is shown as a function of distance in Figure 7. This curve was constructed at the SCF level and results in a bond length of 2.39 Å and a bond energy of 36.8 kcal/mol. This bond energy is due primarily to charge-dipole and charge-induced dipole interactions. Most interestingly, this is the ground state of all ScNH₃⁺ isomers studied. The interaction energy of Sc⁺ in the 3dₓ₃₋₃dᵧ configuration with NH₃ is calculated as 30.5 kcal/mol, and the bond length is 2.48 Å. Interestingly, the removal of the 4s electron from Sc⁺ does not permit the NH₃ to approach as closely as it does when in the 4s3d configuration. The two 3d orbitals both have a component in the direction of the incoming NH₃, and both are more extended than the d electrons in the 4s3d configuration.

The second isomer is the insertion product H-ScNH₂+. The geometry of this molecule was optimized at the GVB(5/10) level.

Summary of the relative energies of the low-lying states of ScNH₂⁺

%Figure 6. Summary of the relative energies of the low-lying states of ScNH₂⁺.

Figure 7. Potential energy of Sc⁺ interacting with NH₃.

relatively granular spacing of the covalently bound doublets.

ScNH₂⁺

Three isomers with the above formula are relevant. The first is the electrostatic or charge-dipole complex in which NH₃ is bound, intact to Sc⁺. The interaction energy for Sc⁺(3D; 4s3d) plus NH₃ is shown as a function of distance in Figure 7. This curve was constructed at the SCF level and results in a bond length of 2.39 Å and a bond energy of 36.8 kcal/mol. This bond energy is due primarily to charge-dipole and charge-induced dipole interactions. Most interestingly, this is the ground state of all ScNH₂⁺ isomers studied. The interaction energy of Sc⁺ in the 3dₓ₃₋₃dᵧ configuration with NH₃ is calculated as 30.5 kcal/mol, and the bond length is 2.48 Å. Interestingly, the removal of the 4s electron from Sc⁺ does not permit the NH₃ to approach as closely as it does when in the 4s3d configuration. The two 3d orbitals both have a component in the direction of the incoming NH₃, and both are more extended than the d electrons in the 4s3d configuration.

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and the H-ScNH₂⁺ bond strength was calculated to be 45.5 kcal/mol—a typical Sc-H bond strength. Combining this with our results on ScNH₂⁺ suggests that the reaction

\[ \text{Sc}^+ + \text{NH}_3 \rightarrow \text{H-ScNH}_2^+ \]

is exothermic by at least 16 kcal/mol.

The third isomer is the electrostatic complex of ScNH₂⁺ with H₂. The Sc-NH₂⁺ bond energy is calculated to be 106 kcal/mol (experimental = 119 kcal/mol) while the Sc-H₂⁺ bond is calculated to be 118.5 kcal/mol. These exceptionally strong bonds result in the reaction

\[ \text{Sc}^+ + \text{NH}_3 \rightarrow \text{H}_2 + \text{ScNH}_2^+ \]

being exothermic by 9 kcal/mol. The subsequent electrostatic attraction between the products (Figure 8) lowers the energy by an additional 5.5 kcal/mol, resulting in the complex

\[ \text{H}_2 + \text{ScNH}_2^+ \]

being bound relative to Sc⁺ and NH₃ by 14 kcal/mol. Note that H₂ is perpendicular to the ScNH₂⁺ axis.

Summary of Energies. The relative energies of the various products of the reaction of Sc⁺ and NH₃ are shown in Figure 9. This figure was constructed by using the previously calculated energies for ScH⁺ and ScH₂⁺ as well as the various fragment energies discussed earlier. Experimental numbers, where available, are in parentheses. These results agree with the experimental observation that ScNH₂⁺ is formed exothermically but also suggest that the insertion product and the electrostatic complex involving intact NH₃ are also formed exothermically. The subsequent electrostatic attraction between the products (Figure 8) lowers the energy by an additional 5.5 kcal/mol, resulting in the complex

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Structures of $^{14}\text{ScNH}_2$ and $^{15}\text{ScNH}_3$ 

$\text{Sc}^+(3D) + \text{NH}_3 \rightarrow \text{Products}$

<table>
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- $^{277}$ Sc$^+ + \text{N} + 3\text{H}^+$
- $^{214}$ Sc$^+$ + NH$_2$ + H$^+$
- $^{201}$ Sc$^+$ + NH + 2H$^+$
- $^{104}$ Sc$^+$ + NH$_2$ + H$^+$
- $^{104}$ Sc$^+$ + NH + 2H$^+$

Figure 9. Summary of the relative energies of Sc$^+$ + NH$_3$ in various low-lying electronic states.

Interfering with either of these mechanisms will reduce the metal–NH$_3$ bond strength and consequently the potential for an exothermic H–M–NH$_3^+$ insertion product. Likewise, reducing the metal–H bond strength would also reduce the possibility of an exothermic insertion product.

For example, Cr$^+$ is a d$^5$ system and the ground 6S state one will always have at least one electron in a d$_{xy}$ orbital. Consequently, the planar configuration is not obviously better than the singly bonded nonplanar structure, and as a result, the M–NH$_3$ bond strength will be smaller for Cr$^+$ than Sc$^+$.

Similar considerations apply to the exothermic products H$_3$ + ScNH$^+$. In this case, the exothermicity results from the strong M–NH bond which arises from (1) each 2p$_x$ electron on N bonding to a singly occupied orbital on Sc$^+$ and (2) the lone pair on N bonding to the empty 4s and 3d orbitals on Sc. It is not possible for Cr$^+$ to satisfy both of these conditions simultaneously, and consequently, CrNH$^+$ should have a relatively weak metal–NH bond strength.

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Appendix

The scandium basis set used in this study consists of the (14s,9p,5d) basis from Wachters, augmented with two diffuse $p$ functions (Dunning) and a diffuse $d$ function as recommended by Hay. This set was contracted to (5s,4p,3d) following Raffenetti. The nitrogen basis set was the 5s,4p,2d AN0 set of Almlof and Taylor. The hydrogen basis set was Huzinaga's contracted to 2s and augmented with a set of $p$ functions ($\alpha = 1.0$).

All ab initio calculations were done on an FPS-164 jointly supported by the Michigan State University Chemistry Department and the Office of the Provost by using the Argonne National Laboratory collection of Quest-164 codes. The integrals were calculated by using the program ARGOS written by Pitzer; the SCF and MCSCF calculations were done by using GVB164 written by Bair and the UEXP program and related utility codes written by Shepard. The configuration interaction calculations were performed by using the program UCI (and related utility codes) written by Lischka et al.

(18) Dunning, T. H., Jr. Private communication.
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(23) The ARGOS integral program was developed by R. M. Pitzer (The Ohio State University).
(24) The GVB164 program was written by R. Bair (Argonne National Laboratory).