Gas-Phase Chemistry of First-Row Transition Metal Ions with Nitrogen-Containing Compounds

Theoretical and Experimental Investigations

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The rich gas phase chemistry of first row transition metal (+1) ions with ammonia, and organic compounds (R-X where X=NH₂, CN, NO₂) is discussed. Ongoing theoretical investigations into the Sc⁺/NH₃ system are presented, which provide some insights into the bonding and energetics of a variety of MNHₓ⁺ complexes.

There are a number of mass spectrometric techniques that have been developed for the study of the low pressure gas phase reactions of ionic species with organic molecules. The earliest experiments involving ion/molecule reactions involved chemical ionization mass spectrometry, and the most recent utilize ion beam and Fourier transform ion cyclotron resonance methods. The earliest studies were predominantly organic in nature. More recently, these methods have been used to study organometallic chemistry in the gas phase. The various ionization techniques available in mass spectrometry allow for the generation of unique gas phase species including bare transition metal ions (such as Co⁺, Ni⁺) and ligated species (such as CoCO⁺, CoNO⁺, NiPF₃⁺, NiC₆H₅⁺). Their chemistry with small molecules and a variety of larger molecules containing the functional groups of organic chemistry has been extensively studied in the past 15 years¹. The earlier studies were largely mechanistic in nature, to gain an understanding of how product ions were formed. Recently, combined experimental and theoretical efforts have provided important insights into how these reactions occur. These insights will become, we believe, the basis for a fresh evaluation of the reactivity of inorganic and organometallic species that are studied and utilized in condensed phases.

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In Bonding Energetics in Organometallic Compounds; Marks, T.; ACS Symposium Series; American Chemical Society: Washington, DC, 1990.
Both polar and nonpolar organic compounds exhibit a rich chemistry with bare transition metal ions (1). Small polar compounds react with ions such as Fe$^+$ and Co$^+$, in a single, bimolecular step to form a metal-olefin complex, reaction (1).

$$\text{Co}^+ + C_3H_7X \rightarrow \text{CoC}_3H_6^+ +HX$$

(1)

Such reactions have been reported for X=Cl, Br, OH, SH, OR and even for X=H and R (R=alkyl substituent). The mechanism by which these products are formed was proposed by Allison and Ridge in 1979 (2), and is shown in reaction (2). The reactants first form a complex (a), which may be simply electrostatically bound. In (b), the transition metal ion inserts into the polar C-X bond (formal "oxidative addition"), followed by the shift of a H atom that is on a C which is β to the metal (β-H shift), across the metal onto X, resulting in the degradation of the molecule into two smaller, stable species that reside as ligands on the metal. The last step (d) is a competitive ligand loss. In this process, it appears that the ligand that is more weakly bound to the metal is preferentially lost (2). In some cases, two products result from this dissociation. For example, Co$^+$ reacts with propanol to form both CoH$_2$O$^+$ and CoC$_3$H$_6^+$ (2). While studies of series of, e.g., alcohols, and labeling studies provided some insights into the mechanisms that are operative in the chemistry, many important questions are difficult to approach experimentally. To understand the chemistry, it is certainly important to understand the bonding of the molecules and fragments involved to the transition metal and the strengths of these bonds. Many features such as the distribution of the charge in the various intermediates may also be important in controlling the types of products that are formed. Thus, theoretical studies are necessary to understand the "driving forces" that dominate these reactions and lead to the rich chemistry.

The chemistry of polar compounds containing many types of functional groups and multifunctional organic compounds, with bare transition metal ions has been...
reported. The richest chemistry certainly involves those functional groups that contain nitrogen, and a few examples will be provided here.

Stepnowski and Allison (4) reported the chemistry of a variety of transition metal ions with a series of alkyl cyanides. While ions such as Fe$^+$ and Co$^+$ insert into the C-X bond in many polar compounds, they do not appear to do so for -X = -CN. Instead, C-C bonds are cleaved, as shown for the Co$^+$/n-propyl nitrile system in reactions (3) and (4).

$$\text{Co}^+ + \text{n}-\text{C}_3\text{H}_7\text{CN} \rightarrow \text{CoCH}_3\text{CN}^+ + \text{C}_2\text{H}_4 \quad (3)$$

$$\rightarrow \text{CoC}_2\text{H}_4^+ + \text{CH}_3\text{CN} \quad (4)$$

The reactivity of nitriles may be dominated by a number of aspects of the chemistry including the fact that C-CN bond dissociation energy (BDE) is substantially larger than the BDE's for C-Cl and C-OH bonds (4). Also, there is evidence that the geometry of the initial complex has a dramatic effect - an "end-on" interaction of the metal ions with the nitrile group may make insertion into the C-CN bond geometrically inaccessible (5).

Another interesting functional group containing nitrogen is the nitro group. The chemistry of Co$^+$ with a series of nitroalkanes has been reported by Cassady et al. (6). Consider the Co$^+$/n-C$_3$H$_7$NO$_2$ system. Fourteen different products were reported. Product ions such as Co(C$_3$H$_7$)$_2^+$ and Co(HNO$_2$)$_2^+$ suggested that Co$^+$ inserted into the C-NO$_2$ bond. Other product ions such as CoC$_3$H$_7$O$_2^+$ and CoNO$_2^+$ suggest that RN$O_2$ may be converted, in part, to RO$^-$ and NO$_2^-$ on the metal center. Thus the -NO$_2$ group actively interacts with the metal. The chemistry of organometallic anions with nitroalkanes has also been reported (7).

The chemistry of NO with transition metal ions has also received some attention, and deserves comment here. One of the first ways in which Co$^+$ ions were generated for mass spectrometric study was by electron impact ionization of the volatile compound Co(CO)$_3$NO. In addition to Co$^+$, ions such as CoCO$_2^+$ and CoNO$_2^+$ were formed. While Co$^+$ and CoCO$_2^+$ ions frequently react with organic molecules in the gas phase, CoNO$_2^+$ is unreactive (8). The reason for this change in chemistry upon change of ligand was unclear, since there was only "traditional" bonding-schemes to consider at the time. However, theoretical studies show that the CO ligand is not bonded to first row transition metal ions via the Dewar-Chatt model, but is electrostatically bound (8,9) - thus it's presence does not change the electronic structure of the metal. Presumably NO acts as a 1 or 3-electron donor with Co$^+$ (which has a 3d$^8$ ground state configuration), so the CoNO$_2^+$ ion has a single unpaired
electron on the metal, and should not participate in reactions that require an insertion step. We also note that the NO ligand does appear to be reactive when bound to Co\(^{2+}\). Jacobson reported the observation of reaction (5) involving CO.

\[
\text{Co}_2\text{NO}^+ + \text{CO} \rightarrow \text{Co}_2\text{N}^+ + \text{CO}_2 \tag{5}
\]

There have been a number of studies reported involving metal ion reactions with amines and ammonia. The first of these involved Co\(^+\) with a series of amines, reported by Radecki and Allison in 1984. Reactions (6-9) were observed for the Co\(^+\)/n-\(\text{C}_3\text{H}_7\text{NH}_2\) system.

\[
\begin{align*}
\text{Co}^+ + n-\text{C}_3\text{H}_7\text{NH}_2 & \rightarrow \text{CoC}_3\text{H}_7\text{N}^+ + \text{H}_2 \tag{6} \\
& \rightarrow \text{CoC}_3\text{H}_5\text{N}^+ + 2 \text{H}_2 \tag{7} \\
& \rightarrow \text{CoCH}_5\text{N}^+ + \text{C}_2\text{H}_4 \tag{8} \\
& \rightarrow \text{C}_3\text{H}_8\text{N}^+ + \text{CoH} \tag{9}
\end{align*}
\]

These results were certainly surprising since insertion into the C-NH\(_2\) bond was not observed, although the reaction (10)

\[
\text{Co}^+ + \text{C}_3\text{H}_7\text{NH}_2 \rightarrow \text{CoC}_3\text{H}_6^+ + \text{NH}_3 \tag{10}
\]

should be exothermic. It was proposed that H\(_2\) elimination occurred by initial insertion into the N-H bond. While Co\(^+\) did not insert into the C-NH\(_2\) bond of primary amines, it does appear to insert into the C-N bond in the tertiary amine, (C\(_2\text{H}_5\))\(_3\)N, and in allyl amine. To explain the failure to observe reaction (10) it was proposed that there was a barrier along the reaction channel - that the insertion intermediate was energetically inaccessible for thermal energy reactions, which could only be due to a weak Co\(^+\)-NH\(_2\) bond. The BDE would have to be unusually small, < 20 kcal/mol. It has since been shown, as discussed below, that this is not the case. Another explanation may be that Co\(^+\) does react with, e.g., propyl amine, to form propene and ammonia, but there is a barrier to the dissociation step of (C\(_3\text{H}_8\))Co\(^+\)(NH\(_3\)) - which cannot be distinguished in the mass spectrum from the complex containing the intact molecule, Co\(^+\)(C\(_3\text{H}_7\text{NH}_2\)). The gas phase chemistry of a number of metal ions with amines has been studied. Babinec and Allison reported the chemistry of Cr\(^+\), Mn\(^+\), Fe\(^+\), Ni\(^+\), Cu\(^+\) and Zn\(^+\) with n-propyl amine. Only Fe\(^+\) clearly inserted into the C-N bond, as evidenced by the observation of the two products FeNH\(_3^+\) and FeC\(_3\text{H}_4^+\). Mn\(^+\) (with a half-filled d-shell, 3d\(^6\)4s\(^1\) ground state) and Zn\(^+\) (with a filled
d-shell, $3d^{10}4s^1$ ground state) were unreactive with propyl amine. In contrast, Cr$^+(3d^5$ ground state) and Cu$^+(3d^{10}$ ground state) were both observed to induce $H_2$ elimination only. Siqsworth and Castleman(13) studied the reactions of Ag$^+$ and Cu$^+$ with methyl amine, dimethyl amine and trimethyl amine. In these studies, hydride abstraction was observed to yield the (amine-$H$)$^+$ ion and the MH neutral product.

In 1987, Buckner and Freiser(14) showed that Co$^+$ does form a strong bond to NH$_2$, and did so as follows. In an FTMS instrument they formed CoOH$^+$, which reacts with ammonia, reaction (11).

$$\text{CoOH}^+ + \text{NH}_3 \rightarrow \text{CoNH}_2^+ + \text{H}_2\text{O} \quad (11)$$

They also found that the NH$_2$ group can be displaced from Co$^+$ by benzene, but not by acetonitrile. With this information, they concluded that the BDE for Co$^+-\text{NH}_2$ is $65 \pm 8$ kcal/mol. In this same work they reported the chemistry of MNH$_2^+$ with some hydrocarbons. They also found that FeO$^+$ reacts with ammonia to form FeNH$^+$, and reported some chemistry for this ionic species. Their work suggested that the BDE for FeNH$^+$ was $> 41$ kcal/mol and $< 81$ kcal/mol. This work was extended in a report by Buckner, Gord and Freiser in 1988(15). They found that a variety of metal ions including Sc$^+$, Ti$^+$ and V$^+$ react with ammonia in an exothermic process by reaction (12), which suggests that these M$^+-\text{NH}$ bonds are stronger than 93 kcal/mol. The BDE for V$^+-\text{NH}$ was determined to be $101 \pm 7$ kcal/mol, and the BDE for Fe$^+-\text{NH}$ to be lower, $54 \pm 14$ kcal/mol.

$$\text{M}^+ + \text{NH}_3 \rightarrow \text{MNH}^+ + \text{H}_2 \quad (12)$$

They also reported a number of reactions for MNH$^+$ with neutral molecules. A variety of mechanisms for reaction (12) was discussed, including dehydrogenation via direct decomposition of the intermediates (H)$_2M^+\text{NH}$ and/or H-M$^+-\text{NH}_2$.

The Reaction of Sc$^+$ with NH$_3$

Our intent is to gain theoretical insights into the initial interaction of M$^+$ with a polar molecule, the insertion step and reductive elimination by a systematic study of the interaction of M$^+$ with NH$_3$. We begin here with Sc$^+$ because it has only two valence electrons and thus its theoretical description and its calculated interaction with NH$_3$ and its fragments will be more reliable than with the latter transition elements. We will first describe the ScN$^+$ core and then build up the various intermediates by adding hydrogens. Specific fragments to be studied include ScNH$^+$, ScNH$_2^+$, HScNH$_2^+$ and ScNH$_3^+$. The calculations will include all electrons and will use both MCSCF and
CI techniques. The basis sets used and the general approach have been described previously(16).

**SCN**

The relative energies of the low lying states of Sc⁺, N, NH and NH₂ are collected in Figure 1. Because the excited states of N are much higher in energy than those of Sc⁺ we will consider the states of SCN⁺ which correlate to the ground state of N and the sd and d² configuration of Sc⁺(16). As Sc⁺ in an sd configuration approaches N we can imagine forming a σ bond between the 4s electron on Sc⁺ and a 2p σ electron on N and a π bond between the 3dxz and 2px electrons. This leaves an unpaired electron on N in the 2py orbital and results in a 2Π state represented by

\[
\begin{array}{c}
\text{Sc}\cdot \sigma \cdot \text{N} \\
\sigma_{\text{Sc}^+}\cdot \pi_{\text{N}}
\end{array}
\]

\[\text{SC} \cdot \text{N}^+ \quad 2\Pi
\]

It is only at large ScN separations that the Sc electron in the σ bond is pure 4s. As the bond forms other orbitals on Sc of σ symmetry mix into the bonding orbital. This is seen most vividly in Figure 2a which shows the occupancies of various atomic orbitals in the 2Π state of SCN⁺ as a function of separation. At equilibrium the atomic orbitals in the σ bond have the occupancy

\[(4s^{0.0} \cdot 4p^{0.0} \cdot 3d^{0.66})_{\text{Sc}}(2p_{1/2}^{1.28})_{\text{N}}\]

and the 4s orbital has gone from an occupancy of 1 to 0. Interestingly the π bond occupancy is equal to that of the σ bond

\[(3d_{xz}^{0.66})_{\text{Sc}}(2p_{x}^{1.28})_{\text{N}}\]

while the unpaired electron remains essentially localized on N.

\[(3d_{yz}^{0.07})_{\text{Sc}}(2p_{y}^{0.91})_{\text{N}}\]

The net result is that Sc⁺ looses 0.49 electrons to N resulting in the charge distribution

\[+1.61 \text{Sc N}^{-0.49}.
\]

If we break the π bond in this state and place the high spin electron on Sc in a dσ orbital we will form a 4Δ state.
Figure 1. Relative Energy Levels (kcal/mol⁻¹) of N(12), NH(20), NH₂(21) and Sc⁺(19).

Figure 2. Orbital occupancy as a function of internuclear distance for ScN⁺ in the a) ²Π and b) ²Σ⁺ states.
In a similar way we can consider states of ScN$^+$ which correlate to the $d^2$ (excited) state of Sc$^+$. For example the $^2\Sigma^+$ state has a $\pi, \pi$ double bond and an unpaired electron on N in the $\sigma$ system

\[
\begin{bmatrix}
\text{Sc} \overset{\pi}{\rightarrow} \overset{\pi}{\text{N}} \\
\end{bmatrix}
\rightarrow
\begin{bmatrix}
\text{Sc} \overset{\pi}{\rightarrow} \overset{\pi}{\text{N}} \\
\end{bmatrix}^+
\]

If we break a $\pi$ bond in this structure and place the then uncoupled $d\pi$ electron in a $d\delta^\pi$ orbital we have ScN$^+$ in a $^4\Phi$ state held together by a single $\pi$ bond

\[
\begin{bmatrix}
\delta\pi \overset{\pi}{\text{Sc}} \overset{\pi}{\rightarrow} \overset{\pi}{\text{N}} \\
\end{bmatrix}
\rightarrow
\begin{bmatrix}
\delta\pi \overset{\pi}{\text{Sc}} \overset{\pi}{\rightarrow} \overset{\pi}{\text{N}} \\
\end{bmatrix}^+
\]

Configuration interaction calculations on these four states result in the potential curves shown in Figure 3. The orbital populations in the $^2\Sigma^+$ state are shown in Figure 2b and the properties of all four states are summarized in Table I.

Table I. Calculated Properties of Several States of ScN$^+$

<table>
<thead>
<tr>
<th>State</th>
<th>Lewis</th>
<th>$D_e$(kcal/mol)</th>
<th>$R_e$(Å)</th>
<th>$\omega$(cm$^{-1}$)</th>
<th>$Q$(Sc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^2\Sigma^+ (d^2)$</td>
<td>$\overset{\pi}{\text{Sc}} \overset{\pi}{\rightarrow} \overset{\pi}{\text{N}} \overset{\pi}{\rightarrow} \overset{\pi}{\text{Sc}}$</td>
<td>63.0</td>
<td>1.738</td>
<td>871</td>
<td>+1.51</td>
</tr>
<tr>
<td>$^2\Pi_X (sd)$</td>
<td>$\overset{\pi}{\text{Sc}} \overset{\pi}{\rightarrow} \overset{\pi}{\text{N}} \overset{\pi}{\rightarrow} \overset{\pi}{\text{Sc}}$</td>
<td>55.3</td>
<td>1.804</td>
<td>811</td>
<td>+1.51</td>
</tr>
<tr>
<td>$^4\Delta (sd)$</td>
<td>$\overset{\pi}{\text{Sc}} \overset{\pi}{\rightarrow} \overset{\pi}{\text{N}} \overset{\pi}{\rightarrow} \overset{\pi}{\text{Sc}}$</td>
<td>26.8</td>
<td>2.101</td>
<td>534</td>
<td>+1.46</td>
</tr>
<tr>
<td>$^4\Phi (d^2)$</td>
<td>$\overset{\pi}{\text{Sc}} \overset{\pi}{\rightarrow} \overset{\pi}{\text{N}} \overset{\pi}{\rightarrow} \overset{\pi}{\text{Sc}}$</td>
<td>21.1</td>
<td>1.979</td>
<td>674</td>
<td>+1.47</td>
</tr>
</tbody>
</table>

Note that all $D_e$'s are reported relative to the ground states of Sc$^+ ({}^3\text{D})$ and N$^+({}^4\text{S})$. Most interestingly, the ground state is the $^2\Sigma^+$ which contains two $\pi$ bonds and which correlates with the excited $d^2$ configuration of
Figure 3. Potential Energy Curves for 4 States of ScN⁺.
Sc\(^+\). It is also noteworthy that the charge on Sc\(^+\), Q, is independent of the number and type of formal bonds in the molecule.

ScNH\(^+\)

We can imagine ScNH\(^+\) being formed by addition of a H to either the \(^2\Sigma^+\) or \(^2\Pi\) state of ScN\(^+\).

Sc = N\(^+\) [\(^2\Sigma^+\)] + H [\(^2S\)] → Sc = N – H\(^+\) [\(^1\Sigma^+\)]

or

Sc = N\(^+\) [\(^2\Pi\)] + H [\(^2S\)] → Sc = N\(^+\) [\(^1\Sigma^+\)]

Optimizing the structure of this system at the CI level results in the linear structure with a \(^+\)ScN–H dissociation energy of 118.5 kcal/mol (Kunze, K.L. and Harrison, J.F., MSU, unpublished results). This is a remarkably strong NH bond (free NH has a \(D_b\) of 80 kcal/mol and we require 108 kcal/mol to break the first N–H bond in NH\(_3\)).

The reason for this enhanced NH bond strength is apparent when one analyzes the electron distribution in the ScNH\(^+\) molecule and compares it with ScN\(^+\) and NH. This analysis shows that when H bonds to ScN\(^+\) the N 2s orbital loses 0.45 electrons, the H 1s loses 0.17e and the N 2p\(_\sigma\) orbital gains 0.30 electrons. If, for bookkeeping purposes, we assume all of the electrons lost by H go into the N 2p\(_\sigma\) and that the remaining gain in the N 2p\(_\sigma\) comes from the N 2s, then we can allot the remaining 0.32 electrons lost by the N 2s to the \(\sigma\) orbitals on Sc\(^+\). This accounts nicely for the increase of 0.33 electrons in the Sc\(^+\) \(\sigma\) system and suggests that the enhanced N–H bond strength in ScNH\(^+\) is due to a significant dative bond formed between Sc and the N 2s electron pair. Alternatively, we may imagine forming ScNH\(^+\) via the lowest state (\(^3\)F) of the excited \(d^2\) configuration.

Sc\(^+\) (\(^3\)F) + NH (\(^3\Sigma^-\)) → ScNH\(^+\) (\(^1\Sigma^+\))

The Sc\(^+\)–NH bond strength is calculated to be 105.9 kcal/mol relative to the ground state fragments (Kunze, K.L. and Harrison, J.F., MSU, unpublished results), which should be compared with recent results by Armentrout et al. (Armentrout, P., Univ. of Utah, private communication, 1989) suggesting a Sc\(^+\)–NH bond strength of 118 kcal/mol. This Sc\(^+\)–NH calculated bond strength is 43 kcal/mol stronger than the 63 kcal/mol calculated for the ScN\(^+\) bond in the \(^2\Sigma^+\) state. Note that the calculated N–H bond strength in ScN\(^+\)–H is also 43 kcal/mol stronger than the 75.5 kcal/mol calculated...
bond strength in NH. This synergistic relationship between the N-H and Sc-N bonds in ScNH\(^+\) is a consequence of the freedom given to the \(\sigma\) system by the unusual \(\pi, \pi\) double bond between the metal and N. As H bonds to the \(\rho\sigma\) electron on N considerable \(2s\) character is mixed into the NH bonding orbital. This hybridization not only strengthens the N-H bond but the companion orbital which points toward the Sc simultaneously stabilizes the ScN bond by a dative interaction. The \(^2\Sigma^+\) state represented above is more accurately written as

\[ ^+\text{Sc} \rightarrow \text{N-H} \left( ^1\Sigma^+ \right) \]

ScNH\(^2+\)

The ground state of NH\(_2\) is of \(^2\text{B}_1\) symmetry and is characterized by a \(\sigma^*\pi^1\) electronic configuration and an NH\(_2\) angle of 104°, whereas, the first excited state is of \(^2\text{A}_1\) symmetry and is 32 kcal/mol above the ground \(^2\text{B}_1\). It is characterized by a \(\sigma^1\pi^2\) electronic configuration and an angle of 144°.

We may imagine the ground state of NH\(_2\), reacting with either the ground or excited state of Sc\(^+\) to form a doublet with a nonplanar structure in which the bonding electron on Sc\(^+\) is formally either 4s or 3d\(\sigma\).

Alternatively we can imagine the ground state of NH\(_2\) reacting with the 3d\(^2\) configuration of Sc\(^+\) to form the planar molecule having a \(\pi\) bond and a (dative) \(\sigma\) bond. The unpaired electron on Sc would most likely be in a \(\delta^\pm\) orbital to optimize the ability to form a \(\pi\) and dative \(\sigma\) bond.

All electron multireference single and double CI calculations (Mavridis, A.; Herrera, F.; and Harrison, J.F., MSU, unpublished work) predict that the ground state of ScNH\(_2\)^+ is of \(^2\text{A}_2\) symmetry and that it is planar with the geometry

\[
\begin{array}{c}
\text{Sc} & \text{N} & \text{H} \\
\sigma & \pi & \text{N} \\
\end{array}
\]

\[ ^+\text{Sc-N-H} \left( ^1\Sigma^+ \right) \text{[107°]} \]

1.98

1.01
Only small energies are required to deviate from the planar structure. Our calculations suggest that 0.3 kcal/mol is required to move Sc $10^\circ$ out of plane and 0.9 kcal/mol to move it $20^\circ$.

The electron distribution at equilibrium suggests that Sc has a total charge of +1.51 having lost 0.49 electrons to the NH$_2$ group. The electrons remaining on Sc are distributed as follows:

\[ 4s^{0.06} 4p_x^{0.04} 4p_y^{0.07} 3d_z^{0.1} 3d_x^{0.22} 3d_y^{1.00} \]

We calculate the $^{+}$Sc=NH$_2$ bond dissociation energy for the $^2$A$_2^*$ state to be 79 kcal/mol which compares favorably with the 85 kcal/mol recently determined by Armentrout et al. (Armentrout, P.B., Univ. of Utah, private communication, 1989). The lowest $^2$A$_1^*$ state has the unpaired electron in a $\delta_+$ orbital and is essentially degenerate with the ground $^2$A$_2^*$ state. The lowest $^2$B$_2^*$ state has a $D_0$ of 70 kcal/mol and results when the unpaired electron is in a $d_y^*$ orbital. Placing the unpaired electron in a $d_x^*$ orbital results in the $^2$B$_1^*$ state which is 22 kcal/mol above the $^2$A$_2^*$ ground state. We have also investigated several quartet states which are bound by ~30 kcal/mol, primarily by charge-dipole interactions.

$^{+}$ScNH$_3^+$

Three isomers with this formula are relevant. The first is a charge-dipole complex in which NH$_3$ is intact. This complex is bound relative to ground state fragments by 36.8 kcal/mol.

The second isomer is the insertion product H-Sc-NH$_2$. Generalized Valence Bond calculations on this system suggest that it is bound relative to Sc$^+$ + NH$_3$ by 16 kcal/mol.

The geometry is

\[
\begin{align*}
H & \quad H \\
1.79 & \quad \text{Sc-N} \\
1.92 & \quad H \\
1.01 & \quad H
\end{align*}
\]

The third isomer is the electrostatic complex ($H_2$)ScNH$_3^+$ that is bound relative to Sc$^+$ + NH$_3$ by 14 kcal/mol. Interestingly the $H_2$ molecule is bound to the ScNH$_3^+$ ion by 5 kcal/mol.

**Summary of Energetics**

The relative energies of the various products of the reaction of Sc$^+$ ($^3D$) with NH$_3$ are collected in Figure 4. This figure was constructed using the energies discussed in the previous section as well as binding energies of ScH$_2^+$ and ScH$_2^+$(18) reported earlier. Energies determined experimentally are shown in parentheses.
Figure 4. Summary of Energetics for Sc⁺ + NH₃.
These calculations suggest that both the insertion product \( \text{H-Sc-NH}_2^+ \) and the complex \( \text{H}_2\cdot\cdot\cdot\text{ScNH}^+ \) are exothermic products of the reaction of Sc\(^+\) with NH\(_3\). The insertion product is formed exothermically because the Sc-NH\(_2\) bond strength and the Sc-H bond strength are large and able to overcome the 108 kcal/mol required to break a N-H bond in NH\(_3\). Our calculations suggest that the \( \text{+Sc-NH}_2 \) bond is strong because:

1. The NH\(_2\) group donates charge to the transition metal ion via the \( \sigma^2 \) pair on N. This dative interaction is optimized when there are no 4s or 3d\(\sigma\) electrons on the metal.

2. The metal donates charge to the \( \pi \) orbital of the NH\(_2\) group. This transfer is optimized when there is one d\(\pi^*\) electron in the \( \pi \) system being coupled with the NH\(_2\) \( \pi \) orbital.

Interfering with either of these mechanisms will reduce the metal-NH\(_2\) bond strength and consequently the potential for an exothermic H-M-NH\(_2^+\) insertion product. Likewise reducing the metal-H bond strength would also reduce the possibility of an exothermic insertion product.

For example, Co\(^+\) is a d\(^4\) system and regardless of the configuration of the electrons in the ground 3\(F\) state one will always have at least one electron in a d\(\sigma\) orbital. Consequently the planar configuration is not obviously better than the singly bonded non-planar structure

\[
\begin{array}{c}
\text{H} \\
\text{N} \\
\text{O} \\
\text{H}
\end{array}
\]

and, as a result, the M-NH\(_2\) bond strength will be smaller for Co than Sc. So while Sc\(^+\) and Co\(^+\) both have two singly occupied d orbitals Co\(^+\) is less energetically favored to react with NH\(_3\) to form

\[
\text{H - Co - NH}_2^+.
\]

Similar considerations apply to the exothermic products \( \text{H}_2^+ + \text{ScNH}^+ \). In this case the exothermicity results from the strong M-NH bond which arises from:

1. Each 2p\(\pi^*\) electron on N bonding to a singly occupied orbital on Sc\(^+\) and

2. The lone pair on N bonding to the empty 4s, 3d orbitals on Sc.
It is not possible for Co$^+$ to satisfy both of these conditions simultaneously and consequently, CoNH$^+$ should have a relatively weak Metal-NH bond strength. The process

$$\text{Co}^+ + \text{NH}_3 \rightarrow \text{Co=NH}^+ + \text{H}_2$$

will be less exothermic if the Co=NH$^+$ bond strength is less than 90 kcal/mol.

Acknowledgments

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