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Solvation of Yttrium with Ammonia Revisited. Di-amide Formation in the Reaction of Yttrium with Ammonia

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The reactivity of yttrium atoms toward ammonia is revisited using expanded density functional theory calculations. The new results reveal that absorption of NH_3 on YNH is dissociative to form $Y(NH_2)_2$.The di-amide species can adsorb further NH_3 molecules molecularly to form $Y(NH_2)_2NH_3$ and $Y(NH_2)_2(NH_3)_2$. The calculations aimed to reveal the detail of the potential energy curves between the imide and the di-amide forms. The $Y(NH_2)_2(NH_3)_x$ species are more stable than those of $YNH(NH_3)_x$ by more than 20 kcal/mol.

Introduction

The reactivity of transition metal−ligand complexes is an important research field. Many reports have focused on the electronic structure and the reaction mechanism for these transcendental systems.[1−17] Understanding the nature of the bonding in transition metal compounds is a topic of great interest, and remarkable progress has been made in the past years.[16] In general, the transition metal−ligand bond is well described with the scheme of ligand donation and transition metal back-donation. The dative bond (another name for a donor−acceptor bond) seems to be the best explanation for these reactions. Despite the progress made toward the understanding of the nature of the chemical bond of transition metal−ligand compounds, it is clear that much work remains to be done. In this context, many authors are focusing in the study of solvation,[1−12] since it can be considered as the first interaction that occurs between the transition metal and ligands. The rationale behind this approach is that the study of the solvation can give some insights concerning the reactivity of these compounds.

Solvation occurs each time a molecule becomes imbedded into a solvent. It involves the formation of molecular complexes resulting from the binding of molecules to form a new species. It is the first (close) approach between the reacting moieties, defining the molecular spatial positions before the actual reaction. There is a great interest in solvation of different metal centers such as clusters by small molecules, unsaturated metal complexes and atoms. The understanding of the chemistry of metal centers in solution benefits from these studies.[1−12]

Ammonia is a molecule that can be used to study the solvation of metal centers, due to its different bonding behavior toward transition metal atoms and clusters.[1−12] The oxidative addition of the N−H bond of ammonia onto second-row transition metal atoms was studied theoretically by Blomberg et al.[2] According to these results, the formation of the $M-NH_3$ molecular complex is the first step of the reaction, followed by the oxidative addition with no activation barrier. Adduct formation for Y, Nb, and Zr is exothermic, and no activation energy was reported for the oxidative addition of the NH bond. Ye et al.[3] reported a theoretical investigation of the reaction $Y^+ + NH_3$ and showed that the mechanism of the reaction is the same, but to form $YNH^+ + H_2$ there is an activation barrier of 11 kcal/mol. They established that the exothermicity of the formation of the $M-NH_3$ molecular complex is large enough to overcome the small activation barrier.

In a previous paper,[1] the results of the interaction of yttrium atoms with ammonia were reported. For this system, multiphoton ionization and kinetic studies have shown that the first reaction step is the rapid formation of yttrium imide (YNH). This occurs via the oxidative addition of the N−H bond of ammonia and the removal of molecular hydrogen. In this paper, new density dunctional theory (DFT) results provide evidence that absorption of NH_3 on YNH is dissociative to form $Y(NH_2)_2$. The di-amide species can adsorb molecularly further NH_3 molecules to form $Y(NH_2)_2NH_3$, $Y(NH_2)_2(NH_3)_2$, and $Y(NH_2)_2(NH_3)_3$. This interpretation is fully supported by the detail of the potential energy curves between the imide and the di-amide forms. In this paper, optimized structures, harmonic vibrational analysis, Mulliken atomic charges, and molecular orbital pictures are discussed.

Computational Details

All calculations were performed using Gaussian 98[18] and the Becke's 1988 functional, that includes the Slater exchange and the corrections involving the gradient of the density. The gradient-corrected correlation functional (BPW91)[19] due to Perdew and Wang's 1991 was employed. The LANL2DZ atomic orbital functions[20−22] were used. To locate different minima on the potential energy surface, starting from several initial geometries, full geometry optimizations without symmetry constrains were performed. To find the most stable spin state, in all calculations different spin multiplicities ($2S_z+1$) were considered. To find the global minimum, several multiplicities and several initial structures for each adduct were considered. It is not possible to exclude the fact that the true global minimum was missed in the optimization procedure. However, the number of different initial geometries and spin multiplicities considered is sufficiently high so as to feel confident that the global minimum has been identified.

Optimized minima and transition states were confirmed with harmonic frequency analysis. To locate transition states, the

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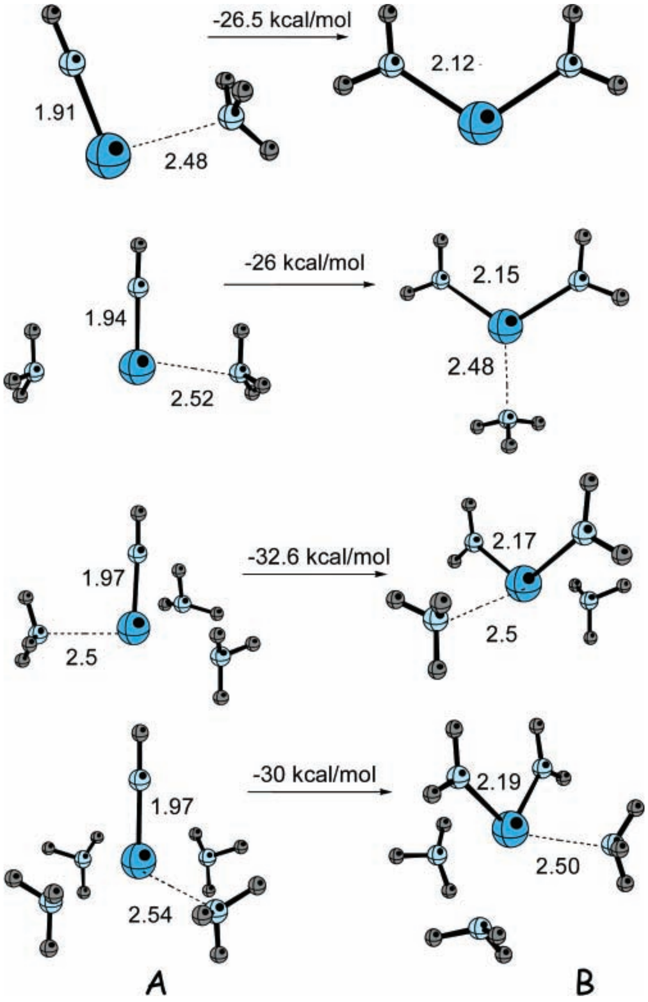

Figure 1. Optimized structures of (A) $YNH(NH_3)_x$ and (B) $Y(NH_2)_2(NH_3)_y$.

Synchronous Transit-Guided Quasi-Newton (STQN) method[23,24] has been used.

There is no universally accepted method of calculating atomic charges, and no experimental technique is available to measure them directly. In a previous work, de Oliveira et al.[25] reported an investigation testing the quality of Mulliken and Bader charges. They found a good agreement between both methods for a qualitative description of the atomic charges. In some cases, the results of Mulliken population analysis are sensitive to the basis set, and for this reason the Natural Bond Orbital (NBO) method is becoming more popular. This method is better than Mulliken's since it is less susceptible to the basis set.[26] To test the quality of Mulliken and NBO charges for the present systems, the calculation of NBO for some examples was performed using the same basis set. As reported in Supporting Information, for these compounds both methods produce the same qualitative description of the atomic charges, namely, the yttrium atom is positive while the N atoms are negative, with the yttrium becoming more positive as the ammonia molecule dissociates. For this reason, in this paper the Mulliken atomic charges are used to discuss the qualitative behavior of the charge-transfer process.

Results and Discussion

Figure 1A shows the optimized geometries for the most stable structures that were considered and reported earlier.[1] In that study, the oxidative addition was considered as the reaction mechanism, followed by the sequential addition of three further NH_3 molecules to YNH. Kinetic modeling and DFT calculations (Figure 1A) on the stability of $YNH(NH)_x$ imide complexes were consistent with a mechanism involving the solvation of yttrium imide by molecular NH_3.[1] However, this interpretation is brought into question by these new DFT results, that reveal evidence that absorption of NH_3 on YNH is dissociative to form $Y(NH_2)_2$ and that these di-amide species can adsorb molecularly additional NH_3 molecules to form $Y(NH_2)_2NH_3$, $Y(NH_2)_2(NH_3)_2$, and $Y(NH_2)_2(NH_3)_3$. The new structures for these compounds are shown in Figure 1B. There are the di-amide species which are more stable than the imide complexes for more than 25 kcal/mol, as indicated in Figure 1. For both compounds, in going from the complex with one ammonia to the four ammonia subunits cluster, the Y−N bond distance increases. The Y−NH bond distance of the di-amide species is larger than the Y−NH bond length of the imide complexes, while the Y−NH_3 bond distance remains approximately the same. The Y−NH distance is shorter than the Y−NH_3 bond length for all the structures displayed in Figure 1.

TABLE 1: Reaction Energies for the Interaction of YNH with NH_3

reaction	ΔE (kcal/mol)
$YNH + NH_3 \rightarrow YNH(NH_3)$	−21.5
$YNH(NH_3) \rightarrow Y(NH)_2$	−26.5
$YNH(NH_3) + NH_3 \rightarrow YNH(NH_3)_2$	−20.8
$Y(NH)_2 + NH_3 \rightarrow Y(NH)_2(NH_3)$	−21.9
$YNH(NH_3)_2 \rightarrow Y(NH)_2(NH_3)$	−26.0
$YNH(NH_3)_2 + NH_3 \rightarrow YNH(NH_3)_3$	−12.3
$Y(NH)_2(NH_3) + NH_3 \rightarrow Y(NH)_2(NH_3)_2$	−20.7
$Y(NH)_2(NH_3)_2 + NH_3 \rightarrow Y(NH)_2(NH_3)_3$	−9.9

The vibrational analysis (see Supporting Information) indicates that the structures are minima on the potential energy surfaces. For two ground states ($Y(NH)_2(NH_3)$ and $YNH(NH_3)_3$) and the transition state of $Y(NH)_2NH_3$, there is one imaginary frequency that corresponds to the rotation of the NH_3 molecules. For the Li atom and for $Na(NH_3)_2$ and $Na(NH_3)_3$ complexes, where NH_3 molecules could rotate almost freely around the M−N bonds, similar results have been found.[28,29] Therefore, it can be assumed that the geometries presented here and their energies are quite similar to the minima and the transition state on the potential energy surface. Table 1 reports the binding energies for the most important reactions of YNH and $Y(NH)_2$. In all cases, the products of the reaction are more stable than the reactants.

It is now apparent that our earlier DFT study, that calculated the structures and energetics of the NH_3 molecular YNH complexes $YNH(NH_3)_x$ ($x = 1$ to 4), only partially explored the reaction potential, although all four species were identified as being stable. YN_2H_4 appears not to contain an −NH_3 group, since the most feasible candidate structure is the di-amide $Y(NH_2)_2$. Figure 2 presents the results of new DFT calculations that explore the reaction pathways opened by this possibility. The figure also summarizes our previous calculations on YNH solvation. $Y(NH_2)_2$ can be formed from the molecular complex $YNH(NH_3)$ by simple internal hydrogen transfer. DFT calculations find that the di-amide form is 26.5 kcal mol^{-1} more stable than the $YNH(NH_3)$ imide−ammonia complex.

According to what is being said, the oxidative addition is the first step of the reaction, followed by the addition of one NH_3 molecule to YNH. $YNH(NH_3)$ can follow two paths: the formation of $Y(NH)_2$ or the absorption of another NH_3 molecule. The data of Table 1 indicate that the binding energies are similar (26.5 and 20.8 kcal/mol, respectively) and both can be present at the experimental conditions. According to these results and

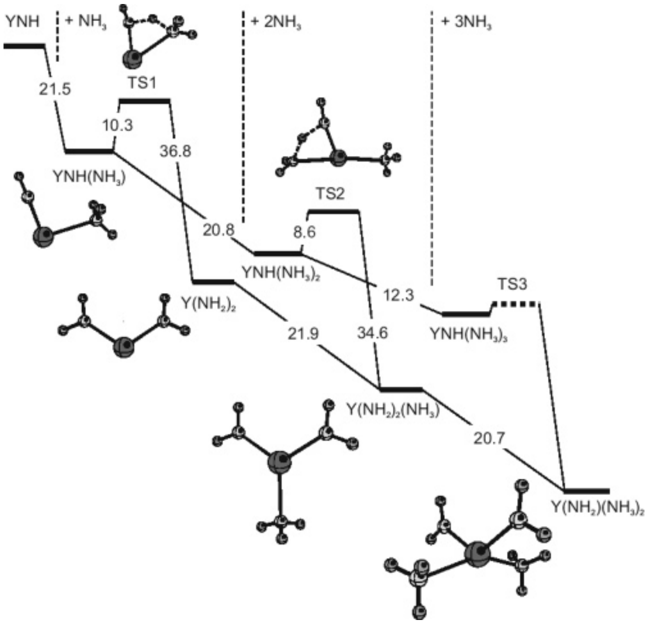

Figure 2. Pathways for the reaction of YNH with NH_3. Values are energy differences in kcal/mol.

following the first route of the reaction, the solvation of YNH is followed by the absorption of NH_3 on YNH. This absorption is dissociative and $Y(NH_2)_2$ is formed. This di-amide species can adsorb further NH_3 molecules molecularly to form $Y(NH_2)_2NH_3$, $Y(NH_2)_2(NH_3)_2$, and $Y(NH_2)_2(NH_3)_3$. In Table 1, the values indicate that the association of the third ammonia molecule to form $Y(NH_2)_2(NH_3)_3$ is fairly weak (9.9 kcal/mol). A species with this stoichemistry was not observed in the experiment, implying that the NH_3 binding is uncertain. Theoretical values agree with the experimental observation, since the reaction energy for the third ammonia molecule is more than half of the other binding energies.

Following the second path, $YNH(NH_3)$ absorbs another NH_3 molecule to form $YNH(NH_3)_2$. The binding energy of this process is 20.8 kcal/mol. This compound ($YNH(NH_3)_2$) can also follow two reaction routes: the dissociative absorption of ammonia, or the absorption of another NH_3 molecule. In the first case, the formation of $Y(NH)_2(NH_3)$ is found with a binding energy of 26.0 kcal/mol. The absorption of the third ammonia molecule is weak (12.3 kcal/mol), and most probably it was not observed in the experiment.

The theoretical results show that the final $YNH(NH_3)$ product does not contain an NH_3 group, but $YNH(NH_3)_2$ and $YNH(NH_3)_3$ have at least one intact NH_3 group. DFT calculations indicate that $YNH(NH_3)$ is less stable than $Y(NH)_2$ by 26 kcal/mol. To have more information about the reaction mechanism, the transition state (TS1 in Figure 2) between the imide and the di-amide forms, where an H atom is moving from the $-NH_3$ group to the NH group, was obtained. This transition state lies 11.2 kcal mol^{-1} below the energy of the separated YNH and NH_3 reactants. The barrier to $Y(NH_2)_2$ formation from $YNH(NH_3)$ is 10.3 kcal mol^{-1}. Because the transition state to dissociate absorption lies well below the energy of the starting reactants, the calculations predict that the reaction proceeds directly through to form $Y(NH_2)_2$. The molecular absorption process will assist in the entrance channel. High buffer gas pressures might temporarily trap some of the population in the molecular absorption well, but at room temperature or above the calculated energetics imply that such trapping is only transient. Following its formation, $Y(NH_2)_2$ can react with NH_3 to successively form the di-amide ammonia complexes $Y(NH_2)_2(NH_3)$ and $Y(NH_2)(NH_3)_2$. The ammonia binding energy is calculated to be 21.9 and 20.7 kcal mol^{-1}, respectively. The calculations also show that the imide complex $YNH(NH_3)_2$ also has a low (8.3 kcal mol^{-1}) barrier to form $Y(NH_2)(NH_3)_2$ by intramolecular hydrogen transfer via transition state TS2.

The reaction scheme must then be written:

$$Y + NH_3 \xrightarrow{k_1} YNH\ (+H_2) \tag{1}$$

$$YNH + NH_3 \xrightarrow{k_2} Y(NH_2)_2 \tag{2}$$

$$Y(NH_2) + NH_3 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Y(NH_2)NH_3 \tag{3}$$

$$Y(NH_2)NH_3 + NH_3 \xrightarrow[k_{-4}]{k_4} Y(NH_2)(NH_3)_2 \tag{4}$$

We previously fitted the experimental results to a similar scheme but with k_{-3} set to zero. The rate constants k_1 and k_2 can still be obtained from analytical fits and remain unchanged at $(1.1 \pm 0.2) \times 10^{-11}$ cm^3 s^{-1} and $(8.0 \pm 1.0) \times 10^{-11}$ cm^3 s^{-1}, respectively. The first three NH_3 molecules are absorbed dissociatively to form rapidly YNH, $Y(NH_2)_2$, and $Y(NH_2)_2NH_3$. The energy barrier is decreasing when one goes from $Y(NH_2)_2$ to $Y(NH_2)_2NH_3$. For $Y(NH)_2(NH_3)_2$ and $Y(NH)_2(NH_3)_3$, the most probable reaction mechanism is the absorption of further NH_3 molecules by the di-amide species. More experiments aimed at a complete characterization of the reaction kinetics are necessary.

The analysis of the net atomic charges from Mulliken population analyses (see Supporting Information) of YNH compounds with ammonia shows that there is a charge-transfer process from the Y atom to the NH moiety. However, at the beginning of the reaction there is a donation of the electron pairs from the ammonia molecule to the metal. For the donation of the electron pairs from the ligands, the vacant orbitals of the yttrium atom play a fundamental role. After this dative bond is formed, there is a back-donation to the p orbitals of N. This is the charge-transfer process from the Y atom to the NH moiety that promotes the dissociation of the ammonia molecule. As the ammonia molecule dissociates, the Y atom becomes more positive. The positive charge of the yttrium atom of the di-amide complex is the largest in all cases. The reaction mechanism involves a charge-transfer process from the Y to the ammonia. This charge transfer is necessary to dissociate the ammonia and to form $Y(NH_2)_2$. The nitrogen atomic charges of the ammonia molecules and the NH_2 groups of the di-amide complexes is similar.

The general appearance of the molecular orbitals (see Supporting Information) for all the other systems is quite similar. A nonbonding 5s5p hybrid orbital of the Y atom is the highest occupied molecular orbital (HOMO). In addition, there is one σ bonding orbital and two π bonding orbitals between Y and NH_2. For all the systems, the energies of these orbitals are quite similar. Hence, the covalent $Y-NH_2$ bond is not affected significantly by the presence of the ammonia molecules.

Conclusion

Although the four species reported before were identified as being stable and we were able to interpret the experimental results in a consistent and coherent form, it appears now that our earlier DFT study only partially explored the potential energy surface.

The DFT study presented here shows that the reaction of yttrium with ammonia most likely proceeds via the di-amide formation. These results revealed evidence that YN_2H_4 appears not to contain an $-NH_3$ group. It became clear that the originally reported structures are not the most feasible possibilities, but instead those discussed here.

The reaction of yttrium with ammonia can be explained in terms of donation and back-donation. Ammonia forms a dative bond with the transition metal at the beginning of the reaction followed by a back-donation to the N p orbitals. The back-donation is crucial for the dissociation of the ammonia.

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Supporting Information Available: Calculated harmonic frequencies and Mulliken atomic charges of the most stable complexes and the transition states reported in this paper. For comparison, Natural Bond Order (NBO) atomic charges are included for some systems. Molecular orbital picture of $Y(NH_2)_2(NH_3)$ is also reported. This material is available free of charge via the Internet at http://pubs.acs.org.

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