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Cooperativity Between Low-Valent Iron and Potassium Promoters in Dinitrogen Fixation

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Abstract

A DFT study was performed to understand the role of cooperativity between iron- β -diketiminato fragments and potassium promoters in N_2 activation. Sequential addition of iron fragments to N_2 reveals that a minimum of three iron centers interact with N_2 in order to break the triple bond. The potassium promoter stabilizes the N^{3-} ligand formed upon N_2 scission, thus making the activated iron-nitride complex more energetically accessible. Reduction of the complex and stabilization of N^{3-} by K^+ have similar impact on the energetics in the gas phase. However, upon inclusion of continuum THF solvent effects, coordination of K^+ has a reduced influence upon the overall energetics of dinitrogen fixation; thus, reduction of the trimetallic Fe complex becomes more impactful than coordination of K^+ vis-à-vis N_2 activation upon the inclusion of solvent effects.

Introduction

Conversion of dinitrogen (N_2) into useful materials is desired for uses such as the production of ammonia (NH_3), one of the most important chemicals used in synthetic fertilizers.¹ However, N_2 is difficult to activate due to the inherent strength of the $N\equiv N$ triple bond (~ 235 kcal/mol). The dominant industrial method for the reductive cleavage of N_2 and formation of NH_3 is the catalytic reduction of N_2 with dihydrogen (H_2) via the Haber-Bosch process. Due to its low cost, iron is commonly used to catalyze the Haber-Bosch process.² Potassium promoters improve the catalytic activity of iron surfaces, partially due to an increase in the rate constant for N_2 dissociation on the iron surface.³ In synthetic compounds, cooperative binding of N_2 by iron and alkali metal ions has been shown to weaken the N-N bond more than iron alone, and this trend has been extended to chromium,⁴ cobalt^{5,6} and nickel.⁷ However, these systems do not cleave the N-N bond. Further progress in cooperative N_2 activation requires better understanding of two key factors: (1) the reductive cleavage of the N_2 bond, and (2) the role of promoters such as potassium.

Recently, Holland and coworkers reported a soluble iron- β -diketiminato ($\equiv [Fe]$) system that can cleave N_2 to give a bis(nitride) intermediate (Figure 1).¹¹ Relatively few Fe-nitride complexes have been reported in the literature that involve more than two iron centers interacting with nitride atoms, and no others are derived from N_2 .^{12,13} The complex in Figure 1 arises from cleavage of N_2 , and has three $[Fe]$ fragments interacting directly with nitrides and a fourth $[Fe]$ interacting indirectly through a series of chlorine and potassium

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Supporting Information. Additional metric data, atomic charges of all calculated species and full citation for ref 15. This material is available free of charge via the Internet at <http://pubs.acs.org>.

interactions. Though this system is not catalytic, the chemistry depicted in Figure 1 is a potential stepping stone to a better understanding of catalysts for solution phase N₂ fixation.

In this study, DFT calculations are employed to understand the role of cooperativity between multiple iron- β -diketiminato fragments. For example, how many iron atoms are needed to cleave the N₂ bond in the reduction step, and what intermediates are potentially involved? Theoretical calculations have greatly aided in understanding N-N bond cleavage.^{8–10} The research reported here indicates that interaction of N₂ with more metal centers increases the N-N activation, and thus N₂ fixation benefits from cooperation between metals. The present calculations also yield insight into the effects of potassium promoters in N₂ fixation.¹⁴

Computational Details

Density Functional Theory (DFT) was used to facilitate comparison between the various ground states of the [Fe]₃N₂ and [Fe]₃(N)₂ species. The Gaussian 09 software package¹⁵ was used for geometry optimizations and frequency calculations. The B3LYP/6–31+G(d) calculated geometries and properties of [Fe]N₂ and [Fe]₂N₂ species are similar to those previously reported from MCSCF computations.^{17–19} Additional continuum solvent corrections are computed in THF using the SMD formulation and are compared to the gas phase energetics.²⁰ Since computations on the monometallic and bimetallic Fe- β -diketiminato species have been reported previously,^{17–19} the present contribution focuses on trimetallic species, the interactions of K⁺ on important intermediates in an array of binding modes, and the role of reduction.

Various isomers of the [Fe]_n-N₂ complexes were calculated in all plausible spin states. Free energies are quoted relative to separated starting materials: (iron- β -diketiminato)_n + N₂ (*n* = number of [Fe] fragments involved in the reaction). Bond lengths are given in Å. Initial attempts to model the tetra-iron complex in Figure 1 molecule with ONIOM techniques revealed that the substituents need to be modeled with full QM techniques due to the importance of K⁺/π-arene interactions. The ligands were thus truncated to C₃N₂H₅[–] for computational expediency; in previous reports, we have found that this truncation gives iron-dinitrogen complexes with metrical and spectroscopic parameters that agree well with experiment and faithfully represents the core electronic properties of larger β -diketiminato supporting ligands.^{6,17–19} The studies here are limited to a single potassium ion and three iron atoms because the fourth iron atom in the complex reported by Holland *et al.*¹¹ interacts indirectly with the Fe₃N₂ core via K⁺/π-arene interactions.

Results and Discussion

This paper explores the effect of sequentially adding Fe- β -diketiminato fragments to free N₂ in various binding modes. The experimental route to the complex in Figure 1 starts from potassium reduction of an iron(II)- β -iketiminato starting material to give a presumed iron(I) species that were modeled here as the unsaturated fragment iron- β -diketiminato. Previous work revealed that three-coordinate iron(I) gives strong backbonding into the π^* orbitals of N₂, and binding of a second fragment enhances N₂ bond lengthening.^{17,19} A single [Fe] binds N₂ in an end-on (E) fashion in a quartet spin state, $\Delta G_{\text{rel}}(^4\text{E-FeN}_2) = -13$ kcal/mol. The lowest energy bimetallic N₂ complex is end-on/end-on (EE) in a septet state, as seen experimentally for closely related compounds,¹⁹ with $\Delta G_{\text{rel}}(^7\text{EE-Fe}_2\text{N}_2) = -40$ kcal/mol. Binding of the second fragment is thus cooperative (defined here as the extra stabilization in a bimetallic complex beyond that expected from two monometallic interactions) by $40 - (2 \times 13) = 14$ kcal/mol. The ligation of a second E-Fe increases the N₂ bond length by 5%, from 1.127 to 1.187 Å.

The key advance here is to explore the interaction of more than two iron(I) fragments with N_2 , and so potential binding modes were explored for a third [Fe] fragment interacting with N_2 . Three isomers of trimetallic complexes were compared: end-on/end-on/side-on (abbreviated EES- Fe_3N_2), end-on/side-on/side-on (abbreviated ESS- Fe_3N_2), and all-side-on (abbreviated SSS- Fe_3N_2). Note that [S-Fe] indicates a side-on interaction of iron with N_2 , which to our knowledge has never been observed experimentally in an iron complex; thus this study gives insight into the expected geometry of such an interaction. Various conformers within each family were explored; the lowest energy geometries are given in the figures.

The lowest energy neutral trimetallic isomer, Figure 2 (left), is calculated to be $^{10}EES-Fe_3N_2$, $\Delta G_{rel} = -62$ kcal/mol, with an N-N bond length of 1.234 Å. A $^{10}ESS-Fe_3N_2$ linkage isomer, Figure 2 (right), $d_{NN} = 1.284$ Å, is only 6 kcal/mol higher than the calculated lowest energy isomer. SSS- Fe_3N_2 isomers were calculated to be thermodynamically unfavorable (by 12 kcal/mol) with respect to those in Figure 2, and are thus not discussed further. Binding of the third [Fe] fragment to $^7EE-Fe_2N_2$ to give EES- Fe_3N_2 is found to release 22 kcal/mol, which is 5 kcal/mol less exergonic than binding of a second [Fe] fragment to $^4E-FeN_2$. Importantly, both EES and ESS isomers are energetically accessible, and each lengthens the N-N bond significantly more than two iron fragments in $^7E-Fe_2N_2$.

Interestingly, $^6ESS-Fe_2(N)_2$, an isomer with a cleaved N-N bond where $(N)_2$ denotes a bis(nitride) complex, was also located (Figure 3). This complex has a N...N distance of 2.598 Å and a relative ΔG_{rel} of -40 kcal/mol. One of the two nitrides in this species is attached to only two iron atoms. This nitride nitrogen forms an apparent double bond to one of the iron atoms with $d_{FeN} = 1.654$ Å, a relatively strained interaction that may explain why it is 16 kcal/mol less stable than $^{10}ESS-Fe_3N_2$ (Figure 4).

Transformation from EES- Fe_3N_2 to ESS- $Fe_3(N)_2$ was explored by scanning the potential energy surfaces of low energy sextet, octet, and decet spin state pathways, Figure 3. The scans reveal low (< 5 kcal/mol) barriers for the transformation on each of the three potential-energy surfaces; see Supporting Information. Thus, calculations imply that isomerization could be kinetically rapid as a part of the reaction leading to N_2 cleavage, but that the N-N cleavage is somewhat thermodynamically unfavorable for the neutral cluster.

Inspection of Figure 1 indicates several K^+ directly interacting with the π -system of the aryl substituents and the nitrides.⁸ Several potential roles of the potassium in the N-N cleavage can be envisioned: K^+ may enforce geometrical constraints, stabilize the nitride (N^{3-}), and/or increase the π -backbonding capacity of the Fe centers as proposed for the heterogeneous catalyst.¹ To assess the impact of K^+ on N_2 fixation, a K^+ ion was placed in several locations in proximity to the N_2 moiety for the low energy dinitrogen and dinitride structures (*i.e.*, $^{10}EES-Fe_3N_2$ with an intact N_2 and $^6ESS-Fe(N)_2$ with a broken N_2 bond), respectively. Addition of K^+ to $^{10}EES-Fe_3N_2$ always rearranges upon DFT geometry optimization to the structure in Figure 5 (left). Binding of K^+ to $^{10}EES-Fe_3N_2$ is exergonic by 19 kcal/mol and the calculated lowest energy multiplicity of EES- Fe_3N_2K remains a decet. The NN bond is elongated from 1.234 to 1.268 Å (3%) upon K^+ addition. Addition of K^+ to $^6ESS-Fe_3(N)_2$ yielded the geometry in Figure 4 (right) with the sextet remaining the lowest energy spin state. Addition of K^+ to $^6ESS-Fe_3(N)_2$ is 11 kcal/mol more exergonic than K^+ addition to $^{10}EES-Fe_3N_2$. Thus, potassium ion addition stabilizes the bis(nitride) product more than the bridged N_2 complex in the gas phase. However, the nitride complex continues to have one unusually short Fe-N bond.

Addition of K^+ to $^6ESS-Fe_3(N)_2$ makes the resulting bis(nitride), Figure 4, more energetically accessible relative to the dinitrogen isomers, with a free energy for $^6ESS-$

$\text{Fe}_3(\text{N})_2\text{K}^+ \rightarrow {}^{10}\text{EES-Fe}_3\text{N}_2\text{K}^+$ of only 12 kcal/mol, roughly half the comparable isomerization free energy in the absence of K^+ . Analysis of calculated atomic charges (see Supporting Information) suggests that greater stabilization of the N^{3-} ligand by K^+ coordination is responsible for the diminution of the endergonicity in the nitrogen scission reaction.

Finally, an electron was added to the ${}^{10}\text{EES-Fe}_3\text{N}_2$ complex to mimic reduction by the fourth Fe(I) fragment in the experimental reaction. This yielded $[{}^9\text{EES-Fe}_3\text{N}_2]^-$ as the lowest energy state, and resulted in only slight geometric distortion (RMSD = 0.22 Å). The largest perturbation was elongation of one Fe–N bond from 1.976 to 2.089 Å for the [S–Fe] fragment, which coincided with an increase of atomic charge on the nitrogen involved in the bond, from –0.19 to –0.58. The added electron occupies a non-bonding, Fe-based orbital, Figure 6, consistent with the minor change in geometry upon reduction. Thus, addition of a single electron to the tri-iron structure has a minor impact on the degree of N_2 activation by trimetallic EES- Fe_3N_2 .

On the other hand, addition of an electron to ${}^6\text{ESS-Fe}_3(\text{N})_2$ gave a significant effect. Reduction yielded $[{}^5\text{ESS-Fe}_3(\text{N})_2]^-$ as the lowest energy state. The distance between the nitride ligands is shortened from 2.598 to 2.587 Å. The added electron was found to occupy a bonding Fe-nitride orbital, Figure 7. A K^+ ion was added to the reduced complexes $[{}^9\text{EES-Fe}_3\text{N}_2]^-$ and $[{}^5\text{ESS-Fe}_3(\text{N})_2]^-$ changing the overall charge on the cluster model to neutral; the resulting complexes were found to possess the same ground spin states as their anionic precursors, Figure 8.

The addition of K^+ to the reduced species makes the $[{}^5\text{ESS-Fe}_3(\text{N})_2\text{K}]$ cluster 3 kcal/mol more stable than $[{}^9\text{EES-Fe}_3\text{N}_2\text{K}]$, Figure 8. It also gives a structure in which the Fe–N bonds are closer to the experimental crystal structure where the Fe–N bonds proximal to coordinated K^+ are shorter than the corresponding distal Fe–N bond lengths. Therefore, addition of three iron(I) fragments, a K^+ ion, and an electron makes N–N cleavage favorable, presumably because of the stronger interaction of the potassium cation with the anionic nitride core.

While gas-phase simulations may more appropriately model an industrial nitrogen fixation catalyst, inclusion of solvent effects is more pertinent to attempts to create a homogeneous version. Continuum solvation corrections in THF were thus computed and compared to the gas phase energetics to assess the impact of solvation on the reactions of interest. The THF thermodynamics, Figure 9 (right, blue border), are calculated to be similar to the gas phase models with one interesting difference. The thermodynamics of ${}^{10}\text{EES-Fe}_3\text{N}_2 \rightarrow {}^6\text{ESS-Fe}_3(\text{N})_2$ is little changed by inclusion of solvent effects, $\Delta G_{\text{gas}} = +22.0$ kcal/mol, $\Delta G_{\text{THF}} = +21.5$ kcal/mol, Figure 9. Similarly, there is a mild solvent influence calculated for the K^+ and K-ligated reactions, *e.g.*, ${}^{10}[\text{EES-Fe}_3\text{N}_2\text{K}]^+ \rightarrow {}^6[\text{ESS-Fe}_3(\text{N})_2\text{K}]^+$, $\Delta G_{\text{gas}} = +11.3$ kcal/mol, $\Delta G_{\text{THF}} = +14.9$ kcal/mol, Figure 9. However, reduction upon the nitride to bis(nitride) transformation is significantly modulated by solvent, going from endergonic, $\Delta G_{\text{gas}} = +8.4$ kcal/mol, to mildly exergonic, $\Delta G_{\text{THF}} = -0.5$ kcal/mol for ${}^9[\text{EES-Fe}_3\text{N}_2]^- \rightarrow {}^5[\text{ESS-Fe}_3(\text{N})]^-$, Figure 9. Comparing the relative ΔG 's in gas ($\Delta\Delta G_{\text{gas}}$) and solvent ($\Delta\Delta G_{\text{THF}}$) indicates that K^+ becomes less impactful ($\Delta\Delta G_{\text{gas}}(\text{K}^+) = 10.7$ kcal/mol, $\Delta\Delta G_{\text{THF}}(\text{K}^+) = 6.6$ kcal/mol) than reduction of the system ($\Delta\Delta G_{\text{gas}}(\text{e}^-) = 13.6$ kcal/mol, $\Delta\Delta G_{\text{THF}}(\text{e}^-) = 22.0$ kcal/mol) upon the inclusion of continuum THF solvent effects.

Conclusions

The present DFT simulations of the sequential addition of Fe- β -diketiminato fragments to dinitrogen are important because they show a reasonable series of metal binding and

reduction events that cleave N₂ to give a Fe₃(N)₂K core like that in a recent experimental report.⁷ In addition to this mechanistic insight, it reveals that three reduced iron centers acting in a cooperative fashion make N₂ cleavage thermodynamically feasible. As summarized in Figure 9, the K⁺ promoter stabilizes the nitride ligand of the “fixed” tri-iron-bis(nitride) isomers by about 10 kcal/mol relative to the N₂ isomers, and N-N cleavage is only favorable when an added electron *and* potassium are present. However, including a polar continuum solvent reduces the impact of the K⁺ on stabilizing the reduced tri-iron-bis(nitride). The results demonstrate that the cleavage of N-N bonds by a reduced iron fragment is greatly influenced by potassium, and also illustrate the impact of cooperative Fe binding upon N₂ activation, indicating that at least three iron fragments are needed to cleave N₂.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.

Structure of the soluble iron- β -diketiminat-nitride complex formed upon cleavage of the N_2 triple bond. Ar = 2,6- $C_6H_3Me_2$.

Figure 2. B3LYP geometries of $^{10}\text{EES-Fe}_3\text{N}_2$ (top) and $^{10}\text{ESS-Fe}_3\text{N}_2$ (bottom). The superscript numeral denotes the lowest energy multiplicity ($2S + 1$). Bond lengths in Å. ΔG_{rel} is calculated relative to isolated [Fe] and N_2 .

Figure 3. Potential energy scans (red/black arrows) between EES-Fe₃N₂ (left) and ESS-Fe₃(N)₂ (right) indicate small barriers to N₂ scission.

Figure 4. B3LYP calculated geometry of ${}^6\text{ESS-Fe}_3(\text{N})_2$ with an broken N_2 bond. Bond lengths in Å. ΔG_{rel} is calculated relative to isolated $[\text{Fe}]$ and N_2 .

Figure 5. B3LYP structures resulting from addition of K^+ to $^{10}\text{EES-Fe}_3\text{N}_2$ (top) and $^6\text{ESS-Fe}_3(\text{N})_2$ (bottom). ΔG_{rel} is calculated relative to isolated $[\text{Fe}]$ and N_2 .

Figure 6. HOMO for ${}^9[\text{EES-Fe}_3\text{N}_2]^-$ complex in which the added electron occupies a non-bonding metal-based orbital.

Figure 7. HOMO for $[^5\text{ESS-Fe}_3(\text{N})_2]^-$ in which the added electron occupies a bonding metal-nitride based orbital.

Figure 8.

B3LYP structures resulting from addition of K^+ to $[\text{}^9\text{EES-Fe}_3\text{N}_2]\text{K}$ (top) and $[\text{}^5\text{ESS-Fe}_3(\text{N})_2]\text{K}$ (bottom). ΔG_{rel} is calculated relative to isolated $[\text{Fe}]$, K^+ and N_2 .

Figure 9.

Ladder of calculated gas phase (red border) and solution phase (blue border) relative free energies (ΔG_{rel}) of dinitrogen (left) and bis(nitride) (right) species. Additions of K⁺ (red) and electron (blue) to the neutral species (black) are compared (ΔG). Also, addition of K⁺ (green) to the reduced species (blue) is also calculated.