Mechanistic Study of Oxy Insertion into Nickel Carbon Bonds with Nitrous Oxide

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S Supporting Information

ABSTRACT: Transition-metal-mediated oxy insertion into metal carbon bonds is useful for the development of catalytic cycles for selective hydrocarbon oxidation. However, there are few bona fide examples of net oxy insertion with transition-metal complexes. An extremely rare example of a 3d metal mediating oxy insertion into metal carbon bonds is a series of Ni^{II} alkyl complexes reacting with nitrous oxide (N₂O) reported by Hillhouse and co-workers; however, the mechanism was never fully elucidated. A computational study has been performed on bipyridyl nickel metallacycles that form nickel alkoxides upon reaction with N₂O to attain insight into future catalyst design for oxygen atom transfer reactions. Two possible mechanisms are explored. Of the two pathways, the computations suggest that the preferred mechanism proceeds through a Ni oxyl intermediate followed by alkyl migration of the nickel carbon bond to form an alkoxide. Oxyl formation was found to be the rate-determining step, with a free energy barrier of 29.4 kcal/mol for bpyNi^{II}(cyclo-(CH₂)₄). Complexes that contain sp²-hybridized molecules at the β -carbon site within the metallacycle ring do not undergo oxy insertion due to elevated barriers. While exploring insertion with another oxidant, namely pyridine *N*-oxide, we found that N₂O is critical for net oxy insertion with this complex due to the substantial thermodynamic advantage of N₂ expulsion. Reaction with pyridine *N*-oxide necessitated expulsion of a “worse” leaving group, resulting in much higher barriers ($\Delta G^\ddagger = 49.7$ kcal/mol) for the oxyl formation step.

INTRODUCTION

Oxy insertion into metal alkyl or metal aryl bonds of middle to late transition metals to give alkoxide or aryloxy ligands is rarely observed. Brown and Mayer have reported alkyl migrations into metal alkyl bonds with Re^{VII} complexes.^{1,2} Ison and co-workers have reported a Re^V oxo complex that was shown to undergo oxy insertion upon coordination of a CO ligand.³ Periana and Goddard reported a reaction of methylrhenium trioxide (MTO) in conjunction with external oxidants, such as, PhIO, H₂O₂, and IO₄. However, the oxy insertion into the Re–Me bond of MTO to form a methoxide did not occur via an oxo intermediate and is thus unlike the Re systems reported by Brown and Mayer.^{4,5} The MTO systems were found to undergo concerted nonredox insertions akin to the Baeyer–Villiger oxidation (BV). Recently, our group has reported several computational studies involving organometallic Baeyer–Villiger (OMBV) reactions with four- and six-coordinate bipyridyl (bpy) complexes.^{6,7} Computations showed the oxidant in a Pt^{II} system showed to have a moderate ($\Delta\Delta G^\ddagger$

3–4 kcal/mol) Hammett impact on the OMBV barrier heights.⁶ A systematic study of the influence on coordination and metal identity for OMBV insertions was performed for group 7–10 metals of the 3d, 4d, and 5d rows, which revealed that earlier, lower coordinate, 3d metals have lower barriers for

OMBV insertions due to weaker metal carbon bonds and more nucleophilic carbons in the alkyl transfer groups.⁷

Hillhouse and co-workers have reported a series of nickel metallacycle complexes, which upon reaction with N₂O yield the respective metal alkoxide complexes. For example, reacting (PMe₃)₂Ni(κ^2 C,C-CH₂CMe₂-*o*-C₆H₄) with N₂O produces [(PMe₃)Ni(κ^2 O,C-O-*o*-C₆H₄CMe₂CH₂)]₂.^{8–10} Examples involving bpy supporting ligation are displayed in Figure 1. Complexes (a) and (b) were found to undergo net oxy insertion upon reaction with N₂O. However, the complexes in which the β -carbon in the alkyl ring is sp²-hybridized (Figure 1, (c) and (d)) did not form alkoxides upon reaction with N₂O. The pathway for oxy insertion was also uncertain, although regioselectivity was displayed when complexes (a) and (b) were compared. The oxygen was found to insert into the more substituted carbon and Ni aryl is preferred over Ni alkyl, much like the classical BV oxidation.¹¹ To our knowledge, the aforementioned nickel complexes are the only examples of 3d metals undergoing net oxy insertion. Thus, understanding this reaction could pave the way for the future design of catalysts for

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Figure 1. Synthesized nickel metallacycle complexes reacting with nitrous oxide to form the respective metal-alkoxide complexes; N.R. indicates that no reaction took place upon reaction with N_2O .

selective partial hydrocarbon oxidation using earth-abundant 3d metals.

An interesting characteristic of nitrous oxide as an oxidant in transition-metal chemistry is its various binding possibilities onto transition-metal centers. Much effort has been put into understanding the chemistry behind N_2O and its interactions with transition metals.^{12,13} Possible linkage isomers are given in Figure 2. In this paper we aim to elucidate the possible

Figure 2. Possible linkage isomers for the interaction of N_2O with a metal alkyl complex.

pathways for oxy insertion into nickel–carbon bonds with N_2O . A better understanding of the fundamental chemistry behind OMBV reactions with 3d metals could guide future experimental efforts at catalyst design.

COMPUTATIONAL METHODS

Density functional theory (DFT) was utilized to elucidate the mechanistic details pertaining to the oxy insertion of various Ni complexes. The Gaussian 09 software package¹⁴ was used for geometry optimizations and vibrational frequency calculations. Minima and transition states were distinguished by the presence of 0 or 1 imaginary frequencies, respectively, obtained from the calculated energy Hessians. The hybrid functionals B3LYP^{15,16} and M06¹⁷ were

compared for a majority of the systems discussed; however, the differences in the geometries and energetics were small (<5 kcal/mol). Thus, the reactions presented will be the results obtained with the B3LYP functional in conjunction with the all-electron basis set 6-31+G(d). All electrons are modeled explicitly with added diffuse and polarization functions to non-hydrogen atoms. All energetics are reported as free energies in kcal/mol and calculated under standard conditions (1 atm and 298.15 K). Singlet and triplet spin states were calculated for each stationary point.

RESULTS AND DISCUSSION

Binding of nitrous oxide to $\text{bpyNi}^{\text{II}}(\text{cyclo}-(\text{CH}_2)_4)$ in a $\eta^1\text{-O}$ or $\eta^1\text{-N}$ fashion yielded a weakly bound adduct (Figure 3) with $\Delta G = 4.6$ kcal/mol in comparison to the separated reactants. Adding N_2O across the nickel–alkyl bond in a $[2+2]$ fashion yields two covalently bound isomers, **2+2a** and **2+2b**, shown in Figure 3. The **2+2a** isomer, in which the oxygen atom is in proximity to the nickel center, is found to be the lower energy isomer ($\Delta G = 0.2$ kcal/mol) by 9.8 kcal/mol in comparison to the **2+2b** addition product. The free energy difference could be attributed to the stabilization of the dangling oxygen atom by the nickel center ($\text{Ni} \cdots \text{O} = 2.6$ Å in **2+2a**).¹³

Two linkage isomers arising from the 1,3-dipolar addition of N_2O into the nickel–carbon bond were calculated. The 1,3-dipolar addition product in which the oxygen is connected to the carbon ($\text{Ni}-\text{N}-\text{N}-\text{O}-\text{C}$ cycle) was found to be unstable. The 1,3-dipolar addition product in which the oxygen is connected to the nickel atom ($\text{Ni}-\text{O}-\text{N}-\text{N}-\text{C}$ cycle) was found to have $\Delta G = 4.7$ kcal/mol (Figure 3). Calculations investigating the possibility of $\kappa^1\text{-bpy}$ conformations resulted in higher energies and will not be discussed further. Singlet and triplet spin states were investigated for each isomer in Figure 3; however, in each case the singlet was found to be lower in energy.

Figure 3. Calculated lowest energy isomers for the addition of N_2O onto $\text{bpyNi}^{\text{II}}(\text{cyclo}-(\text{CH}_2)_4)$. Free energies are relative to separated reactants. Bond lengths are given in Å.

Figure 4. Proposed mechanisms of the reaction of N_2O with complex [1] to form the respective nickel alkoxide complex. Spin states are given as superscripts in the upper left corner of the respective geometries. OAT TS = oxygen atom transfer transition state.

Figure 5. Calculated transition state geometries for oxygen atom transfer by nitrous oxide ([2]) and alkyl migration into a nickel carbon bond ([5b]). Bond lengths are given in Å.

Proposed Reaction Pathway. The free nickel metallacycle [1] (Figure 4) was found to possess a singlet ground state with a square-planar geometry. Given the possible binding isomers of N_2O just discussed, one can envision several pathways for the formation of the nickel alkoxide product [6]. One possible pathway consists of a 1,3-dipolar addition of N_2O to a Ni–C bond followed by a [2 + 2] release of N_2 to form the Ni^{II} alkoxide product.

However, this pathway yielded very large calculated barriers: $\Delta G = 44.1$ and 71.0 kcal/mol for the initial 1,3-dipolar addition and subsequent [2 + 2] elimination of N_2 , respectively. Thus, the large barriers suggest that this pathway is improbable and it will not be discussed further. Cartesian coordinates for these transition states and all other stationary points are given in the Supporting Information.

Another possible pathway (Figure 4) consists of attack in a κ^1 fashion through the oxygen atom of N_2O onto the nickel center, forming the square-pyramidal oxo complex [3], coupled with expulsion of N_2 . The B3LYP/6-31+G(d) OAT (oxygen atom transfer) transition state geometry [2] in the triplet spin state is given in Figure 5, which yields a calculated barrier, ΔG_{OAT} , of 29.4 kcal/mol relative to N_2O plus [1] that is exergonic by 8.5 kcal/mol upon formation of the oxo complex

[3]. The oxo complex [3] is predicted to have a triplet ground state, and from here two plausible routes for oxy insertion are (1) alkyl migration or insertion, [5a], of the apical oxo ligand of [3] into the Ni–CH₂ bond of the ring and (2) pseudorotation of [3] to form a pseudo-trigonal-bipyramidal oxo complex, [4] (Figure 4), followed by oxo insertion into the nickel alkyl bond. The triplet oxo complex [4] is found to have a trigonal-bipyramidal (TBPS) geometry that is 6.1 kcal/mol more stable than the triplet oxo complex [3] with a square-pyramidal geometry (SPS). The extra stability could be attributed to the shortening of the oxo bond in complex [4], from 1.83 to 1.75 Å ($\sim 2.2\%$). Oxo insertion into the metal–carbon bond is found to be facile with an effective transition state barrier, ΔG_{eff} , of 6.2 kcal/mol for [4] [5b]. The resulting product is the singlet nickel alkoxide [6], which is calculated to be exergonic by 67.0 kcal/mol relative to the separated reactants [1].

Pseudorotation from Square Pyramidal to Trigonal Bipyramidal. The pseudorotation transition state connecting [3] and [4] was not isolated, despite numerous attempts; however, pseudorotation from SP5 to TBP would be expected to be facile with an oxo ligand.¹⁸ The isomerization of [3] to [4] is thermodynamically favored by 6.1 kcal/mol. The HOMO for a d^6 complex with SP5 geometry (e in Figure 6) would be

Figure 6. Orbital correlation diagram for metal d orbitals which connect trigonal-bipyramidal and square-pyramidal geometries (adapted from ref 18).

Figure 7. Calculated Ni^{III} oxyl geometries in the triplet ground states. Bond lengths are given in Å.

lower compared to the HOMO for a TBP structure (e' in Figure 6), and thus SP5 would be the preferred orientation.

However, the predicted barrier for a pseudorotation to TBP from an SP5 geometry with an apical oxo ligand would be low for a d^6 complex along the “ b_2 pathway” from the Walsh diagram in Figure 6. The orbital energy differences between the e'' and e' terms will be reduced due to the π -donor effects of the oxo ligands upon the d_{xz}/d_{yz} orbitals in the SP5 geometry likely making the b_2 pathway in Figure 6 even more accessible than for σ -only ligands. The geometries for the oxo complexes [3] and [4] are given in Figure 7.

The extra stability of the TBP structure may be attributed to the HOMO orbitals (xz and yz) of the SP5 attaining more π -antibonding character, reducing the bond order of the nickel oxo bond, and resulting in a bond length of 1.83 Å. Switching to a TBP geometry alleviates these π -antibonding interactions, thus yielding a stronger metal oxo bond, which is evident in the 1.75 Å metal oxo bond length. Note that the spin densities on the oxygen atoms of [3] and [4] are both 1.0e, suggesting

that these species are best thought of as Ni^{III} oxyl (i.e., $\text{O}^\bullet$) entities.

Oxy insertion into the nickel alkyl carbon of [1] (Figure 8, red) has been experimentally shown to occur at 50 °C in 48 h.¹⁰ However, a complex in which the β -carbon is sp^2 -hybridized, such as the examples given in blue and green in Figure 8, does not yield oxy insertion products and leads to decomposition at elevated temperatures. Calculations revealed that for each complex in Figure 8 the rate-determining step was the OAT transition state.

There exists a spin “flip” from the singlet ground state for complex [1] to the triplet surface in the transition state [2] to form the Ni^{III} oxyl intermediates [3] and [4]. Another spin state flip occurs from the triplet oxyl intermediate to the singlet oxy insertion transition state [5b], forming the alkoxide product [6]. The free energy barrier to oxyl formation for the parent complex [1] is calculated to be 2–3 kcal/mol lower than for the derivatives with sp^2 -hybridized carbons in the β -positions. As 1 kcal/mol translates into approximately 1 order

Figure 8. Comparison of the proposed oxy-insertion pathway between the sp^3 -hybridized $\text{bpyNi}^{\text{II}}(\text{cyclo}-(\text{CH}_2)_4)$ system [1] and related compounds with sp^2 -hybridized β -carbons ([1'] and [1'']).

of magnitude for the rate constant according to Arrhenius theory, the computations are consistent with the experimental reactivity trends.

Regioselectivity of Oxy Insertion. Oxy insertion into the nickel alkyl bond was shown to have a certain degree of selectivity. For instance, Hillhouse et al. found that the oxygen atom from N_2O would selectively insert into the more substituted nickel carbon bond (i.e., secondary over primary).¹⁰ Methyl, primary, and secondary nickel systems were studied in order to elucidate selectivity trends. The three systems studied are given in Figure 9. The barriers for the alkyl migration transition states akin to [5b] were calculated to be 9.1, 6.2, and 2.7 kcal/mol for methyl-, primary-, and secondary-substituted alkyls. The insertion for this organometallic system follows the same pattern as expected for organic Baeyer

Villiger oxidation. Note, however, these reactions are best thought of as two-step oxy insertions with initial Ni^{III} oxyl formation followed by alkyl migration to the oxyl ligand.

Connection between BV and Alkyl Migrations. A Baeyer Villiger-type reaction involves a single step in which the metal carbon bond is cleaved while the oxygen carbon bond is formed in concert (Figure 10). While the Hillhouse

Figure 10. Organometallic Baeyer Villiger transition state where R = alkyl or aryl transfer group, YO = oxidant, and L_n = ancillary ligand.

Figure 9. Oxy insertion selectivity patterns for $(\text{bpy})\text{Ni}(\text{alkyl})$ systems. Barriers for alkyl migration are given on the right.

system shows selectivity trends reminiscent of BV-type insertions, the simulations indicate that the nickel systems under study first form a Ni^{III} oxyl intermediate before oxy insertion to make the alkoxide. Repeated attempts to isolate a Baeyer Villiger transition state led to the oxy insertion transition state [5b].

This may be attributed to the “good” leaving group capacity of N_2 generated by the N_2O oxidant. There exists a connection in oxy insertion transformations, a BV or nonredox pathway or an oxo (redox) pathway, which can be thought to lie on a continuum that is linked to the identity of the oxidant (YO) and the degree of participation of the leaving group (Y) in the TS active site (Figure 11).

In the present case N_2O affords the excellent leaving group N_2 and thus does not directly participate in the oxy insertion. Hence, N_2O may be expected to move the oxy insertion TS toward the oxo end of the continuum stylized in Figure 11. On

Figure 11. Proposed connection between Baeyer Villiger and oxo pathways for oxy insertion ($MR + [O] \rightarrow MOR$) where M = metal, R = alkyl or aryl transfer group, Y = leaving group, and L_n = ancillary ligand.

the other side of the continuum there exists a BV-type transformation in which the leaving group directly participates in the oxy insertion transition state.

To test this hypothesis, a “worse” leaving group in comparison to N_2 such as pyridine N -oxide was utilized to test the link between leaving group capacity and the nature of oxy insertion. Pyridine N -oxide has been utilized in previous examples of oxy insertion of the BV variety.⁵ The transition state involving a κ^1O OAT transition state afforded a much larger barrier ($\Delta G = 49.7$ kcal/mol) and was found to be slightly endergonic in comparison to the separated reactants ($\Delta G = 10.0$ kcal/mol), consistent with the Hammond postulate and the weaker oxidizing potential of PyO versus N_2O .¹⁹ Attempts to isolate a BV-type insertion TS for PyO led to an $N-O$ oxidative addition transition state for which was found to have an even larger barrier ($\Delta G = 62.6$ kcal/mol). The transition state geometries for the OAT and oxidative addition of pyridine N -oxide to **1** are given in Figure 12.

CONCLUSIONS

DFT calculations were performed to elucidate the oxy insertion mechanism of various Ni^{II} alkyl complexes with N_2O as oxidant. The complexes showed selectivity patterns for oxy insertion upon the introduction of additional methyl groups to the α -carbon in the metallacycle ring that are similar to classic Baeyer Villiger oxidations. However, unlike BV insertions, which are concerted nonredox transformations, the reaction was found to proceed through an oxo intermediate that is coupled with a formal 2e reduction (if the oxo ligand is considered as O^{2-}) of the nickel center. Note, however, analysis of the electronic structure implies that the “oxo” intermediates are best thought of as Ni^{III} oxyl (i.e., $O^\bullet$) entities.

The DFT-proposed pathway involved a two-step mechanism: (1) formation of a Ni^{III} oxyl intermediate and (2) oxo insertion into the nickel carbon bond to form the alkoxide product. The rate-determining step was found to be the initial oxygen atom transfer, with a barrier height of 29.4 kcal/mol for N_2O plus $bpyNi^{II}(cyclo-(CH_2)_4)$. Complexes that contain sp^2 -hybridized β -carbons within the metallacycle were found to not undergo net oxy insertion experimentally. These complexes were calculated to have higher barriers (2–3 kcal/mol) in comparison to the systems that underwent oxy insertion. Factors such as rigidity of the nickelacycle rings could also play a role in the outcome of this reaction. A key advantage of utilizing N_2O for these reactions is the large thermodynamic driving forces afforded by expulsion of N_2 . Oxidants such as pyridine N -oxide which afford “worse” leaving groups were found to have much higher barriers for oxyl formation due to a loss in the thermodynamic driving force.

ASSOCIATED CONTENT

Supporting Information

A figure giving a comparison of the B3LYP and M06 functionals for the proposed pathway, tables giving Cartesian coordinates of all calculated species, and text giving the full citation for ref 14. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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Figure 12. Oxyl formation transition states via a κ^1O OATS (left) and oxidative addition (right) in the triplet spin states. Bond lengths are given in Å.

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