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Theoretical Study of Ethylene Oligomerization by an Organometallic Nickel Catalyst

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The mechanism for ethylene oligomerization by (acac)NiH has been studied using density functional theory (DFT). The transition states for chain propagation and chain termination were optimized and the related reaction barriers calculated. Several possible mechanisms were considered for the chain termination step. Chain termination by β-hydrogen elimination was found to be energetically unfavorable, and is not likely to be important. Instead, β-hydrogen transfer to the incoming ethylene unit seems to be operative. The most favorable β-hydrogen transfer pathway has two transition states. The first leads from a weak π-complex between an incoming ethylene unit and (acac)$NiCH_2CH_2R$ to an intermediate in which the two olefins C_2H_4 and H_2CCHR both are strongly π-complexed to the nickel hydride (acac)NiH. The second barrier takes the intermediate to another weak π-complex between (acac)$NiCH_2CH_3$ and $H_2C{=}CHR$ from which the oligomer $H_2C{=}CHR$ can be released and the catalyst (acac)$NiCH_2CH_3$ regenerated. Due to the mechanism of chain termination, the actual catalyst is proposed to be (acac)$NiCH_2CH_3$ whereas (acac)NiH serves as a precursor or precatalyst.

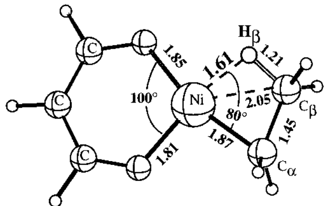
Introduction

Dimerization and oligomerization of ethylene to 1-butene and higher α-olefins are processes of considerable industrial importance. A variety of catalysts have been reported to be active in producing α-olefins by oligomerizing ethylene. A number of nickel−based catalysts have been developed by Keim and co-workers[1] and by others.[2] All of these catalysts contain a bidentate chelating ligand, X-Y, where X, Y = O, S, N, P. The reaction mechanism for the oligomerization has not yet been fully established. It is suggested[1] that the actual catalyst is a nickel hydride and that the oligomerization processes follow the mechanism shown in Scheme 1.

In the initial step, an ethylene unit approaches the coordinately unsaturated nickel hydride to form a π-complex, followed by a four-center transition state that leads to the insertion of the ethylene into the Ni−H bond. The vacant coordination site is released when the insertion is completed, and subsequent insertion reactions can take place until the oligomer chain is eliminated, Scheme 1.

We have in a previous study[3] made use of density functional theory (DFT) to determine the structures of some of the important intermediates involved in Scheme 1. We have shown that the nickel hydride (acac)NiH, where acetylacetonate (acac) was modeled by 1,3-propanedione, is very active in the presence of ethylene and leads to (acac)NiC_2H_5 with an exothermicity of 44.7 kcal/mol. On the other hand, the butene elimination process in Scheme 1 was found to be energetically unfavorable with an endothermicity of 44.7 kcal/mol. Thus, the mechanism in Scheme 1 based on the regeneration of nickel hydride is not viable although the complete cycle is essentially thermoneutral.

We have therefore proposed a modified mechanism for the catalytic cycle, Scheme 2, in which the nickel hydride is a precursor or precatalyst whereas the actual catalyst is considered to be (acac)NiC_2H_5. The optimized structure of the model catalyst (1,3-propanedionato)NiC_2H_5 is shown as structure **1**.



Catalyst

1

The emphasis in the previous study[3] was on the thermochemistry of the different steps in the catalytic oligomerization cycles shown in Schemes 1 and 2. We shall in the present investigation turn to the kinetic aspects of the catalytic cycle in Scheme 2 by probing the transition states and activation barriers for the chain growing insertion process as well as the chain-terminating elimination step.

Computational Details

Density functional theory[4] (DFT) has been widely recognized as a powerful alternative computational method to traditional *ab initio* schemes, particularly in the studies of transition metal complexes where large-size basis sets and an explicit treatment of electron correlation are required. The local spin density approximation[5] (LDA) is the most frequently applied approach within the families of approximate DFT schemes. It has been used extensively in studies on solids and molecules. Most properties obtained by the LDA scheme are in better agreement with experiments[4a] than data estimated by *ab initio* calculations at the Hartree−Fock level. However, bond energies are usually overestimated by LDA. Thus, gradient or nonlocal corrections[6] have

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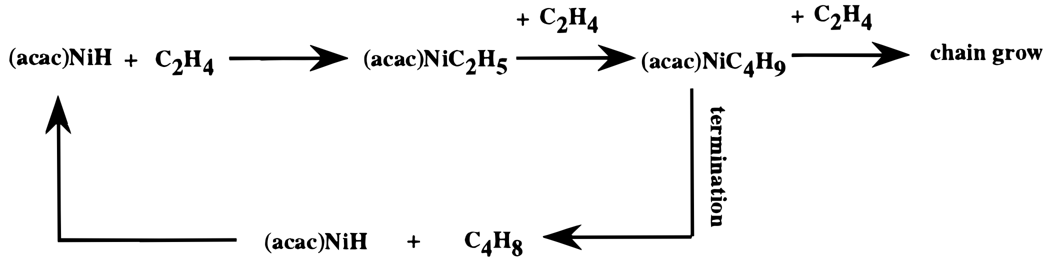
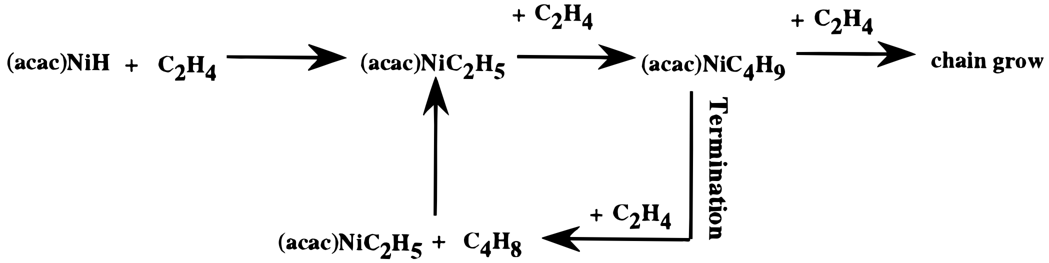
Scheme 1. Original Mechanism for Ethylene Oligomerization Based on Nickel Hydride as the Catalyst



Scheme 2. Modified Mechanism for Ethylene Oligomerization with (acac)NiC_2H_5 as the Catalyst



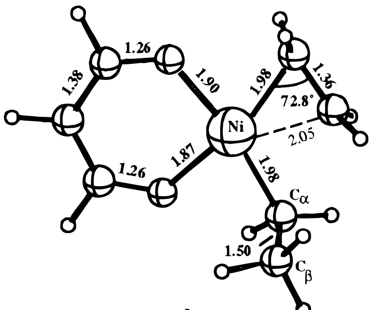
been introduced to rectify the shortcomings in the LDA. The nonlocal corrections can be introduced as a perturbation or incorporated into a fully variational calculation. In the perturbative approach, the nonlocal energy functional is evaluated on the basis of the LDA electronic density, while in the variational approach the electronic density itself is determined by optimizing the gradient-corrected energy. The variational procedure is computationally more demanding than the perturbative approach. We have shown in previous studies[7] that the density change induced by nonlocal corrections is minor and the two approaches lead to similar results for most of the molecular properties that have been studied.

In the present investigation all calculations were carried out by the ADF program due to Baerends[8] *et al.* and the molecular geometries were optimized on the basis of the LDA method in the parametrization due to Vosko[9] e*t al.* Single-point energy evaluations were then carried out with Becke's nonlocal exchange correction[6b] and Perdew's nonlocal correlation correction.[6c] The basis set[10] used for the 3s, 3p, 3d, and 4s valence shells on nickel was of triple-ζ quality and augmented by three 4p Slater-type orbitals (STO). A double-ζ basis set was applied for the 2s and 2p shells of oxygen and carbon as well as the 1s shell of hydrogen. An additional 3d STO was added to oxygen and carbon whereas hydrogen was given a single 2p STO. All inner shell orbitals were kept frozen in the variational calculations.[8] A set of auxiliary[11] s, p, d, f, and g type of STOs centered on each atom was used to fit the electronic density. The numerical integrations were carried out according to the scheme[12] proposed by Boerrigter *et al.*

Results and Discussion

The insertion step in Scheme 2 starts with the nickel−ethyl complex **1,** which is postulated to be the catalyst for the ethylene oligomerization on the basis of our previous investigation.[3] Complex **1** displays a strong agostic interaction between a β-hydrogen on ethyl and the metal center. This interaction results in a close Ni−H_β contact of 1.61 Å as well as a C_β-H bond stretched to 1.21 Å. The strength of the agostic interaction was estimated[3] to be 11 kcal/mol.

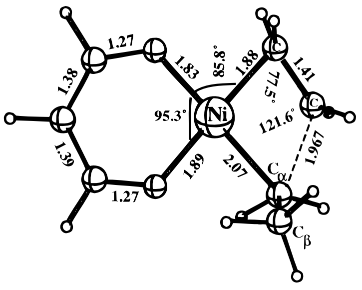
The insertion step is initiated by an ethylene monomer approaching the catalyst, **1**, leading to the formation of a π-complex **2a** in which the original ethyl unit now is moved out of the chelate plane by a rotation around the Ni−C_α axis. The coordination of C_2H_4 in **2a** leads to two relatively short Ni−C(ethylene) bonds of 1.98 and 2.05 Å and a slight elongation of the ethylene double bond by 0.02 Å to 1.36 Å. The nickel−ethyl bond has at the same time stretched from 1.85 Å in **1** to 1.98 Å in **2a**, and the agostic bond is completely broken**.** The total π-complexation energy for the process **1** → 2**a** amounts to 6.0 kcal/mol.



π–complex

2a

The insertion process proceeds after the formation of the π-complex **2a** to the transition state **2b**. The geometry for **2b** has been determined by the standard algorithm of transition state



Transition State for Insertion

2b

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(7) (a) Fan, L.; Ziegler, T. *J. Chem. Phys.* **1991**, *94*, 6057. (b) Fan, L.; Ziegler, T. *J. Chem. Phys.* **1991**, *95*, 7401. (c) Fan, L.; Ziegler, T. *J. Chem. Phys.* **1992**, *96*, 9005. (d) Fan, L.; Ziegler, T. *J. Phys. Chem.* **1992**, *96*, 6937.

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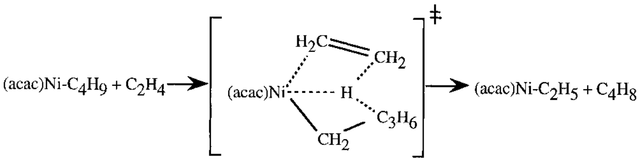
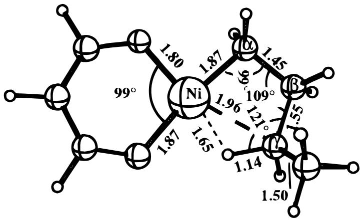


Figure 1. Chain termination by associative β-hydrogen transfer.

optimization.[13] The Ni−C(ethyl) bond is elongated from 1.98 Å in the reactant **2a** to 2.07 Å in **2b**, and a partial C−C bond of 1.97 Å is formed in **2b**. Thus the structure **2b** is a typical four-center transition state similar to those found in ethylene polymerization by metallocene catalysts.[14] The barrier associated with **2b** was calculated to be 5.7 kcal/mol relative to π-complex **2a**.

The kinetic insertion product formed from the transition state **2b** is the γ-agostic butyl complex **2c**. It is 8.6 kcal/mol more stable than the π-complex **2a**. Thus, the reaction enthalpy for the total insertion step, **1** + $C_2H_4 \rightarrow$ **2c**, is 14.6 kcal/mol. As discussed previously,[3] the γ-agostic butyl complex **2c** formed as the kinetic insertion product can rearrange to a thermodynamically more stable β-agostic product which is 10.4 kcal/mol lower in energy. The β-agostic product might then serve as the starting point for the next insertion, Scheme 2.



Insertion Product

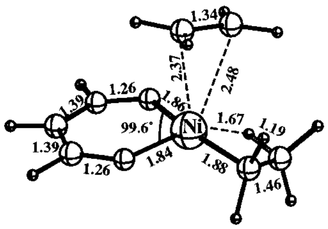
2c

The chain-terminating step in olefin oligomerization might conceivably take place by β-hydrogen elimination as shown in Scheme 1 where the butyl complex is converted into 1-butene and nickel hydride. However, it was found[3] that the β-hydrogen elimination step in Scheme 1 is highly endothermic with a reaction enthalpy of 44.7 kcal/mol. Thus, it is not likely that β-hydrogen elimination is an integral part of olefin oligomerization.

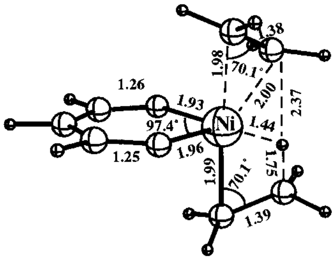
We have proposed[3] an alternative mechanism for the chain termination step in olefin oligomerization, Scheme 2. This mechanism is based on hydrogen transfer between the incoming ethylene monomer and the oligomer chain, Figure 1.

The transition state shown in Figure 1 is schematic. It might represent a direct hydrogen transfer from the β-carbon of the butyl group to the β-carbon of the incoming ethylene monomer with little or no interaction between the migrating hydrogen and the metal center. Alternatively, the hydrogen shift reaction could be aided by a strong Ni−H bond in the transition state. It is also possible that the structure shown as a transition state in Figure 1 in fact is an intermediate. We have looked for reaction paths with a single barrier and associated transition state. For R = H the transition state must in this case have at least a plane, C_s, or axis, C_2, of symmetry to satisfy the requirement of microscopic irreversibility. However, the lowest path with a single symmetrical (C_s) transition state has[3] a rather high barrier of 17.3 kcal/mol, mainly due to the strain imposed by the symmetry requirements.

This requirement does not have to be fulfilled if the reaction profile has a double-welled shape. In this case, the process will involve one symmetrical intermediate with at least C_s or C_2 symmetry, as well as two equivalent transition states. However, neither of the transition states will have to possess any symmetry. We have found a favorable path for which the energy profile has a double-welled shape, Scheme 3. The first step in this path is the formation of a very weak five-coordinated ethylene adduct, **3a**, with a complexation energy of only 1.8 kcal/mol compared to **1** and free ethylene. The next step leads to the transition state **3b.** Here the ethyl group has been pushed away from chelating plane by the ethylene. The hydrogen about to migrate has moved from a Ni−H distance of 1.67 Å in **3a** to 1.44 Å in **3b** and has thus established a strong bond to the metal center. The C−H bond has at the same time increased from 1.19 Å in **3a** to 1.75 Å in **3b** and is thus virtually broken. The C−C link in the former ethyl unit has finally gained considerable double-bond character with a C−C distance of 1.39 Å. The transition state can be characterized as an (acac)Ni−H system coordinated unsymmetrically to two ethylene units, and its energy is 6.5 kcal/mol above **3a**. The transition state structure was initially determined by decreasing the distance between the migrating hydrogen and the β-carbon on the incoming ethylene step by step while the other geometric parameters were optimized. The final converged structure **3b** was obtained by standard optimization procedures.[13] The single imaginary frequency of 235.4i cm^{-1} ensures that **3b** indeed is a transition state.

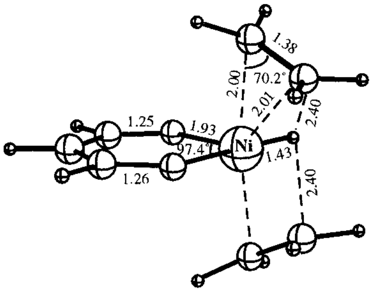


3a



3b

The two ethylene units become equivalent in the intermediate **3c** which represents the minimum-energy point on the reaction profile, Scheme 3. Structure **3c** is clearly a five-coordinated nickel hydride with the a Ni−H distance of 1.43 Å. The two



3c

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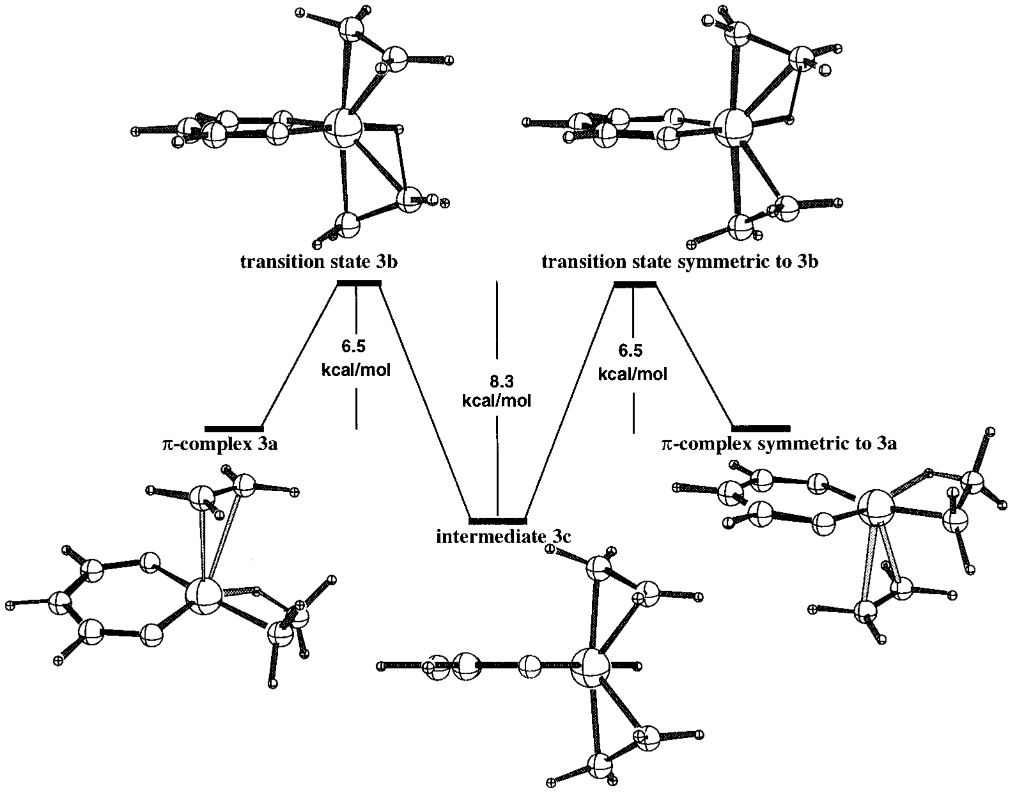
[14] (a) Fan, L.; Harrison, D.; Deng, L.; Woo, T.; Swerehone, D.; Ziegler, T. *J. Can. Chem.* **1995**, in press. (b)Woo, T.; Fan, L.; Ziegler, T. *Organometallics* **1994**, *13*, 432. (c) Woo, T.; Fan, L.; Ziegler, T. *Organometallics* **1994**, *13*, 2252.

Scheme 3. Proposed Mechanism for Chain Termination Involving One Intermediate and Two Transition States



ethylene ligands are connected by a symmetry plane containing the chelating ligand, and **3c** is of C_s symmetry. The intermediate is 8.3 kcal/mol below **3b** in energy and is primarily more stable than **3b** because the migrating hydrogen now is situated in the chelating plane where it has the strongest interaction with the metal d orbitals.[3] Keim[15] *et al.* were able to observe a ^{1}H NMR shift in the catalytic mixture which is consistent with the presence of a nickel−hydride species. They associated it with (acac)Ni−H; however, it could also be due to the five-coordinated intermediate **3c**. The last part of the reaction in Scheme 3 is degenerate to the first steps **3a** → **3b** → **3c** and results in a new π-complex that might eliminate the olefin. The reaction path in Scheme 3 does not exhibit a β-hydride elimination mechanism in a traditional sense. It can however be considered as a β-hydride elimination aided by an incoming olefin.[5]

The last question remaining for Scheme 3 to be a plausible chain-terminating mechanism is whether there exists a low-energy path which will lead either **3a** or **3c** away from the elimination pathway. We have carried out a linear transit calculation from **3a** to **2a**, and the barrier is estimated to be over 20 kcal/mol. This barrier is apparently due to the strong β-agostic interaction in **3a**. A similar high barrier was found for the path **3c** → **2c**. Thus, it would appear that the profile shown in Scheme 3 represents a viable path for the termination process.

Conclusion

The chain termination mechanism for catalytic ethylene oligomerization has been studied. Chain termination by β-hydrogen elimination is energetically unfavorable (44.7 kcal/mol), which leads to the conclusion that the catalytic cycle, Scheme 1, involving nickel hydride needs to be modified. We propose instead that a nickel−ethyl species, **1**, is the actual catalyst and that the termination takes place by transfer of the β-hydrogen to the incoming olefin, Scheme 2. A two-step mechanism for the β-hydrogen transfer reaction has been shown to represent the lowest energy path for termination, Scheme 3. The transition state **3b** for the path in Scheme 3 has been identified by an imaginary frequency of 235.4i cm^{-1}.

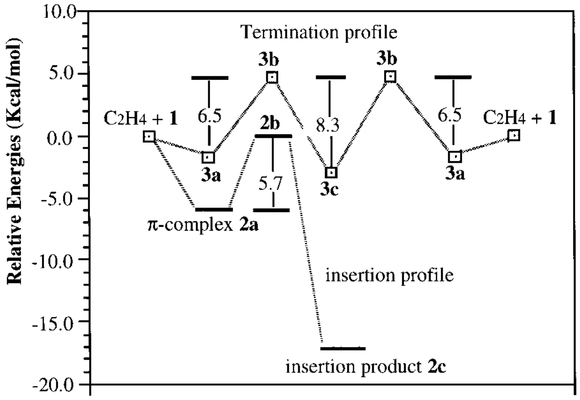


Figure 2. Energy profiles of ethylene insertion and chain termination.

The calculated energetics for the elementary reaction steps in olefin oligomerization catalyzed by (acac)NiC_2H_5 with (acac)-NiH as a precursor is shown in Figure 2. The figure displays the energy profile for the chain-growing insertion process of Scheme 2 as well as the chain-terminating hydrogen transfer process of Scheme 3. The reaction barrier of 8.3 kcal/mol for the termination path is somewhat higher than the insertion barrier of 5.7 kcal/mol. Keim[15] and co-workers have identified a hydride system in the oligomerization mixture. We suggest that this hydride might be the intermediate **3c** rather than (acac)-NiH of Scheme 1.

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