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Theoretical Study on the Reaction Complexing Olefins with Nickel Dithiolene

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Economic and powerful olefins separation is the most important technology for the energy optimisation and reduction of fossil fuel in petrochemical industry. On account of that the specific structures of olefins will make some influences on the separation, in this work, by means of density functional theory, we perform a theoretical estimation of the olefin-structure-induced effects on the reaction of nickel dithiolene with olefins. It is shown that the reaction complexing olefins with Ni dithioloene is a two-step process with the first step being the rate-determining one. As the number of carbon atoms in the olefins increases, the activation energy of any step will increase, while the reaction rate and the equilibrium constant will decrease. Furthermore, it demonstrates that the increase of the carbon atom number in olefins will suppress the reaction, and decrease the production rate, which provides a way of separating the olefins with different numbers of carbon atoms. Then we consider the influences on the reaction induced by the *trans*- or *cis*-structure in olefins. It is verified that the reaction between nickel dithiolene and *trans*-structure olefin will be much easier and faster to occur, but the product has a smaller stability than that of *cis*-structure olefin. This work should be of some significance for estimating the reaction rate and product rate in olefin separation.

1. Introduction

Due to the important roles in petrochemical industry played by olefins, it becomes more urgent to explore an approach used to separate olefins with high reagent selectivity and low energy consumption (Wang and Stiefel, 2001). In order to find reversible and high selective reagents for separating olefins, many experimental (Wang and Stiefel, 2000 and 2001, Harrison et al., 2006) and theoretical (Fan and Hall, 2002) (Brinkmann et al., 2009) researches have been performed recently. Wang and Stiefel (2001) reported that, because the olefin binding occurs through the sulfur atoms rather than the metal center, the neutral nickel 1,2-enedithiolate (dithiolene) complexes can reversibly and selectively react with simple aliphatic olefins to form adducts even in the presence of H_2S and CO, which are commonly present in olefin streams. In addition, Schrauzer et al. (1970) found that $M(S_2C_2Ph_2)_2$ (M = Ni, Pd, Pt; Ph = Phenyl group) reacts with norbornadiene, and Wing et al. (1970) also proposed that $Ni[S_2C_2(CF_3)_2]_2$ reacts with norbornadiene and 2,3-dimethyl-1,3-butadiene to form 1/1 olefin adducts, where the olefin binds to ligand S atoms rather than the metal. Theoretically, studies on the

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reaction of ethylene and $Ni(S_2C_2R_2)_2$ (R = H, CN, CF_3) in gas phase were carried out by Fan et al.(2002), using density functional theory (DFT) with B3LYP. It was found that this reaction show a two-step mechanism, and the electron-withdrawing groups will lower the barrier for the association of olefins and Ni dithiolene complexes, and stabilize the intermediates and products relative to the reactants. All the aforementioned researches have shown that the nickel dithiolene can be used in olefin separation and purification scheme, where the dithiolene-bound olefin is released through reduction and regenerated by oxidation. However, to the best of our knowledge, there are few studies that discuss the reactions between nickel dithiolene and other olefins.

In the present work, we theoretically studied the reactions of nickel dithiolene with eight kinds of olefins by using density functional theory (DFT) and B3LYP. We found that the nickel dithiolene can be used to separate the olefins with different numbers of carbon atoms. Also we find that the reaction between nickel dithiolene and trans-structure olefin has smaller product stability and will be easier and faster to occur than that of cis-structure olefin.

2. Computational Methods

All calculations of the present work are performed with Gaussian03 program package. The geometries of reactants, transition states, intermediates and products are optimized, as well as the corresponding frequency calculations, by means of DFT with B3LYP. A slightly modified version of Hay and Wadt's LANL2DZ (1985) with the two outermost *p* functions replaced by a new function with (41) split (Couty and Hall, 1996), and a relativistic effective core potential (ECP) is used for Ni, while the 6-31G(d) basis set is utilized for all the other atoms. In addition, the nature of all transition states is characterized by the imaginary frequency and verified by the intrinsic reaction coordinate (IRC) approach. All of the calculations are performed in gas phase at temperature T = 298.15 K and pressure P = 101.33 kPa, and the energies have been modified by zero point corrections.

The rate constants at temperature T can be obtained by the general statistical thermodynamics and Eyring transition state theory (TST) from partition function:

$$k(T)=\frac{N_A k_B T}{h}\left[\frac{Q_{\mathrm{TS}}^{\neq}/V_{\mathrm{TS}}}{\prod_i (Q_{\mathrm{R}i}/V_{\mathrm{R}i})}\right]\exp\left(-\frac{\Delta E_0}{RT}\right), \tag{1}$$

where $N_A = 6.022\times10^{23}\,\mathrm{mol}\cdot\mathrm{l}^{-1}$ is the Avogadro' number, k_B = 1.380662×10^{-26} kJ·K^{-1} the Boltzmann constant, h = 6.626176×10^{-37} kJ·s^{-1} the Planck's constant, R = 8.314×10^{-3} kJ·mol^{-1}·K^{-1} the gas constant, $Q_{TS}^{\neq}$ and Q_{Ri} represent the molecular total partition function of transition state and reactant i, V_{TS} and V_{Ri} the molar volume of transition states and reactant i, ΔE_0 is the energy barrier of activation by zero point corrections. The equilibrium constant K_{eq} can be obtained straightforwardly by the general statistical thermodynamic relationship.

3. Results and Discussions

In this section we presented the numerical results and explored the selectivity of the nickel dithiolene in the olefin separation. It has been found that the reaction between nickel dithiolene and each olefin is a two-step process. In every reaction the first step is, by coordinating the double-bond-carbon atoms in olefin molecule to the S atoms in dithiolene, to form a trans-structural intermediate

$$Ni(S_2C_2H_2)_2 + R_1CH = CHR_2 \rightarrow Ni(S_2C_2H_2)_2 \cdot R_1CH\text{-}CHR_2 \quad (2)$$

Here R_1 and R_2 can represent substitutes -H, -CH_3, -C_2H_5, and -C_4H_9. The structure of the intermediate is mainly decided by the matching principle of the symmetry in the frontier orbit of the olefins and the nickel dithiolene. In the second step, the unstable trans-structural intermediate will be quickly transformed into the steady cis-structural product. For clarity, the reaction of complexing 1-butylene with nickel dithiolene is schematically presented as an example in Figure 1.

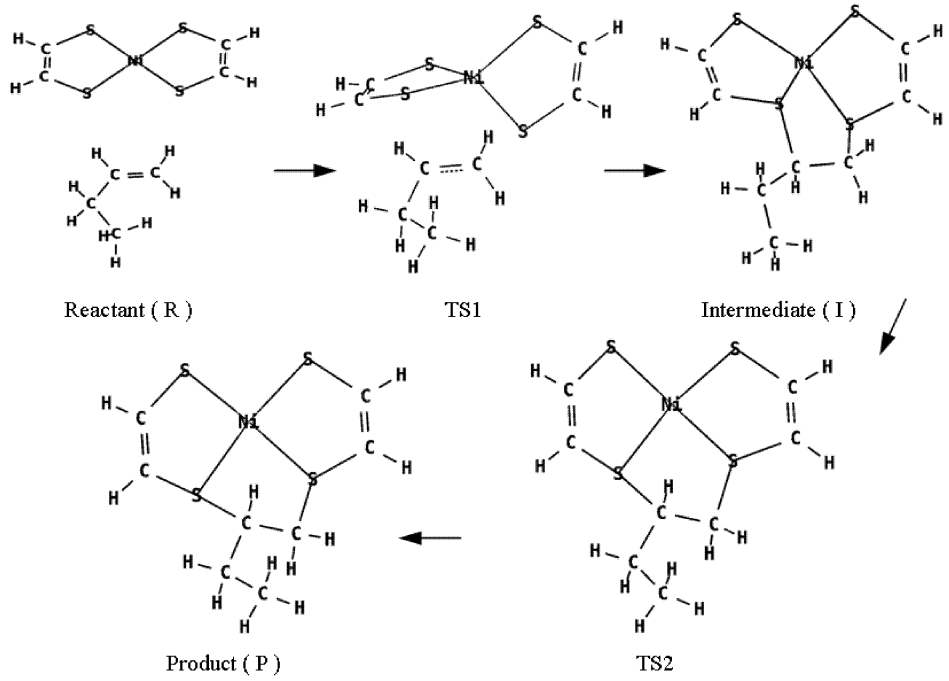

Figure 1: The approach of the reaction complexing Ni dithiolene with 1-butylene.

In order to study the selectivity of nickel dithiolene we modeled all the reactions occurred between nickel dithiolene and olefins. The activation energies and the gap energy (defined as $\Delta E = E_P - E_R$ with E_P and E_R being the energy of the product and the reactants) are shown in Figure 2. By comparing the activation energies $\Delta^{\neq}E_1$ and $\Delta^{\neq}E_2$ corresponding to the first and second steps in each reaction, we can find $\Delta^{\neq}E_1$ is always larger than $\Delta^{\neq}E_2$, clearly demonstrating that the first step is the rate determining

one. Furthermore, we can find that the activation energy $\Delta^{\neq}E_1$ of the first step will changes from 122.9 kJ·mol^{-1} to 130.2 kJ·mol^{-1} when C_2H_4 is changed to 1-C_6H_{12}, which seemly indicates that the activation energy becomes large when the number of carbon atoms in the 1-olefin increases. In the same way, the activation energy of the second step changes from 89.90 kJ·mol^{-1} to 104.9 kJ·mol^{-1}. For the olefins with 6 carbon atoms we can find the activation energy of the step-1 increases from 135.4 kJ·mol^{-1} to 140.1 kJ·mol^{-1}, while that of the step-2 will decrease from 113.8 kJ·mol^{-1} to 110.2 kJ·mol^{-1}, when the structure of 3-hexene becomes from *trans-* to *cis-*. It is demonstrated that the reaction between nickel dithiolene and *trans-* structure olefin will be much easier to occur than that of *cis-* structure, but will have a more unstable product. All of these results verified that the reaction is inclined to be blocked with the increase of the complexity of olefin's structure, and the reaction is easier to occur between nickel dithiolene and simple olefins. It is practical to separate the simple olefins from the others with relatively more complex structures, consistent with a great many experimental studies.

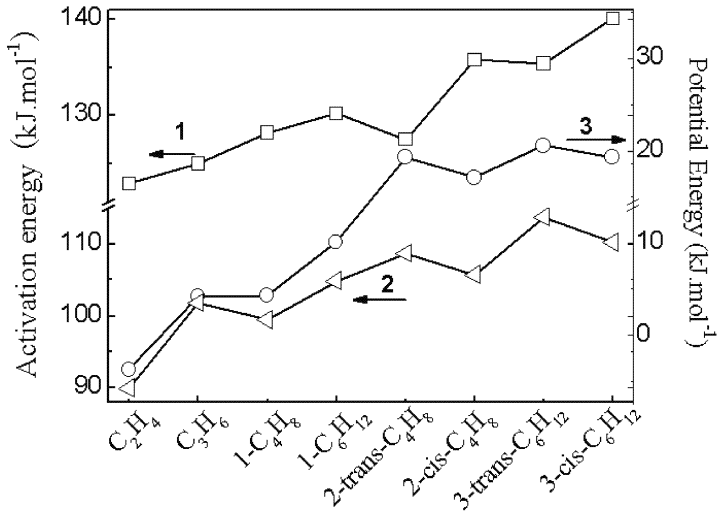

Figure 2: Activation energies and potential energy differences variations of the reactions between $Ni(S_2C_2H_2)_2$ and olefins (1: $\Delta^{\neq}E_1$, 2: $\Delta^{\neq}E_2$, 3: ΔE)

These results are also able to be found from the gap energy, as well as the rate constant k_1 of the rate-determining step (as shown in Figure 3). In the reaction of complexing nickel dithiolene and C_2H_4 the gap energy is -3.706 kJ·mol^{-1}, which implies that the product is more stable than the reactants. Otherwise, the product produced by nickel dithiolene and 3-cis-C_6H_{12} becomes more unstable than the reactants since the gap energy is positive (19.31 kJ·mol^{-1}). This implies that the product of the reaction

between nickel dithiolene and simple olefins will be much more stable than that of more complex olefins. Obviously this is a reasonable explanation on the above results from an energy point of view. On the other hand, let us take into account the rate constant k_1. From Figure 3 we can find that the rate constant k_1 of the rate-determined step decreases sharply from 1.177×10^{-11} l·mol^{-1}·s^{-1} to 2.113×10^{-17} l·mol^{-1}·s^{-1} when the olefin changes from a simple (C_2H_4) to a relatively complex (3-cis-C_6H_{12}) structure. This indicates that the rate of reaction complexing olefins with nickel dithiolene will become much faster for an olefin with a much simpler structure.

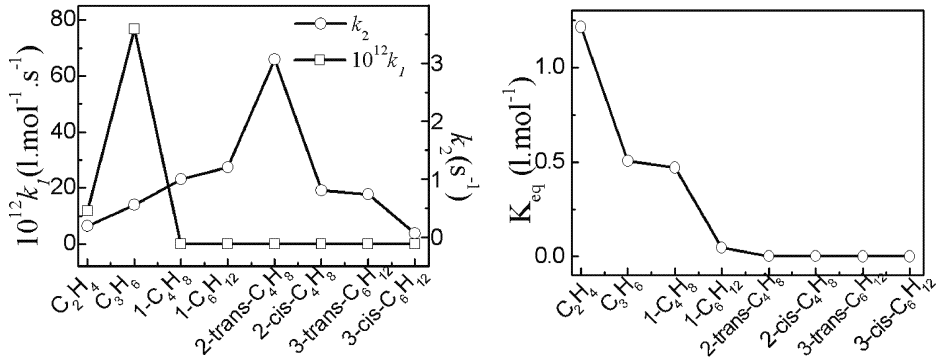

Figure 3: Rate constants(k_1 and k_2) and equilibrium constants(K_{eq}) of the reaction between $Ni(S_2C_2H_2)_2$ and olefins

Finally, we consider the variation of the equilibrium constant for the different olefin reactant. It is also very clear that the equilibrium constant rapidly decreases from 12.12 to 8.435×10^{-6} l·mol^{-1} when one of the reactant, olefin, changes from a simple olefin C_2H_4 to a relatively complex olefin 3-cis-C_6H_{12}. This indicates that the production rate decreases with the increasing of the olefin structure complexity. It is believed that the reaction of adding olefins to nickel dithiolene is sensitive to the structure complexity of olefins.

4. Conclusion

In conclusion, we have studied the reaction of nickel dithiolene with eight kinds of olefins. By comparing and analyzing the activation energies, the gap energy, the rate constant, and the equilibrium constant. It is shown that the increase of the carbon atom number in certain olefin will block the reaction, and decrease the production rate. This is beneficial to separate the olefins with less carbon atoms (e.g. ethylene and propylene) from the others with relatively more carbon atoms. Therefore, we may draw that the nickel dithiolene has a good selectivity to the simple olefins (such as ethylene and propylene) in the separation of olefins with different numbers of carbon atoms, indicating that the nickel dithiolene can be used to separate the ethylene and propylene

from other olefins with more complex structure in petrochemical industry. The results of this work can be seen as a parameter to estimate the reaction rate and product rate in olefin separation production, it also can be beneficial to improve the reagent selectivity, increase the product rate of ethylene, reduce the energy consumption and reaction time in the current separation methods.

5. Acknowledgement

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