

# Theoretical Study on the C-H Activation in Decarbonylation of Acetaldehyde by $\text{NiL}_2$ ( $\text{L}=\text{SO}_3\text{CH}_3$ ) Using Density Functional Theory

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**Abstract:** Density functional theory calculations were carried out to explore the potential energy surface (PES) associated with the gas-phase reaction of  $\text{NiL}_2$  ( $\text{L}=\text{SO}_3\text{CH}_3$ ) with acetone. The geometries and energies of the reactants, intermediates, products and transition states of the triplet ground potential energy surfaces of  $[\text{Ni}, \text{O}, \text{C}_2, \text{H}_4]$  were obtained at the B3LYP/6-311++G(d,p) levels in C, H, O atoms and B3LYP/LanL2dz in Ni atom. It was found through our calculations that the decarbonylation of acetaldehyde contains four steps including encounter complexation, C-C activation, aldehyde H-shift and nonreactive dissociation. The results revealed that C-C activation induced by  $\text{NiL}_2$  ( $\text{L}=\text{SO}_3\text{CH}_3$ ) led to the decarbonylation of acetaldehyde.

**Key words:** density functional theory; decarbonylation; transition state; energy; C-C activation

## 1 Introduction

Nowadays, the reaction of transition metal ions with hydrocarbons is considered to be one of the most active research areas in contemporary gas-phase ion chemistry. In this area, C-H and C-C bond activations in small hydrocarbons induced by transition metal ions are being attracted increasing the enormous practical importance to the petroleum chemistry as well as the fundamental importance of bonds as among the simplest, strongest, and most ubiquitous of chemical bonds. Considerable efforts in the past years have been directed at exploring the mechanisms<sup>[1-7]</sup>. A variety of fundamental thermodynamic, kinetic, and mechanistic information about gas-phase organometallic chemistry are obtained from these studies<sup>[2-8]</sup>. However, the reaction mechanism is explicit. On the other hand, quantum chemical calculations in first principle have played a great role in the studies which offer a complementary source of information on the structure and energy details of the potential energy surfaces (PES) for the reactions. Various techniques have been used for the investigation of gas-phase reactions of first-row transition-metal ions ( $\text{M}^+$ ) with acetaldehyde, such as

ion beam mass spectrometry and crossed-beam, etc. In the previous studies<sup>[2]</sup>, decarbonylation of acetaldehyde (reaction 1) by  $\text{M}^+$  was considered to be a dominant process at low reaction energies and the formula was expressed as follows<sup>[8]</sup>:



Significant thermodynamic and kinetic clues were obtained, however, reports about theoretical studies of the mechanistic details of decarbonylation are limited. Theoretical studies of the mechanistic details of decarbonylation are still scarce. Based on the above, the occurrence of the reaction and the formed products by  $\text{M}^+$  ions insertion into the H-CO or C-CO bond is urgent to be determined. Hence, theoretical study on the reaction is still needed. In this paper,  $\text{NiL}_2$  ( $\text{L}=\text{SO}_3\text{CH}_3$ ) was selected as a probe of first-row transition metal ions compounds to carry out the theoretical investigation on the  $\text{NiL}_2$  ( $\text{L}=\text{SO}_3\text{CH}_3$ )-assisted decarbonylation of acetaldehyde using DFT method (B3LYP) and compute energies of key reaction. This method has been widely applied to electronic structure calculations on systems containing transition metals, which combines reasonable computational costs with accuracy sufficient for describing open-shell metal systems.

## 2 Computational method

The density functional method in its three-

parameter hybrid B3LYP functional was used in the calculations. We optimized the structures of all the stationary points involved in the title reaction at both 6-311++G(d,p) basis sets in C, H, O atoms and Lanl2dz basis sets in Ni atom levels of theory<sup>[9,10]</sup>, the later of which is flexible enough to give a good account of longer range ion-ligand interactions, and it is also large enough to generally reduce the basis set superposition error (BSSE) to less than the errors inherent in the method, so that BSSE corrections become unnecessary. Frequency calculations were carried out at the same levels to identify the optimized stationary points (minima or transition states) and to estimate the zero point energy (ZPE) corrections that are applied to all reported energies. In order to confirm the transition states and their connected minima, intrinsic reaction coordinate (IRC) calculations were performed to follow the reaction pathways. All the calculations were carried out with GAUSSIAN 03 package.

### 3 Results and discussion

The optimized geometries and structural parameters for the reactants, intermediates, products, and saddle points along the decarbonylation pathway are shown in Fig.1. It can be found that both the basis sets result in almost the same results for the reaction system, indicating the ability of basis set to describe the features of the PES of [Ni, O, C<sub>2</sub>, H<sub>4</sub>]. For convenience, in the following the results calculated at 6-31+G\*\* basis sets in C,H,O atoms and Lanl2dz basis sets in Cr atom level will be used in the discussion.

As shown in Fig.1, three minima (noted as M1, M2, and P, respectively) and two first-order saddle points (noted as TS1 and TS2, respectively) were located along the decarbonylation coordinate on the triplet surface of [Ni, O, C<sub>2</sub>, H<sub>4</sub>]. The encounter complex (L=SO<sub>3</sub>CH<sub>3</sub>)<sub>2</sub>Ni-OCHCH<sub>3</sub>-OCHCH<sub>3</sub> is featured by the linkage of Ni to the O atom of acetaldehyde. The overall symmetries of the encounter complexes are nearly C<sub>s</sub> with the symmetry plane

defined by Ni-O<sup>2</sup>-C<sup>3</sup>-C<sup>5</sup> (M1). Upon binding with Ni<sup>1</sup>, the largest change in CH<sub>3</sub>CHO is the increase in the O<sup>2</sup>-C<sup>3</sup> bond length. This is a result of oxygen polarizing charge toward Ni<sup>1</sup>, weakening the O-C<sup>3</sup> bond. The equilibrium Ni<sup>1</sup>-O<sup>2</sup> distances are 1.919 Å, the net charge of Ni<sup>1</sup> and O<sup>2</sup> are 0.49 and -0.353. Correspondingly, the Ni<sup>1</sup>-O<sup>2</sup> binding energy is 5.2 kcal/mol less than the sum of NiL<sub>2</sub> and CH<sub>3</sub>CHO. The obtained result at least partially validates our theoretical approach to the electronic and geometric structures of the species

The inserted species H<sub>3</sub>C-Ni-CHO (TS1) may be formed by the metal ion insertion into the C-C bond of acetaldehyde. As shown in Fig.1, complex TS1 has an overall C<sub>s</sub> symmetry with the symmetry plane defined by O<sup>2</sup>-C<sup>3</sup>-Ni<sup>1</sup>-C<sup>5</sup>. The C<sup>3</sup>-Ni<sup>1</sup>-C<sup>5</sup> angle of TS1 is calculated to be 92.7°, slightly larger than 90°, The Ni<sup>1</sup>-H<sup>6</sup>, Ni<sup>1</sup>-C<sup>5</sup>, Ni<sup>1</sup>-C<sup>3</sup> and Ni<sup>1</sup>-O<sup>2</sup> distances are 2.205 Å, 2.203 Å, 1.98 Å, and 2.184 Å, respectively, indicating that the Ni<sup>+</sup> center interacts with all these atoms. From Table 1, it can be seen that the charge of O<sup>2</sup> transfers to Ni<sup>1</sup> from -0.353 to -0.237, the charge of H<sup>4</sup> drops from 0.179 to 0.250. However, the C<sup>3</sup>-C<sup>5</sup> distance is 2.03 Å, suggesting rupture of the C-C bond, s and d orbital of Ni<sup>1</sup> is preferably sd hybridization. The transition state TS1 is the first saddle between the intermediate M1 and M2, and the bond distance is close to the M2. Therefore, it is the late transition state of potential energy surface, the energy of TS1 is 48.2 kcal/mol above that of M1.

In response to the second intermediate M2, the energy is lower than TS1 5.6 kcal/mol. It can be seen that the direct break of (H<sub>3</sub>C)Ni<sup>1</sup>-CHO bond gives rise to NiCH<sub>3</sub> and CHO. Structurally, It can be seen that Ni<sup>1</sup> proceeds inserting the C<sup>3</sup>-C<sup>5</sup> band. M2 has the C<sub>s</sub> symmetry, and the symmetry surface is O<sup>2</sup>-C<sup>3</sup>-Ni-C<sup>5</sup>. The Ni<sup>1</sup>-H<sup>6</sup>, Ni<sup>1</sup>-C<sup>5</sup>, Ni<sup>1</sup>-C<sup>3</sup> and Ni<sup>1</sup>-O<sup>2</sup> distances are 2.372 Å, 2.029 Å, 1.93 Å and 2.815 Å, respectively. It shows that the central atom Ni still interacts with all these atoms, however, C<sup>3</sup>-C<sup>5</sup> distance is 2.725 Å, the charge of C<sup>3</sup> drops from 0.278 to 0.296, and the charge of C<sup>5</sup> continues to lose charge from -0.571 to -0.517.

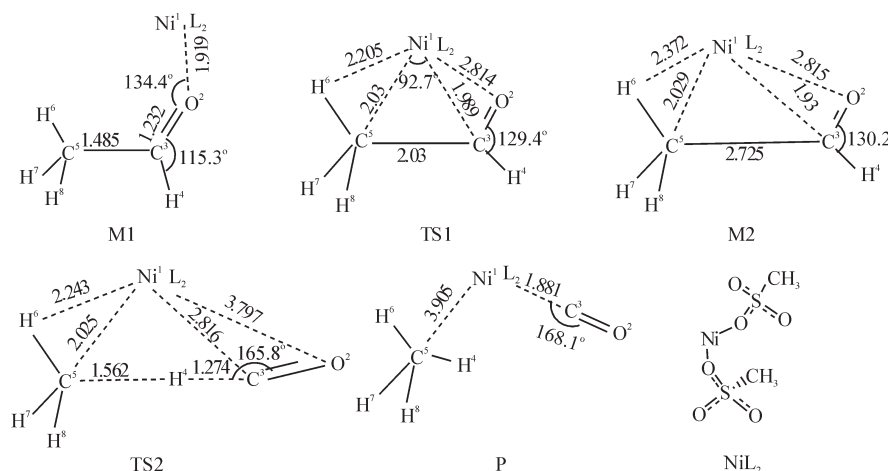


Fig.1 The geometries of the decarbonylation reaction of CH<sub>3</sub>CHO with NiL<sub>2</sub>(L=SO<sub>3</sub>CH<sub>3</sub>)

It means that C<sup>3</sup>-C<sup>5</sup> bond has been broken. M2 can be rearranged to an H-shifted species H<sub>4</sub>C-Ni<sup>1</sup>(CO) (p), which can be a direct precursor of the decarbonylation products (CH<sub>4</sub> and Ni<sup>1</sup>(CO)). It can be seen that complex P has no symmetry elements (Fig.1).

**Table 1** The net charges distribution of intermediates and transition

Atomic number	M1	TS1	M2	TS2
Ni <sup>1</sup>	0.49	0.212	0.077	0.320
O <sup>2</sup>	-0.353	-0.237	-0.22	-0.181
C <sup>3</sup>	0.278	0.194	0.296	0.388
H <sup>4</sup>	0.179	0.250	0.259	0.253
C <sup>5</sup>	-0.553	-0.571	-0.517	-0.704

**Table 2** The relative energies (kcal/mol) for the decarbonylation with NiL<sub>2</sub>(L=SO<sub>3</sub>CH<sub>3</sub>)

	ΔE	Δ(E+ZPE)	Δ(E+H)	Δ(E+G)
NiL <sub>2</sub> +CH <sub>3</sub> CHO	0.0	0.0	0.0	0.0
M1	-5.2	-3.7	-3.5	7.0
TS1	43.0	42.5	42.4	54.6
M2	37.4	36.8	37.2	48.5
TS2	64.4	60.2	60.8	70.1
P	-2.8	-4.0	-2.3	-3.6

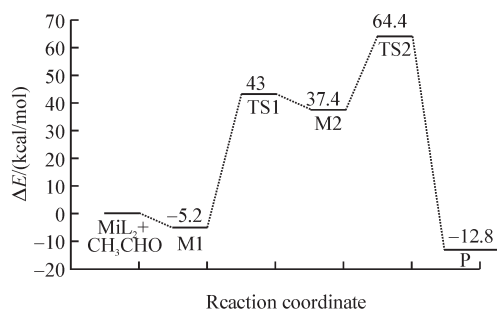


Fig.2 Diagram of relative energies along the channels for the decarbonylation

M2 and P are connected through a direct, one-step H<sup>4</sup> shift occurring via saddle point TS2. The charge of O<sup>2</sup> continues to lose charge, drop from -0.22 to -0.181, the charge of C<sup>3</sup> loses charge to -0.181, and the change of the charge of H<sup>4</sup> is small. Structurally, the transition state is featured by one elongated and one shortened C-Ni bond as well as the both elongated C<sup>3</sup>-C<sup>5</sup> and C<sup>3</sup>-H<sup>4</sup> bonds, suggesting that it may be a saddle point that connects P to either M2 via Ni<sup>1</sup> insertion into C-C bond. Structurally, the C<sup>3</sup>-C<sup>5</sup> and C<sup>3</sup>-H<sup>4</sup> distances become long, whereas the C<sup>5</sup>-H<sup>4</sup> distances become short. Table.2 presents the relative potential energy from the IRC calculation. Fig.2 is some selected structures along the reaction pathway. It is clear that TS2 is indeed the saddle point connecting minima M2 and P. All our attempts to locate such a minimum as H(CH<sub>3</sub>) Ni<sup>1</sup>(CO) on the [Ni, O, C<sub>2</sub>, H<sub>4</sub>] lead instead to 2 or P, suggesting that only species P can be the precursor of products CH<sub>4</sub> and Ni<sup>1</sup>(CO). TS2 is found to be the most demanding point along the whole decarbonylation pathway, and the energy of TS2 is 64.4 kcal/mol and

67.2 kcal/mol above that of the separated reactant and P, respectively.

The potential energy surface profile of the decarbonylation of acetaldehyde at the Ni<sup>1</sup> center has also been generalized in Fig.2 and Table 1. It is very clear that the reaction occurs through Ni<sup>1</sup> insertion into C-C bond followed by an aldehyde H-shift and then a nonreactive-dissociation of the H<sub>4</sub>C-Ni<sup>1</sup>(CO) bond. The rate-determining step of the reaction is the aldehyde H-shift, which has an energy barrier of 64.4 kcal/mol with respect to the separated reactants. The stable precursor for the decarbonylation products is H<sub>4</sub>C-Ni<sup>1</sup>(CO). According to the above calculations, it comes to a conclusion that the C-H activation by NiL<sub>2</sub> leads not to the decarbonylation of acetaldehyde but to the elimination of both NiH and NiH<sup>2</sup>.

## 4 Conclusions

a) The decarbonylation of CH<sub>3</sub>CHO with NiL<sub>2</sub> follows C-C activation rather than aldehyde C-H activation. This reaction proceeds through four elementary steps, *i e*, encounter complexation, C-C activation, H-shift and nonreactive dissociation, and the third step of the process constitutes the rate-determining step. Along the Cr<sup>3+</sup> mediated decarbonylation coordinate, there are two high-energy barriers (43 and 64.4 kcal/mol for the second and third steps, respectively)

b) The stable precursor of the decarbonylation products CH<sub>4</sub> and (L=SO<sub>3</sub>CH<sub>3</sub>) L<sub>2</sub>Ni<sup>1</sup>(CO) has a structure of (CH<sub>4</sub>) Ni(CO) rather than (CH<sub>3</sub>)<sub>3</sub>Ni(CO), while the later is isolated as a transition structure.

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