



Computational Investigation of Carbonyl Positioning Mechanism in Mn (CO)₅CH₂F Complex by Functional Density Theory

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Abstract

In this study, quantum computation was performed by density functional theory (DFT) on carbon monoxide placement in the Mn (CO)₅CH₂F complex. First, all geometric optimization structures and then CO depositional mechanisms were evaluated in different states. it placed. The pathway for the placement reaction was through the migration of the alkyl group. The initial complex will have four different paths to reach the product. The computational results indicate that a route is preferable to other paths, which is attributed to spatial and electron effects.

Keywords: Density Function Theory, Mn (CO)₅CH₂F, Reaction Reaction.

1. Introduction

Carbonyl placement is a very important primary reaction [1]. For this reason, many researchers have attracted the attention of both researchers and researchers in two experimental and theoretical fields [2]. As a major elemental reactor, in 1960 the CO placement was observed by Calderazzo and colleagues [3], many studies were carried out thereafter. Mainly in carbonyl complexes, Rh Mo, Fe, Zn are useful as catalysts, a similar reaction [4], migration reactions from the NO ligand to Co-CH₃ by Hall and colleagues from a quantum chemistry perspective [5]. There are three possible ways to realize the CO deposition in the reaction [6-8]:

-CO positioning mechanism

-Migration Mechanism CO

-Alkyl migration mechanism

In this paper, CO placement in the Mn (CO) 5CH₂F complex has been studied based on the alkyl group migration mechanism .

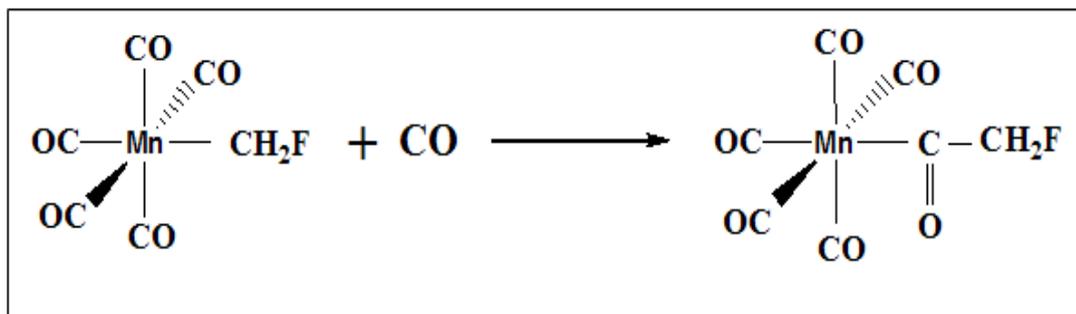
2 .Computational method:

All calculations were performed using Gaussian software 03 [9]. The calculations have been used for all interfaces and transition states using the functional density theory (DFT) with three applied parameters (B3) plus Lee, Young, and Par (LYP). For all standard series atoms 6-31G is used for the central metal atom of LANL2DZ.

3 .description and calculations:

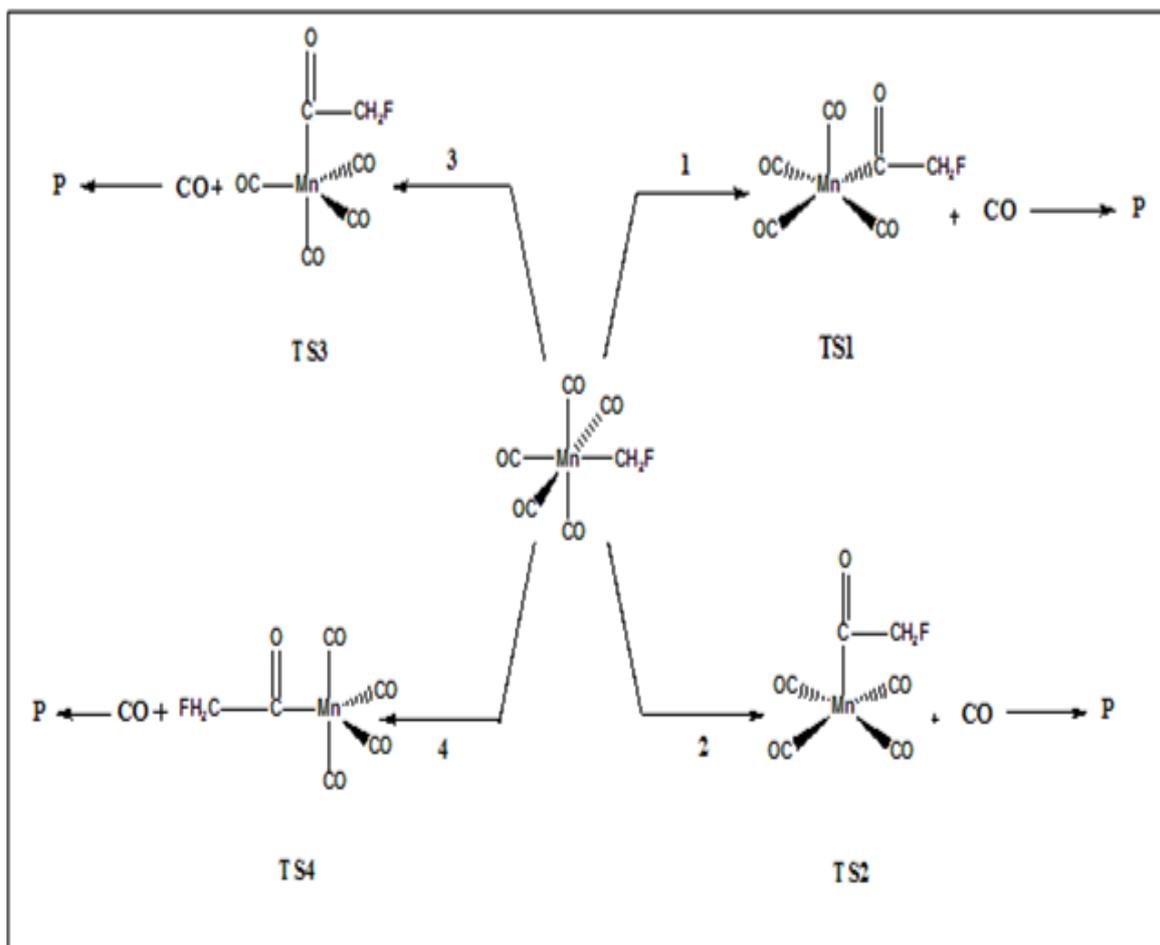
In the following sections, the carbon monoxide CO positioning in the metal-alkaline bond, which is an example of the placement-removal reaction of the ligand, is discussed. This reaction is a key step in some catalytic processes. The placement will take place so that after completion of the process,

CO is introduced into the metal-alkaline bond. CO reaction with Mn (CO)₅CH₂F is an indicator of the carbonyl position[1].



Schema (1) Carbonyl Positioning Response

If we just take into account the reaction equation, CO may be thought to fit directly into the Mn-CH₂F bond, such a view is fully consistent with the name CO (CO), but other mechanisms with the same stoichiometry for Other ligands other than CO are possible. In this paper, the results of initial quantum mechanics methods were evaluated to evaluate the carbonyl residue reaction in Mn (CO)₅CH₂F. Energy is calculated and structural parameters and results are obtained using the methods mentioned in the tables. In this reaction, a reactive species reacts with CO and CO is produced by CO. Carbon monoxide shows a great tendency to be placed on a metal-alkaline bond. The reaction of the reactive species begins with Mn (CO)₅CH₂F. In the reagent, manganese has a quasi-octagonal makeup, and manganese metal in the composition has an electron d₆ arrangement and six corundum. This composition has 18 electrons. In the first-order placement reaction, the migration of the methyl group to the CO group at the position of the Cis (Cis) is faster and more reversible. In this migration, the Acyl group is formed and an intermediate 5 Curtain that can have a triangular borehole structure (TBP) and a square pyramid, which has an empty site for entering the CO. In the next step, the CO enters the empty site and produces the Mn (CO)₅COCH₂F product[13-16].



In Scheme 2, four paths are proposed to examine the mechanism.

This reaction has been investigated with the interfaces of the square pyramid and the two pyramidal triangles, in which each of these structures was considered as substrates in two tropical and axial positions.

4 .The paths studied reactions

Route number 1:

The reaction of the reactor $\text{Mn}(\text{CO})_5\text{CH}_2\text{F}$ begins and goes toward the TS1 transition state; the migration of the CH_2F group occurs on one of the carbonyls located in the Cis position relative to the alkyl group and the CH_2FCO group forms To be During this migration, the TS1 transition mode, which has an appropriate CO space entry point, is formed. This intermediate has a square pyramid structure, in which the acyl group is in a tropical position. In the next step, the CO enters the place and the product $\text{Mn}(\text{CO})_5\text{COCH}_2\text{F}$ is obtained.

Route No. 2:

This reaction is in accordance with the mechanism of path number 1 and goes towards the TS2 transition state, and like the pre-intermediate path has a quadrilateral pyramid structure, with the difference that the acyl group is in a pivotal position. This path, like the path 1 of Mn (CO)₅COCH₂F, gives us [17-19].

Route No. 3:

This path starts at the same path as the above mentioned reactor and goes on to the TS3 transition state, and it should be noted that the TS3 has two triangular pyramidal structures and the acyl group is located in a pivotal position.

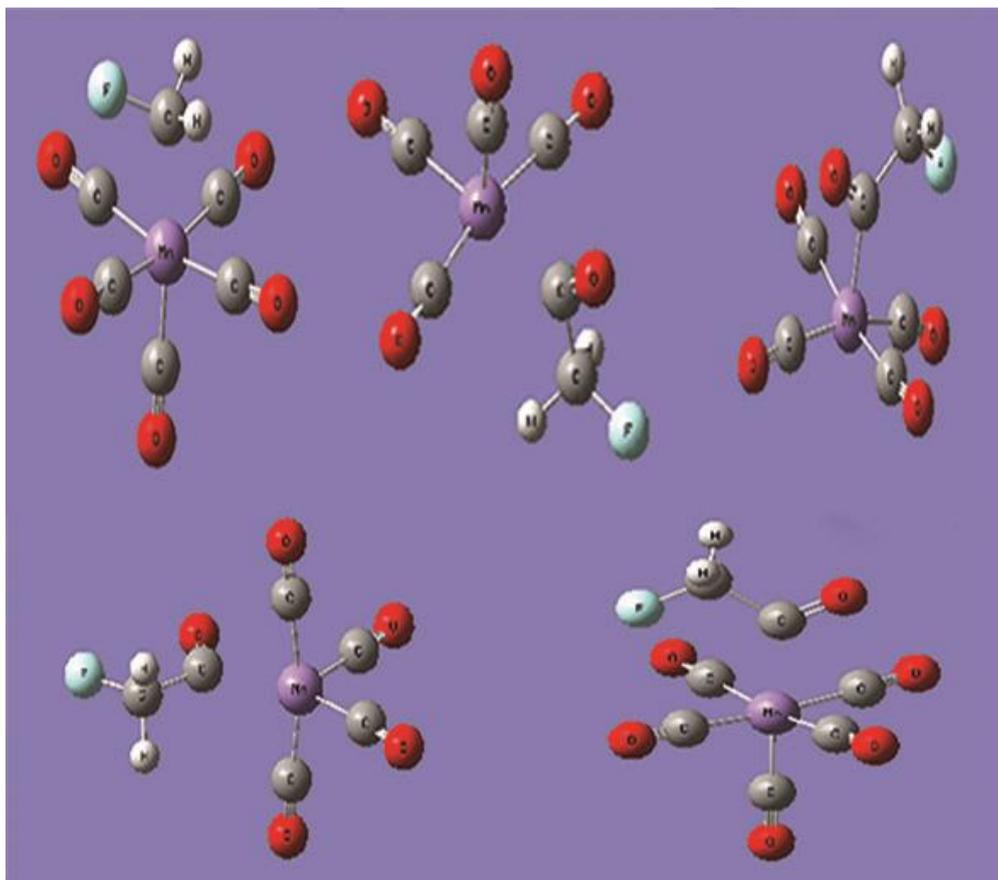
Route No. 4:

The path to this transition towards the TS4 transition mode has a transition mode with a two-pronged triangular pyramidal structure and the acyl group is in a tropical position.

It should be noted that in all of the studies, the path No. 3, which was preceded by the TS3 transition, was removed due to spatial and electron effects, and these structures changed to the TS4 direction.

5 .Discussion in the results

In this research, all the basic structures, interfaces and products are optimized. The calculations, which include zero point energy (ZPE), total calculated energy (E₀) and electron energy (E_{ele}), are arranged in tables and charts.



The schema (3) of the optimized shape of the molecules is from the upper left: Reactor, TS1, TS2, TS4 and product for Mn (CO) 5CH2F

Table 1 shows the total calculated energy (E0), zero point energy (ZPE) and electron energy (Eele) for Mn (CO) 5CH2F

| B3LYP/6-31G | | | |
|--|-------------|------------------|-----------------|
| Kcal/mol | ZPE | E _{ele} | E ₀ |
| <i>Mn(CO)₅CH₂F</i> | | | |
| react | 45.89168883 | -508124.0281 | -508078.1364 |
| CO | 3.15763032 | -71102.81610705 | -71099.65847673 |
| TS1 | 45.64946997 | -508097.6332 | -508051.9837 |
| TS2 | 45.89419887 | -508100.2649 | -508054.3707 |
| TS4 | 45.39219087 | -508095.5266 | -508050.1344 |
| Product | 51.81663825 | -5792422.237 | -579190.207 |

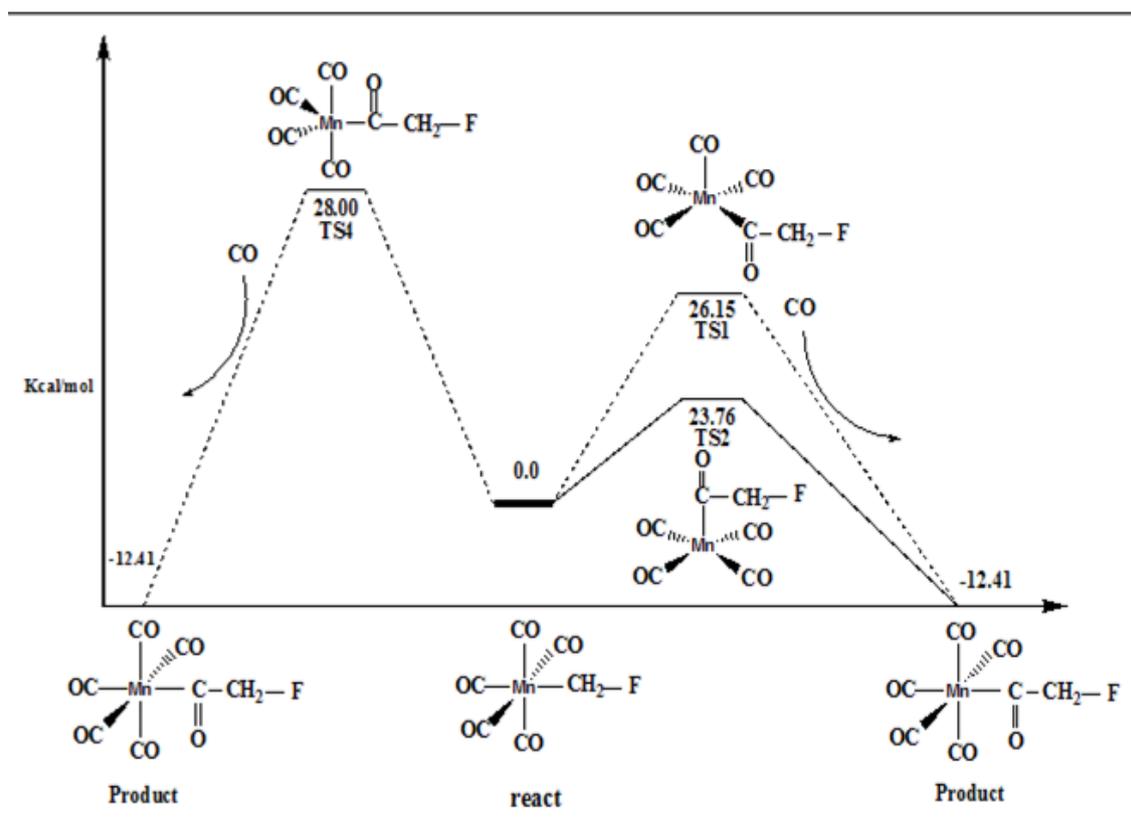


Figure (1) Placement reaction-migration diagram of CO in the complex according to (kcal / mol)

The high energy graph has three paths. In the direction where the TS4 with the closed formula $\text{Mn(CO)}_5\text{CH}_2\text{F}$ is two triangular pyramidal (TBP), the energy (28) is. On other paths TS1 and TS2 with the closed formula above, have a square pyramid structure that is solvable in TS1 on the page and in TS2 in a pivotal position having respectively 26.25 and (23.76) energies. In all three ways, the product produced $\text{Mn(CO)}_5\text{COCH}_2\text{F}$, which has an octahedral structure with energy (12.41). With regard to the energies mentioned and calculated, the path in which the medium is in the form of a square pyramid and the pivot point in the axial position (TS2) has the lowest energy, so the energy barrier is less in this reaction, and it can be concluded that this The route is thermodynamically preferred to the TS1 and TS4 paths.

6. Discussion and Conclusion.

From the quantum computation of the density function (DFT), the migration of the alkyl group in the Mn (CO) 5CH2F complex and the 4 paths of the different transition state of the 1 path is eliminated, and from the remaining 3 tracks, only one path is considered for computational results with less energy and the velocity And it is preferable that this superiority can be attributed to spatial and electron effects.

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