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DFT Study on Hydrogenation Reaction of 1-hydroxypropan-2-one

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Abstract

1-hydroxypropan-2-one is an important bio-oil compound obtained after pyrolysis of biomass. The model bio-oil compound for this study, i.e. 1-hydroxypropan-2-one has two oxygen atoms which degrades the quality of bio-oil as fuel thus needs to be upgraded. To remove all the oxygen atoms, three simultaneous hydrogenation reactions are required to get propane as the final product. However, in this study we have reported one hydrogenation reaction and acetone as an intermediate compound is targeted. This study investigates the reaction pathway and barrier height for hydrogenation reaction. Optimization calculation has been performed to find the transition state and a frequency calculation has been done to recognize the transition state. An IRC calculation task was given to find out the minima in both direction to get an optimized structure of reactant and product which also reaffirms the transition state. Optimization, frequency and IRC calculation has been performed at M06-2X level of theory with 6-31g+(d,p) basis set. Energy has been calculated for all the optimized structures at B3LYP/6-311g+(d,p) level of theory. All calculations have been performed using Gaussian 09 and Gauss View 5 software package.

Keywords: DFT, Hydrogenation, IRC calculation, Optimazation

1. Introduction

Energy has ever been a hot topic worldwide whether it is renewable energy or non-renewable energy source, energy demands or supply, green and sustainable energy etc. Developed nations like USA, Russia etc. and some developing countries like China, India, and Brazil etc. have already understood the energy values and its future fortune but a lot of developing countries are not giving importance to renewable and sustainable energy. Since non-renewable energy sources, e.g. petroleum and natural gas mainly, are depleting at the unbelievable fast rate and it also causes the serious concern to carbon emission therefore most of the countries have diverted to renewable energy. Renewable energy sources are wide, including wind energy, tidal energy, solar energy, hydropower, biomass etc. Out of all the renewable energy resources, only biomass is the renewable energy resource which provides sustainable carbon source for the production of transportation fuel[1,2]. For the production of bio-oil from biomass, there are several routes such as pyrolysis, liquefaction, catalytic liquefaction and catalytic pyrolysis[3].

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After pyrolysis of biomass, bio-oil forms and it is a mixture of hundreds of small-small compounds in functional groups, such as sugars, alcohols, esters, acids, ketones, furans, aldehydes and ethers etc[3–7]. Since the bio-oils have a lot of oxygenates which in turn degrades its quality as fuel therefore it needs to be upgraded. Hydrodeoxygenation[8,9] is an important route for hydrogenation of the molecule and getting rid of the oxygen atoms as well. Unlike other deoxygenation route such as decarboxylation and decarbonylation, hydrodeoxygenation doesn't let molecule's carbon atom separate as in the form of product which associates carbon and oxygen both as well. Decarboxylation forms the CO_2 in the product whereas decarbonylation forms CO in the product[10].

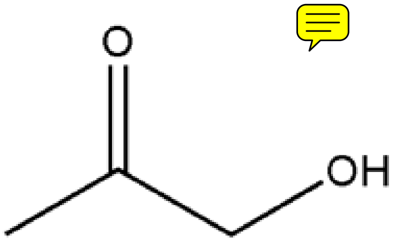

Figure 1. Structure of 1-hydroxypropan-2-one.

1-hydroxypropan-2-one is an important bio-oil compound obtained after fast pyrolysis of biomass. It is also known as hydroxyacetone or acetoland it comes under ketones functional group in the bio-oil. (We'll use 1-hydroxyprpan-2-one as acetol in this article). Zhe Tang et al. have studied the bio-oil upgrading from various means including esterification, hydrotreatment and cracking. They have taken the crude bio-oil into acids, esters, phenols, aldehydes, ketones and others. In this study acetol percentage in the crude bio-oil is 2.8 %[4].

Acetol has two oxygen atoms which lowers its stability in bio-oil and therefore the oxygen atom removal process becomes necessary so that it can be stable and will be more valuable product. For removal of oxygen atoms along with hydrogen attached with this, i.e. the hydroxyl group, we usually introduce additional hydrogen molecule (H_2) to hydrogenate the hydroxyl group and get it as water molecule. Then hydrogenation of another oxygen atom which is having pi bonding with the carbon, requires two molecule of H_2, first H_2 to make it sigma bond and make oxygen atom as hydroxyl group followed by introduction of another H_2 molecule to dehydrate the hydroxyl group as water and the final product would be propane, which is very useful in LPG (liquefied petroleum gas) for cooking. However, in this study we have taken only one hydrogenation reaction and the intermediate we have got as acetone and water. Acetone is also a very useful chemical as laboratory perspective.

2. Computational Details

Transition state optimization for the transition state structure has been done with M06-2X[11] functional of density functional theory[12,13] with the basis set of 6-31+g(d,p)[14]. M06-2X functional is a density functional theory functional and comes under Minnesota functional of 06 family. In the basis set used for transition state optimization has been packaged with special diffuse and polarization function to predict an accurate structure. 1-hydroxypropan-2-one (R1) and hydrogen molecule (R2) are taken as the reactant, acetone and water molecule are taken as product fragment and third fragment is for the "guess structure" of transition state using QST3 keyword in Gaussian 09 and Gauss View software package to get the transition state. QST stands for quadratic synchronous transit search operation and the integer number shows that how much fragment or interface of Gauss View is required to apply the keyword. After getting a transition state structure, a normal mode vibrational frequency calculation has been ran for recognizing and affirming the transition state at the same level of theory as of transition state optimization theory. Vibrational frequency results also provides the thermochemistry required for the reaction, e.g. enthalpy, entropy, Gibbs free energy etc. An imaginary frequency affirms the transition state structure from optimization calculation, as the actual transition state structure. Now to link the transition state with its two minima in both directions, also known as the reactant and product, an intrinsic reaction coordinate (IRC) calculation has been carried out at the same level of theory, i.e. M06-2X/6-31+g(d,p). This IRC calculation connects the transition state with actual reactant and product, and by IRC calculation, the transition state structure gets confirmed once again that this transition state is the one which connects the actual reactant and product otherwise by vibrational frequency calculation, only transition state can be confirmed but a potential energy surface (PES) might have a lot of transition states. After getting the reactant and product structure, another vibrational frequency calculation has been ran just to be assured that the structure gotten, is a stationary point at equilibrium and getting zero imaginary frequency in both structure's vibrational frequency calculation thus confirms them as the minima. To get an accurate energetics of reactant, product and transition state, a single point energy (SPE) has been carried out at B3LYP functional[15] with 6-311+g(d,p)[16] on optimized geometries therefore whole keyword for single point energy (SPE) in this case would be B3LYP/6-311+g(d,p)//M06-2X/6-31+g(d,p). All the calculations have been performed using Gaussian 09[17] and Gauss View 5[18].

3. Result and Discussion

In this theoretical study we have investigated the hydrogenation reaction of acetol to make it as acetone and water molecules by M06-2X density functional theory (DFT) functional with the basis set of 6-31+g(d,p). Figure 2, represents the reactants structure, R1 as aceol and R2 as hydrogen. Figure 3, represents the transition state structure and Figure 4 represents the intermediate and product structures. All the distances in the Figure 2, 3 and 4 are in angstroms. Table 1 contains the energies of all the species involved in the reaction. E_T is the total energy of the species as the sum of electronic energy and zero point energy (ZPE). E_{Rel} is the total relative energy of the species with respect to the reactant's energy and SPE_{Rel} is the single point relative energy with respect to the reactant's energy at B3LYP/6-311+g(d,p) level of theory on the optimized geometry of M06-2X/6-31+g(d,p) level of theory. In this section we'll have two sub-sections as following:

3.1 M06-2X/6-31+g(d,p)

As we can see in Figure 2, R1 is 1-hydroxypropan-2-one and R2 is hydrogen molecule in optimized state. All the bonding details in the Figure 2, are in angstroms. These two reactant molecules are put in specified proper atomic distances so that it could find the saddle point in between the reaction coordinate. Transition state optimization has been performed at the aforementioned level of theory, i.e. M06-2X/6-

31+g(d,p). In the basis set, we have included the diffuse and polarisation function to predict a good transition state in potential energy surface (PES). As we can see in the Figure 3, the transition state for the reaction. This transition state structure must be having the highest energy pint in the minimum energy path and this structure would be connecting the other two minima in both directions as reactant and product. Hydrogenation reaction (introduction of H-H molecule) upon acetol cleaves the C-O sigma bond to form another sigma bond with one hydrogen atom to saturate it as acetone and other hydrogen atom to saturate the separate water molecule. If we focus our attention to hydrogen atoms of R2 then we can find that those two hydrogen atoms are not attached to any atoms but free in space with some specified distances and since we know that if the bonding distances are excess of the equilibrium bonding distance then that molecule's energy would go higher.

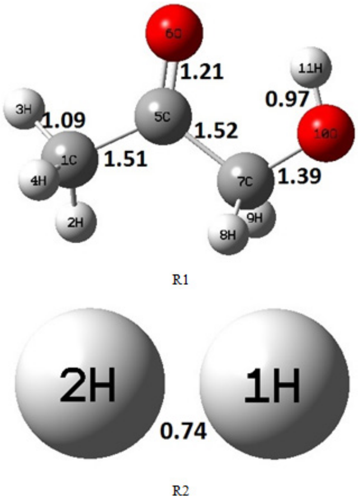

Figure 2. R1 and R2 structural details. All distances are in angstroms.

Like wise in the Figure 3, the distance between the two hydrogen atoms is 1.24 Å while it should be ~0.75 Å at the equilibrium bond distance. See the Figure 2, R2 has the distance of 0.74 Å between two hydrogen atoms at equilibrium.

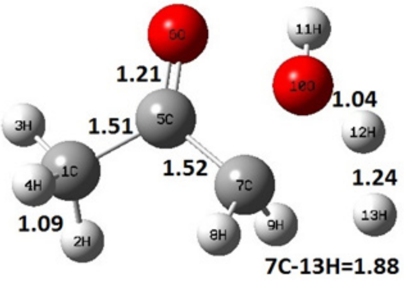

Figure 3. Transition state structure details. All distances are in angstroms.

Figure 5, contains the intermediate and the product. The hydrogen molecule in the intermediate attacks the hydroxyl group of acetol compound thus forming the water and acetone as products.

Table 1. Energy of the species from basic optimization theory, i.e. M06-2X/6-31+g(d,p) and single point energy by B3LYP/6-311+g(d,p)//M06-2X/6-31+g(d,p)

Species	**E_T (E+ZPE) (hartrees)**	**E_{Rel}(kcal/mol)**	**SPE_{Rel} (kcal/mol)**
R=R1+R2	-269.332	0	0
IM	-269.33	1.25	-0.25
TS	-269.175	98.52	93.12
P	-269.37	-23.85	-29.68

The distance of C = O pi bond in both the structure has the deviation of 0.01 Å and except this distance no other, non-reacting atom, bonding distances are deviating. As Table 1, predicts that reactants would require 1.25 kcal/mol of energy

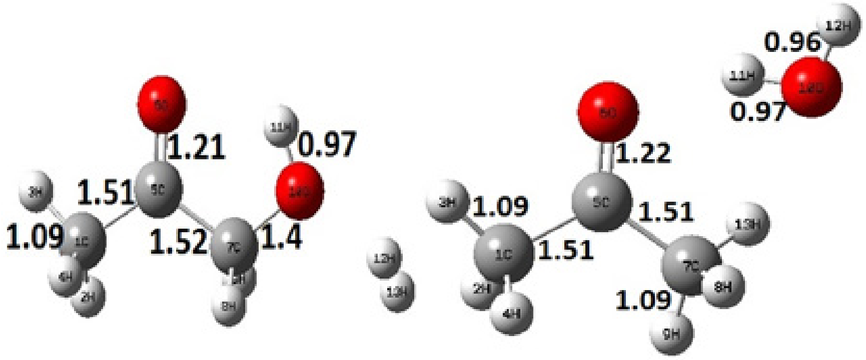

Figure 4. Structure of intermediate (acetol and hydrogen) and product (acetone and water molecule). All distances are in angstroms.

to come into the intermediate state for M06-2X/6-31+g(d,p) level of theory while for SPE by B3LYP/6-311+g(d,p)//M06-2X/6-31+g(d,p) level of theory, we will have to extract out 0.25 kcal/mol of energy to form the reactant as the intermediate structure.

3.2 Reaction Pathway

The Figure 5, shows the reaction pathways for the hydrogenation reaction of acetol to form the acetone and water as the product. There are two pathways, the black colour pathway's energies are from the basic optimization theory, i.e. M06-2X/6-31+g(d,p) while the green colour pathway's energies are from the single point energies at the B3LYP/6-311+g(d,p) level of theory on the optimized geometry by M06-2X/6-31+g(d,p) level of theory.

As we can see that, the total energies of R1 and R2 are kept as the zero kcal/mol for reference to the other specie's energies. If we follow the black colour pathway then we would be required to add 1.25 kcal/mol energy to form the reactant as the intermediate from where it will start to react while for green colour pathway is exothermic at first, that is, we'd be required to extract the 0.25 kcal/mol energy to form the reactant state to intermediate. Now from intermediate, the rate determining step is requiring

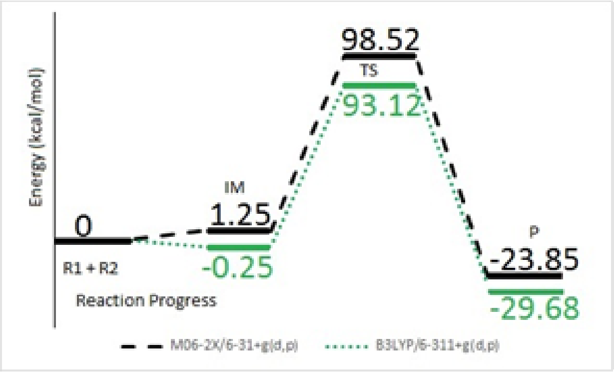

Figure 5. Reaction pathway for the hydrogenation reaction of acetol to form acetone and water. All energies are in kcal/mol.

97.27 kcal/mol and 93.37kcal/mol energy to surpass the barrier height for black colour and green colour pathway respectively. Here the attention should be paid at the green colour pathway, i.e. B3LYP/6-311+g(d,p)//M06-2X/6-31+g(d,p) energy pathway. The green colour pathway is requiring less amount of energy to cross the barrier height comparatively to black colour pathway, thus the green colour pathway should be favourable.

4. Conclusion

The hydrogenation reaction on 1-hydroxypropan-2-one has been studied using density functional theory (DFT). Acetone and water molecule have been found to be the product after one hydrogenation reaction. M06-2X functional of density functional theory with 6-31+g(d,p) basis set has been employed to optimize the transition state, to predict the thermochemistry by calculating the normal mode vibrational frequency and the same functional has been used to find out the reaction pathway.

Reaction pathway suggests that the basic optimization theory, M06-2X/6-31+g(d,p) predicts the higher barrier height while B3LYP/6-311+g(d,p)//M06-2X/6-31+g(d,p) predicts he lower barrier height comparing to the basic optimization theory. This phenomenon can be explained and understood by the level of theory. Since optimization theory is not using the diffuse function in the basis set and the functional is M06-2X, which is good at the prediction of the barrier height but associated with less quality basis set. This only can't be the sole explanation to this phenomenon but holds good place to explain. 97.27 kcal/mol of energy is required to surpass the barrier height from the basic optimization theory and lead to the products, combining acetone and water, which are showing -23.85 kcal/mol of energy with respect to the reactant's energy while green colour pathway requires only 93.37 kcal/mol of energy to surpass the barrier height and links with the products having combined energy of -29.68 kcal/mol with respect to the reactant's energy.

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