DFT STUDY ON HYDROGENATION REACTION OF ACETALDEHYDE TO ETHANOL IN GAS AND WATER PHASE

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Abstract
Numerical investigation of hydrogenation reaction of acetaldehyde to ethyl alcohol has been done in two phases, i.e. gaseous and aqueous phase separately using Gaussian 09 software package. For aqueous phase calculations, solvation approach has been taken and applied SMD model with water as solvent. Geometries were optimized at B3LYP functional of density functional theory (DFT) with the basis set of 6-31g(d) in both the phases. An imaginary frequency in frequency calculation result affirms the transition state. For getting an optimized structures of reactant and product, intrinsic reaction coordinate (IRC) calculation is carried out on the transition state structure at the same level of theory, in both phases. IRC connects the both minima in both forward and backward directions linking with transition state structure. Single point energy (SPE) has been calculated to get more accurate values of the optimized structures of reactant, product and transition state in both phases, i.e., gas and water at CCSD/6-311+g(3df,2p) theory.

Keywords: Acetaldehyde, Ethyl Alcohol, Solvation, DFT, B3LYP, Reaction Pathway

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1. INTRODUCTION

In recent years, energy demand has been increased since increased demand by developing nations and constantly increasing population. To accommodate the energy demand among all in proper proportion, relying on fossil fuel might not be a good idea since fossil fuels are also depleting very fast and causing environmental concerns. Therefore in this scenario, one has to go for renewable energy resource, like wind energy, solar energy, tidal energy, hydro power, biomass etc. Out of all above renewable energy resources, biomass is the only renewable energy resource which provides sustainable carbon for transportation fuel. Gasification, pyrolysis and liquefaction, and hydrolysis are the main routes to transform biomass into bio-oil [1]. Raw bio-oil from fast pyrolysis has been reported to contain more than 300 hundred of compounds and the bio-oil produced from biomass happens to have many oxy-functionals which degrades its quality as transportation fuel [2]. Due to many oxy-functionals in bio-oil after pyrolysis, it comes with many disadvantages including low heating value, low pH, low carbon and high oxygen content, less stability etc. [1, 3]. Therefore it needs to be channelized through upgradation processes. The current status of upgradation of bio-oil has been reviewed recently [4, 5, 6].

Acetaldehyde is an important bio-oil compound which comes under aldehyde catalogue of bio-oil. Guo et al. [7] performed the pyrolysis bio-oil experimentally and found that acetaldehyde is an integral part of aldehyde category of biomass and it is present in 1.72 wt. % in pine sawdust derived bio-oil. Guo et al. [8] repeated the experiments for the characterization of rice husk derived bio-oil and in this experiment acetaldehyde was found to be in 3.58 wt. %. Therefore acetaldehyde can be considered as a promising model compound to represent the aldehyde catalogue of bio-oil.

In the early days acetaldehyde has been produced by the dehydrogenation and selective oxidation of ethanol to produce hydrogen. Zaccheria et al. [9] produced acetaldehyde by dehydrogenation of ethanol over Cu catalysts and Santacesaria et al. [10] produced acetaldehyde by selective oxidation of ethanol over V_2O_5/TiO_2-SiO_2 catalysts. Recently Elena et al. [11] performed selective oxidation of acetaldehyde over Au-Cu catalysts. Since the first generation bio-fuels involve ethanol as the primary source for transportation fuel, the process has been reversed now. As we have discussed that pyrolysis derived bio-oil contains acetaldehyde in good weight percentage therefore the process of getting ethanol can be done by hydrogenation of acetaldehyde. Logsdon et al. [12] in one of his patent discussed about the hydrogenation of acetaldehyde and its catalytic effects. They reported that most of hydrogenation catalysts such as nickel, copper chormite, cobalt compounds etc. exhibit less selectivity than the required one. Burch and Petch [13] reported the hydrogenation of acetaldehyde over pure rhodium and iron oxide promoted rhodium. They concluded that pure rhodium acts as a poor catalyst whereas iron oxide promoted rhodium catalysts shows an excellent behavior as more active and selective. Feng et al. [14] performed the hydrogenation of bio-oil compounds and related aldehyde compounds using homogeneous catalyst, $RuCl_2(PPh_3)_3$. They concluded that acetaldehyde is more reactive and can easily be converted to ethanol by

hydrogenation than furfural and vanillin under mild conditions of 70 °C, 2.3 MPa and 3 hr. Qingsen et al. [15] performed mechanistic study of hydrogenation reaction of acetaldehyde over Au(111) catalyst and reported hydroxyethyl as the key intermediate product for the hydrogenation of acetaldehyde. Throughout the literature review, authors have not found any literature regarding the solvation study of hydrogenation of acetaldehyde therefore in this study, acetaldehyde has been considered as the model compound and numerically carried out the hydrogenation reaction to transform it into ethyl alcohol in the gas phase and aqueous phase using Gaussian 09 [16] and Gauss View 5 [17] software packages.

2. COMPUTATIONAL DETAILS

Geometries and transition state optimization have been carried out for both phases by B3LYP (Becke 3-parameter Lee-Yang-Parr) functional [18] of density functional theory (DFT) [19-20] using 6-31g(d) basis set [21-22]. To recognize and affirm the transition state structure, a normal mode vibrational frequency calculation has been performed by the same level of theory for both phases. An imaginary frequency has been found out in normal mode vibrational frequency calculation and therefore it confirms the structure as an actual transition state structure. To link the highest energy state to the minima, an IRC calculation has been carried out in both phases at the same level of theory as of the transition state optimization and normal mode vibrational frequency calculation. Two minima in each direction of transition state have been obtained as the reactant and product. Another normal mode vibrational frequency calculation has been performed to ensure that the structures of reactant and product are the true minima and by obtaining zero imaginary frequency, ensures the structures as the true minima. Since the energy from optimization theory happens not to be that accurate as it should be therefore an additional single point energy (SPE) calculation has been carried out on each stationary points. SPE has been performed at CCSD/6-311+g(3df,2p)//B3LYP/6-31g(d) level of theory in both the media, i.e., gaseous and aqueous phases [23-24]. To accommodate the aqueous phase calculation, solvation model has been employed. SMD model has been taken as the solvation model and water as solvent to put the aqueous nature [25].

3. RESULTS AND DISCUSSION

Acetaldehyde to ethyl alcohol reaction results have been separated in two sections as gaseous phase section and aqueous phase section for ease in discussion. Gaseous phase calculation results are as follows:

3.1 Phase behavior

3.1.1 Gaseous Phase

The reaction between acetaldehyde and hydrogen forms ethyl alcohol, has been studied in gaseous phase by quantum chemical simulations. Figure 1 represents the structural details of the gas phase reaction of acetaldehyde to ethyl

alcohol reaction. In Figure 1, R1 and R2 corresponds to acetaldehyde and hydrogen respectively, IM shows the intermediate, TS stands for transition state and P is showing the product details. All the bonding parameters are in angstroms.
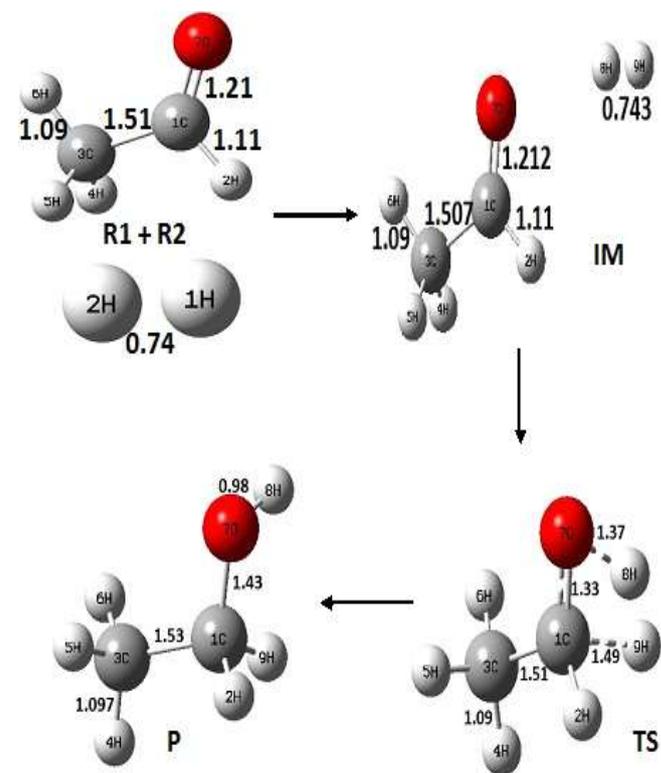

Fig -1: Structural details of R1 and R2, IM, TS and P. All bonding distances are in Å.

R1 and R2, i.e., acetaldehyde and hydrogen are in ground state and in intermediate, IM, acetaldehyde and hydrogen are at the proper bonding distances from which the reaction is about to start. One can see that in IM, the C=O and H-H bonding distances are distorted from R1 and R2 because C=O is the site where H-H is going to attack. In transition state, TS, one can clearly see that one hydrogen atom is attacking oxygen atom of C=O and other hydrogen on C of C=O. C=O bond length has been stretched out at 1.33 Å in TS from 1.212 Å in IM. Although the C=O bond in TS is not proper pi bond but in the broken condition because transition state shows highest energy in minimum energy path and whenever the bond lengths shortens or lengthens from its equilibrium length, the energy of that molecule goes high. The transition state here has been confirmed by running a normal mode vibrational frequency calculation and an imaginary frequency in the frequency result certifies the structure as an actual transition state. Product, P, can be clearly seen as an optimized geometry of ethyl alcohol. 8H and 9H of H-H have made the sigma bond with oxygen and carbon atom of C=O bond after the reaction. All the minima are also affirmed by running vibrational frequency calculation and zero imaginary frequency affirms the structures as true minima. Reaction progress in the Figure 1 is going in clockwise in order of arrows.

3.1.2 Aqueous Phase

The hydrogenation reaction of acetaldehyde to ethyl alcohol in aqueous phase has been discussed in this subsection. The reactants, intermediate, transition state and product structure with their bonding details are represented in Figure 2.
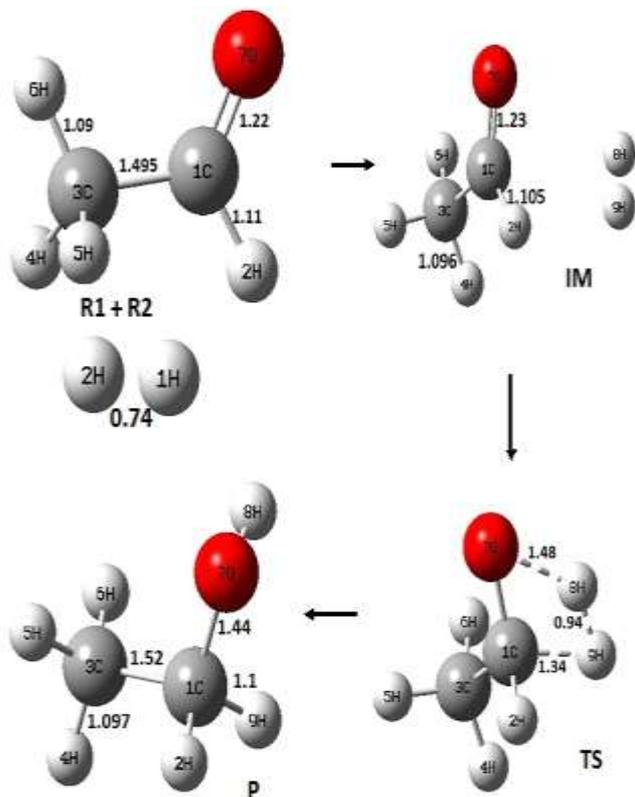
Fig -2: Bonding details of acetaldehyde (R1), hydrogen (R2), intermediate (IM), transition state (TS), and product (P).

To introduce aqueous phase environment, we have applied solvation model in Gaussian 09 using SMD solvation model and water as solvent. The dielectric constant value for water is kept as 78.3553 as in the default given by Gaussian package.

The structural details are given in Figure 2 where one can see that R1 and R2 are forming an intermediate (IM) which goes to the first order saddle point followed by the minima which is nothing but the product, ethyl alcohol. The transition state here has been affirmed by running a normal mode vibrational frequency calculation and an imaginary frequency in the frequency result certifies the structure as an actual transition state. All the minima are also affirmed by running vibrational frequency calculation and zero imaginary frequency affirms the structures as true minima. The C-C sigma bond distance is 1.51 Å in gas phase whereas in the aqueous phase it happens to be 1.495 Å. Similarly in the product also the C-C bond length is 1.53 Å and 1.52 Å in gas phase and aqueous phase respectively. The similar trend of the reaction progress has been followed in the aqueous phase compared to the gas phase but the structures differ in the energies.

Single point energies of the structure at the CCSD/6-311+g(3df, 2p)//B3LYP/6-31g(d) level of theory are given in the Table 1 for both phases, i.e., gaseous phase and aqueous phase. Two types of energies are given in the Table 1, first E_T is the total energy corresponding to the respective structure and E_T(Rel) which are the energies of the structures relative to the reactants' energy.

Table -1: Single point energies of structure are given in kcal/mol at the CCSD/6-311+g(3df, 2p)//B3LYP/6-31g(d) level of theory. E_T shows the total energy whereas E_T (Rel) shows the relative energy to the reactants' energy.
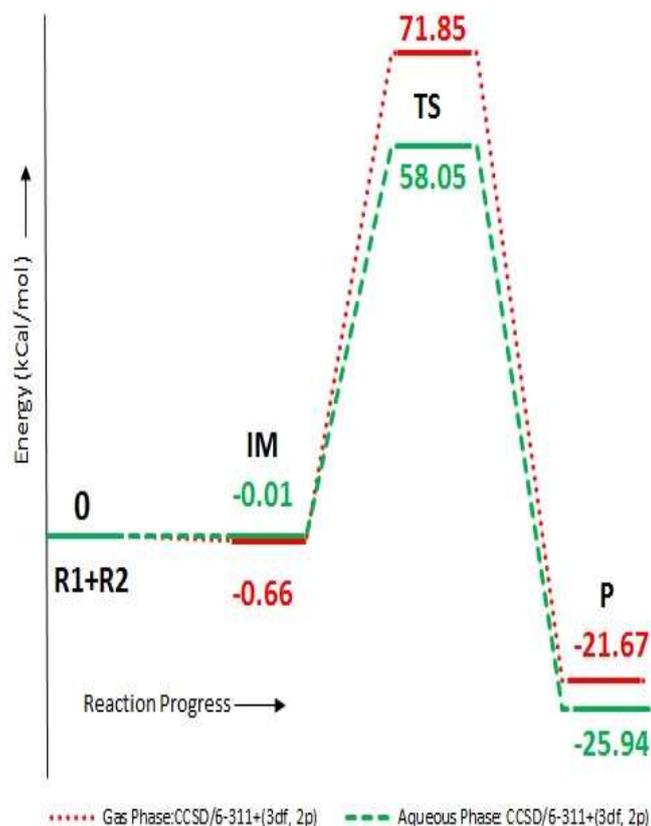
Species	Gas Phase		Aqueous Phase	
	E_T	E_T(Rel)	E_T	E_T(Rel)
R1+R2	-97094.33	0	-97096.19	0
IM	-97094.99	-0.66	-97096.2	-0.01
TS	-97022.48	71.85	-97038.14	58.05
P	-97116	-21.67	-97122.13	-25.94

As we can see in the Table 1 that gas phase intermediate's SPE is -0.66 kcal/mol with respect to the sum of energies of R1 and R2 whereas in aqueous phase this energy requirement is only -0.01 kcal/mol with respect to the reactants' energy. Similarly the deviation can be seen in the case of transition states and products also. But the main focus point is the transition state which plays a vital role in prediction of the activation energy. The gas phase transition state structure shows the energy of 71.85 kcal/mol whereas the aqueous phase shows 58.05 kcal/mol.

3.2 Reaction Pathways

The reaction pathways of acetaldehyde to ethyl alcohol reaction are in Figure 3 for both the phases, i.e., gas phase and aqueous phase. All the energies except R1 + R2, are relative energy to the reactants' energy. R1 and R2 are the first and second reactant, IM is the intermediate, TS is transition state and P's are product. The green colour pathway (dashed line) corresponds to the energies from aqueous phase whereas black colour pathway (dotted line) corresponds to the energies at the gas phase. All the single point energies are calculated at CCSD/6-311+g(3df,2p)//B3LYP/6-31g(d) level of theory.

Hydrogenation reaction of acetaldehyde which leads to form the ethyl alcohol is an exothermic reaction and to reach the intermediate structure it loses energy by -0.01 and -0.66 kcal/mol for aqueous phase and gas phase respectively. The reaction profile or minimum energy path says that reactants first form the intermediate then goes to the transition state followed by the formation of product.

Fig -3: Reaction pathways of acetaldehyde to ethyl alcohol reaction for gas phase and aqueous phase. All energies are single point energies in kcal/mol at CCSD/6-311+g(3df, 2p)//B3LYP/6-31g(d) level of theory.

The activation energy for the gas phase reaction is obtained as 71.86 kcal/mol whereas the aqueous phase offers this activation energy as only 58.71 kcal/mol. Thus one can objectify that hydrogenation reaction of acetaldehyde is favorable in aqueous phase comparing to gas phase reaction. Since we have not done the thermochemistry study of this reaction so that we cannot tell exactly how much exothermic is this reaction but from a glance to the above reaction profile (Figure 3), one can easily predict that both phase reactions are exothermic reaction.

4. CONCLUSIONS

DFT study on the hydrogenation reaction of acetaldehyde in two phases has been carried out in this paper with B3LYP/6-31g(d) level of theory and SPE with CCSD/6-311+g (3df, 2p) level of theory. The conclusions to this study are: 1) hydrogenation reaction of acetaldehyde yielding ethanol is an exothermic reaction in both gas and aqueous phase. 2) In both phases the reaction progress of hydrogenation reaction of acetaldehyde is same. 3) Aqueous phase offers less activation energy (58.71 kcal/mol) than the gas phase (71.86 kcal/mol). 4) Both reactions lose energy to form the intermediate.

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