

Theoretical Study on Gaseous Hydrogenation Reaction of Crotonaldehyde

Yonglun Tang

Anhui Technical College of Industry and Economy, Hefei 230051, China
 hefeitt@163.com

On the basis of quantum chemistry calculations, gaseous reactions including molecular and atomic hydrogenation of crotonaldehyde have been systematically examined in this paper. Firstly, the structures of initial states, transition states and final states along each reaction pathway were completely optimized at the level of B3LYP/6-31G (d, p) and PW91/6-31G (d, p). The total energies were adjusted by zero-point energy correction, and the obtained activation energies were compared with those of more accurate calculation method of CBS-APNO. Through comparing the results obtained from B3LYP, PW91 and CBS-APNO, it was found that the data from B3LYP are closer to those of CBS-APNO. Moreover, both the molecular and atomic hydrogenation reactions of crotonaldehyde are exothermic and the heat effect of C=C is higher than that of C=O, indicating that both H₂ and H prefer to attack C=C double bond, resulting in the formation of butaldehyde or free radical. On the other hand, from the viewpoint of dynamics, the difference of activation barriers between C=C and C=O in the reaction of molecular hydrogenation is very small while the barrier of C=C atomic hydrogenation is pronounced lower than that of C=O. Comparing with the results of acrolein hydrogenation, C=C hydrogenation can be hindered by introducing heavy end groups because of the steric effect. Finally, through comparing the mechanisms of hydrogenation reactions of the isolated C=C (in propene) and C=O (in formaldehyde), the conjugate effect is revealed in which the difference in kinetics between C=C and C=O hydrogenation of crotonaldehyde is greatly decreased. Thus, it is reasonable to design a rational catalyst that the selectivity can be favorably controlled.

1. Introduction

As important industrial raw materials and intermediates (Baillie et al., 2001), α , β -unsaturated alcohols have a wide range of applications in the fields of chemical production, organic synthesis etc, which is usually synthesized by the selective hydrogenation of α , β -unsaturated aldehyde. The α , β -unsaturated aldehydes have both C=O and C=C double bonds (Bi et al., 2010). However, on the surface of most catalysts, C=C double bonds are more prone to be hydrogenated than C=O from both thermodynamic and kinetic points of view, leading to the main product of saturated aldehyde (Breen et al., 2004). In recent years, researchers have devoted to seek the selective hydrogenation catalysts for acquiring α , β -unsaturated alcohols. Precious metal catalysts, such as Pt (Bus et al., 2007), Au (Delbecq and Sautet, 2002), and Ir, can effectively improve the selectivity of C=O during the hydrogenation process of α , β -unsaturated aldehydes (Gebauer-Henke et al., 2007). Due to more economic, employment of theoretical calculations for the design of an effective catalyst and the investigation on reaction mechanism has a great advantage over experiment (Kennedy et al., 2014). For example, Delbecq and Sautet (1995) have concluded the most favorable adsorption surface for hydrogenation of C=O bond via the calculations of α , β -unsaturated aldehydes adsorption on Pt surfaces. Although hydrogenation reactions of α , β -unsaturated aldehyde are mostly catalyzed by heterogeneous catalysis, its catalytic mechanism is still in controversy, thus the catalysts still need to be optimized (Luza et al., 2017). Obviously, it would be helpful for understanding the heterogeneous catalytic hydrogenation process of α , β -unsaturated aldehydes through investigation of gaseous hydrogenation. For example, Li et al., (2008) have explored the mechanism of gaseous hydrogenation of acrolein by density functional theory. Using quantum chemistry calculations, all the possible reaction channels for the hydrogenation of crotonaldehyde with hydrogen molecule (hereinafter referred to as molecular hydrogenation) and hydrogen

atom (atomic hydrogenation) as well as the structures and energies of each stationary point along the channels were systematically investigated. By comparing the hydrogenation mechanisms of formaldehyde and propylene, the effect of conjugation effect was summarized. Further by comparing the results of hydrogenation with acrolein, the effect of steric hindrance on the reaction was revealed. We expect our results would offer some hints to the hydrogenation mechanism catalyzed by the catalyst surface.

2. Computational Methods

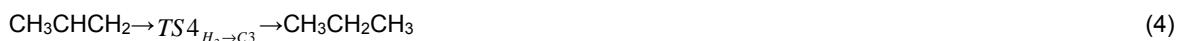
All the calculations were carried out by using the Gaussian 09 package. First, the reactants, transition states and products of the crotonaldehyde hydrogenation reaction system were optimized by using the 6-31G (d, p) basis set at the B3LYP, PW91 and CBS-APNO levels of theory (Mäki-Arvela et al., 2005). The correctness of the structures was verified by the frequency calculations (reactants and products have no imaginary frequencies while transition state has only one imaginary frequency). Then, the correlation between the reactants, the transition states and the products in each channel was verified by the intrinsic reaction coordinate calculation (IRC). Among the three methods, CBS-APNO has the highest accuracy because it uses a QCISD/6-31G (d, p) optimized geometrical structure to perform a higher level of single point energy correction, resulting in an absolute mean deviation of less than 0.5 kcal/mol (Marinelli et al., 1995). Thus, the CBS-APNO results can be used as a benchmark for other methods. Our results showed that results from B3LYP level are very close to those of CBS-APNO. In fact, plenty of similar theoretical studies have revealed that B3LYP can achieve reasonable results with lower time-consuming (Mohr et al., 2003). Therefore, on the investigation of atomic hydrogenation of crotonaldehyde, only B3LYP results were reported. Note that all the structural diagrams in this paper are the results of B3LYP/6-31G (d, p) level.

3. Results and Discussion

3.1 Hydrogenation of Formaldehyde and Propylene

Because C=C and C=O double bonds are simultaneously existed in the crotonaldehyde molecule, the selectivity of hydrogenation reaction will be definitely affected by conjugation effect. Therefore, it is necessary to study the hydrogenation reactions of formaldehyde and propylene with the isolated C=O and C=C double (Ochterski et al., 1996) bonds before the study of hydrogenation reaction of crotonaldehyde.

Due to presence of the C=O double bond in formaldehyde, hydrogen can attack either C or O atom, leading to the product of methanol for molecular addition. Therefore, two transition states, named $TS1_{H_2 \rightarrow C}$ and $TS2_{H_2 \rightarrow O}$, are presented in the reaction of formaldehyde and hydrogen (Pettersson, et al., 1998). Likewise, in the reaction of propylene and hydrogen, hydrogen can also attack C2 or C3, producing the same product of propane. This reaction also has two different transition states ($TS3_{H_2 \rightarrow C2}$ and $TS4_{H_2 \rightarrow C3}$). The possible reaction channels are designed as follows (Reyes et al., 2002):



In Table 1, we list the total energies of all stationary points along hydrogenation reactions of formaldehyde and propylene. It can be seen that, at the level of CBS-APNO, the calculated energy barriers are 291.72, 400.79, 345.56 and 366.12 kJ/mol (Reye, et al., 2000) when the reactions experience the transition states of $TS1_{H_2 \rightarrow C}$, $TS2_{H_2 \rightarrow O}$, $TS3_{H_2 \rightarrow C2}$, $TS4_{H_2 \rightarrow C3}$, respectively. Note that these values are close to the corresponding results obtained at the B3LYP level (the difference is less than 5.4 kJ/mol except TS2), but deviate somewhat largely from those of PW91 (~ 29-99 kJ/mol). Moreover, the relative potential energy surface in the hydrogenation reaction is shown in Fig. 1. It can be intuitively seen that hydrogenation of formaldehyde releases heat of 74.80 kJ/mol while hydrogenation of propylene releases heat of 124.62 kJ/mol at the B3LYP level. Therefore, hydrogenation of C=C bond is more favorable than C=O bond from the viewpoint of thermodynamics, but the dynamic results are opposite.

Table 1: Energies of reaction complex (RC), transition states (TS) and products (P) in the hydrogenation reaction of formaldehyde and propylene.^a

		E(a.u.)			ZPE(a.u.)			ΔE (kJ/mol)		
		B3LYP	PW91	CBS-APNO	B3LYP	PW91	CBS-APNO	B3LYP	PW91	CBS-APNO
Channel s 1, 2	RC	-115.6837	-115.6314	-115.4989	0.0396	0.0390	0.0382	0	0	0
	P	-115.7240	-115.7240	-115.5449	0.0514	0.0514	0.0508	-74.80	-79.47	-87.64
	TS _{1H₂->c}	-115.5731	-115.5336	-115.3918	0.0423	0.0411	0.0422	297.16	262.50	291.72
	TS _{2H₂->o}	-115.5569	-115.5165	-115.3499	0.0405	0.0390	0.0419	335.01	301.52	400.79
Channel s 3, 4	RC	-119.0960	-119.0185	-118.8130	0.0918	0.0898	0.0887	0	0	0
	P	-119.1554	-119.0802	-118.8727	0.1037	0.1015	0.1009	-124.62	-131.58	-
	TS _{3H₂->c2}	-118.9651	-118.9026	-118.6825	0.0932	0.0913	0.0898	347.38	308.10	345.56
	TS _{4H₂->c3}	-118.9587	-118.8972	-118.6743	0.0925	0.0908	0.0894	362.33	320.99	366.12

^a Basis sets of 6-31G(d, p).

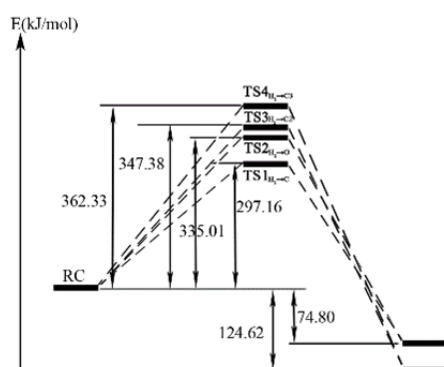


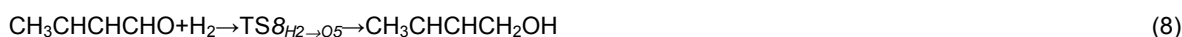
Figure 1: Relative energy difference diagram of reaction complex, transition states and products along hydrogenation reaction of formaldehyde and propylene

The reaction barrier of molecular hydrogenation of formaldehyde has been reported. At the same level of theory, the results are almost identical to us. In addition, we have also got the transition state of hydrogen attacking oxygen atom. In this process, the hydrogen molecule begins to dissociate firstly, at the same time two hydrogen atoms respectively approach to the C1 and O2 atoms. When the distance between H6 and C1 atoms is about 0.21 nm, H6 starts to shift slowly to C1 until the bond formation between H5 and O2. After that, the distance between H6 and C1 atoms is drastically reduced, and finally H6-C1 bond is formed.

3.2 Molecular Hydrogenation of Crotonaldehyde

There are four isomers of crotonaldehyde, i.e., E-trans-CH₃CHCHCHO, E-cis-CH₃CHCHCHO, Z-cis-CH₃CHCHCHO and Z-trans-CH₃CHCHCHO. We first optimized the geometrical structures for these four isomers at the B3LYP level. Results showed that relative to E-trans-CH₃CHCHCHO, the energy differences for E-cis-CH₃CHCHCHO, Z-cis-CH₃CHCHCHO and Z-trans-CH₃CHCHCHO are 5.69, 12.00 and 12.41 kJ/mol, respectively. According to the classical Boltzmann distribution, the magnitude ratio of four isomers at room temperature is 1: 0.101: 0.008: 0.007, meaning the proportion of E-trans-CH₃CHCHCHO is about 89.6%. Therefore, only E-trans-CH₃CHCHCHO was considered in the following.

Reaction Channel: The possible channels for the hydrogenation of crotonaldehyde are as follows:



Among these, channel (5) and (6) generate butyraldehyde as H₂ attacks C2 and C3 atoms, respectively; and channel (7) and (8) produce croton alcohol which is the result of H₂ attacking C4 and O5.

IRC Analysis: In order to verify the correctness of the reaction mechanism, the intrinsic reaction coordinates (IRC) calculations were performed.

$TS_{H_2 \rightarrow C_2}$ is formed by H₂ attacking C2, which connects the reaction complex of CH₃CHCHCHO and H₂ and the product of CH₃CH₂CH₂CHO. The variations of C2 = C3, C2-H13, C3-H12 and H12-H13 distances in the reaction process are shown in Fig. 2. As can be seen, the distance between H12 and H13 is increasing, eventually H-H bond is broken and the dissociated H atoms approach C3 and C2, respectively. With the progress of the reaction, the distance of C2-H13 gradually reduces, and finally forms the chemical bonding. Similar variation is found for the change of C3-H12, leading to the equal bond lengths of C2-H13 and C3-H12 finally. The distance of C2=C3 in this process gradually increases but the growth rate is relatively slow, and finally this bond changes into that having a single bond characteristic.

$TS_{H_2 \rightarrow C_3}$ is the transition state produced by H₂ attacking C3 of CH₃CHCHCHO. The variations of bond distances for C2=C3, C2-H13, C3-H12 and H12-H13 are essentially the same to those of $TS_{H_2 \rightarrow C_2}$ (Fig. 2).

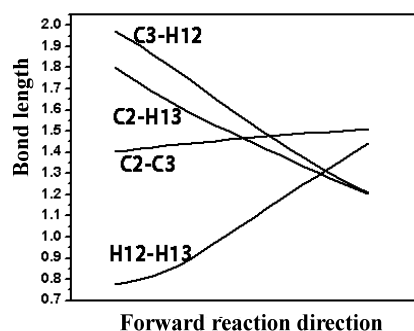


Figure 2: Variation of bond length on the progress of the reaction in channel 5 and 6

$TS_{H_2 \rightarrow C_4}$ links the reactant complex of CH₃CHCHCHO and H₂ and the product of crotonaldehyde in the process of H₂ attacking C4. During the reaction, C4=O5 double bond and H12-H13 single bond begin to break, at the same time, C4 is close to H12 and O5 approaches H13, leading to the bonds formation finally.

Similarly, $TS_{H_2 \rightarrow O_5}$ is the transition state of H₂ attacking O atom of C=O double bond in crotonaldehyde. In Fig. 3, we also plot the bond distances variations of C4=O5, C4-H12, O5-H13 and H12-H13. As is seen, with the reaction proceeding, H₂ begins to approach crotonaldehyde. When the distance of C4-H12 reaches 0.23 nm, the dissociation of H₂ happens, subsequently the distance of H12-H13 sharply increases. At this moment, H13 starts to attack O5, and the distance of C4-H12 keeps unchanged. After the bond formation for O5 and H13, distance is nearly unvaried. At this time H12 begins to close to C4, making the distance sharply reduce, and finally forms the chemical bond. Similar to the previous mentioned channels, the bond length of C4=O5 double bond grows slowly in the reaction process until the bond breaks and finally becomes a single bond.

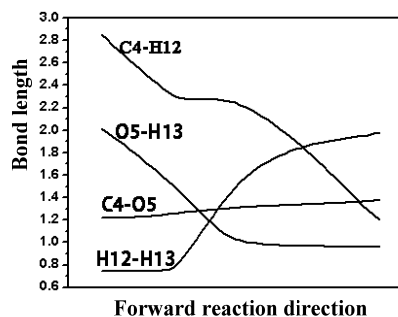


Figure 3: Variation of bond length on the progress of the reaction in channel 8

Potential Energy Profile of the Reaction:

The energy barriers of channels (5), (6), (7) and (8) were calculated to be 311.79, 390.23, 316.61 and 329.07 kJ/mol, respectively, at the B3LYP level. In comparison with CBS-APNO, it can be seen the results are very close. In contrast, the difference seems somewhat greater for PW91. At the meanwhile, free energies of the reaction were calculated at the level of CBS-APNO. Results show that the free energy of producing butyraldehyde is -76.8 kJ/mol, and the free energy of generating crotonol is -33.0 kJ/mol, which are in nice agreement with the corresponding experimental results (-70.8 and -30.6 kJ/mol for the production of butyraldehyde and crotonol, respectively). Thus, from both thermodynamics and dynamics points of view, C = C is easier to be hydrogenated than C=O.

Conjugation Effect on C=O Double Bond and C=C Double Bond:

By comparing the activation energies of C=O and C=C double bonds in the hydrogenation of formaldehyde, propylene and crotonaldehyde processes, the conjugation effect can be easily understood. Firstly, the heat release for C=C hydrogenation of crotonaldehyde is 52.10 kJ/mol more than that of C=O at the CBS-APNO level of theory. This value is increased by 15.02 kJ/mol compared with the difference between C=C hydrogenation of propylene and C=O hydrogenation of formaldehyde. Secondly, the activation energy difference between C=C and C=O double bond hydrogenation of crotonaldehyde is 0.05 kJ/mol, but the difference between C=C hydrogenation of propylene and C=O hydrogenation of formaldehyde is 53.84 kJ/mol. Therefore, the conjugation effect makes the energy barrier difference of C=C and C=O greatly reduce while the difference of hydrogenation heat is enhanced. This result indicates that by using catalysis of the catalyst, the selectivity can be effectively tuned by promoting activity of C=O hydrogenation while inhibiting C=C hydrogenation.

3.3 Atomic Hydrogenation of Crotonaldehyde

The mechanism of atomic hydrogenation catalyzed by the catalyst surface is different from that of the aforementioned molecular hydrogenation mechanism. Generally, H₂ is dissociated into H atoms firstly and then H is added stepwise to unsaturated atoms. Therefore, it is necessary to investigate the atomic hydrogenation in gas phase before understanding the mechanism on catalyst. As mentioned above, for the molecular hydrogenation system of crotonaldehyde, the results of B3LYP are more reliable and less time-consuming. So, for the atomic hydrogenation, we still use this level of theory.

The designed channel for the atomic hydrogenation of crotonaldehyde is as follows:



For channel (9), H atom attacks C2 to generate CH₃CH₂CHCHO radical. This process needs to surmount an activation energy of 6.79 kJ/mol; for channel (10), energy barrier of 8.64 kJ/mol is needed for H atom attacking C3, resulting in the product of CH₃CHCH₂CHO free radical; for channel (11), H atom attacks C4 to generate CH₃CHCHCH₂O free radical. This step needs to overcome the barrier of 20.83 kJ/mol; and for the channel (12), the activation energy is calculated to be 17.01 kJ/mol for H attacking O5 in which CH₃CHCHCHOH free radical is generated. Thus, the lowest activation energy is found in the channel (9), and meanwhile, the heat release is also the least. Therefore, among the four channels, H atom tends to follow the channel (9) to react with crotonaldehyde, that is, H attacks C2 to generate CH₃CH₂CHCHO free radical is most favorable.

Comparing with the molecular hydrogenation, the activation energy of atomic hydrogenation is relatively lower, but the difference in energy barrier between C=C and C=O is slightly increased. This result further indicates that the selectivity of C=C and C=O hydrogenation can be subtly controlled on the catalyst surface.

4. Conclusion

These results indicate that the selectivity of C=C and C=O hydrogenation can be tuned by using the catalyst. Through comparing the results obtained from B3LYP, PW91 and CBS-APNO, it was found the results of B3LYP are very close to those of more accurate method of CBS-APNO. In consideration of less time-

consuming for B3LYP, it was concluded B3LYP has the highest efficiency for gaseous hydrogenation of such an unsaturated aldehyde system.

Reference

- Baillie J.E., Abdullah H.A., Anderson J.A., Rochester C.H., Richardson N.V., Hodge N., Hutchings G.J., 2001, Hydrogenation of but-2-enal over supported Au/ZnO catalysts, *Physical Chemistry Chemical Physics*, 3(18), 4113-4121, DOI: 10.1039/b103880j
- Bi H.M., Xie P.T., Li Y., You F.Y., Hu J.P., 2010, Theoretical studies on the reaction mechanism of formaldehyde photocatalytic degradation, *Journal of Molecular Science*, 6, 010, DOI: 10.14233/ajchem.2013.13154
- Breen J.P., Burch R., Gomez-Lopez J., Griffin K., Hayes M., 2004, Steric effects in the selective hydrogenation of cinnamaldehyde to cinnamyl alcohol using an Ir/C catalyst, *Applied Catalysis A: General*, 268(1-2), 267-274, DOI: 10.1016/j.apcata.2004.04.002
- Bus E., Prins R., van Bokhoven J.A., 2007, Origin of the cluster-size effect in the hydrogenation of cinnamaldehyde over supported Au catalysts, *Catalysis Communications*, 8(9), 1397-1402, DOI: 10.1016/j.catcom.2006.11.040
- Delbecq F., Sautet P., 2002, A density functional study of adsorption structures of unsaturated aldehydes on Pt (111): A key factor for hydrogenation selectivity, *Journal of Catalysis*, 211(2), 398-406, DOI: 10.1006/jcat.2002.3744
- Delbecq F., Sautet P., 1995, Competitive C=C and C=O Adsorption of α - β -Unsaturated Aldehydes on Pt and Pd Surfaces in Relation with the Selectivity of Hydrogenation Reactions: A Theoretical Approach, *Journal of Catalysis*, 152(2), 217-236, DOI: 10.1006/jcat.1995.1077
- Gebauer-Henke E., Grams J., Szubiakiewicz E., Farbotko J., Touroude R., Rynkowski J., 2007, Pt/Ga₂O₃ catalysts of selective hydrogenation of crotonaldehyde, *Journal of Catalysis*, 250(2), 195-208, DOI: 10.1016/j.jcat.2007.06.021
- Kennedy G., Baker L.R., Somorjai G.A., 2014, Selective Amplification of C=O Bond Hydrogenation on Pt/TiO₂: Catalytic Reaction and Sum - Frequency Generation Vibrational Spectroscopy Studies of Crotonaldehyde Hydrogenation, *Angewandte Chemie*, 126(13), 3473-3476, DOI: 10.1002/ange.201400081
- Li Z., Chen Z.X., Kang G., He X., 2008, Hydrogenation of conjugated CC and CO bonds: Quantum chemical preview before metal catalysis, *Journal of Molecular Structure: THEOCHEM*, 870(1-3), 61-64, DOI: 10.1016/j.theochem.2008.09.003
- Luza L., Rambor C.P., Gual A., Alves Fernandes J., Eberhardt D., Dupont J., 2017, Revealing Hydrogenation Reaction Pathways on Naked Gold Nanoparticles, *ACS Catalysis*, 7(4), 2791-2799, DOI: 10.1021/acscatal.7b00391
- Mäki-Arvela P., Hájek J., Salmi T., Murzin D.Y., 2005, Chemoselective hydrogenation of carbonyl compounds over heterogeneous catalysts, *Applied Catalysis A: General*, 292, 1-49, DOI: 10.1016/j.apcata.2005.05.045
- Marinelli T.B.L.W., Nabuurs S., Ponc V., 1995, Activity and Selectivity in the Reactions of Substituted α , β -Unsaturated Aldehydes, *Journal of Catalysis*, 151(2), 431-438, DOI: 10.1006/jcat.1995.1045
- Mohr C., Hofmeister H., Radnik J., Claus P., 2003, Identification of active sites in gold-catalyzed hydrogenation of acrolein, *Journal of the American Chemical Society*, 125(7), 1905-1911, DOI: 10.1021/ja027321q
- Ochterski J.W., Petersson G.A., Montgomery Jr J.A., 1996, A complete basis set model chemistry. V. Extensions to six or more heavy atoms, *The Journal of chemical physics*, 104(7), 2598-2619, DOI: 10.1063/1.470985
- Petersson G.A., Malick D.K., Wilson W.G., Ochterski J.W., Montgomery Jr J.A., Frisch M.J., 1998, Calibration and comparison of the Gaussian-2, complete basis set, and density functional methods for computational thermochemistry, *The Journal of chemical physics*, 109(24), 10570-10579, DOI: 10.1063/1.477794
- Reyes P., Aguirre M.C., Melián-Cabrera I., Granados M.L., Fierro J.L.G., 2002, Interfacial properties of an Ir/TiO₂ system and their relevance in crotonaldehyde hydrogenation, *Journal of Catalysis*, 208(1), 229-237, DOI: 10.1006/jcat.2002.3566
- Reyes P., Aguirre M.D.C., Pecchi G., Fierro J.L.G., 2000, Crotonaldehyde hydrogenation on Ir supported catalysts, *Journal of Molecular Catalysis A: Chemical*, 164(1-2), 245-251, DOI: 10.1016/s1381-1169(00)00329-0