

Mechanism of Oxalic Acid Formation from Acetylene on Pt (111) Surface: A DFT Investigation

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The mechanism of electrochemical synthesis of oxalic acid from acetylene on Pt (111) surface has been comprehensively investigated using first-principles method based on density functional theory (DFT). The calculation results show that CHCH firstly react with OH to form CHCHOH, then, the product takes off hydrogen to form CHCHO. Next, CHCHO oxidize to obtain CHOCHO. During the process of CHOCOOH formation, CHOCHO firstly dehydrogenize to form CHOCO, then, CHOCO interact with OH to produce CHOCOOH. Finally, CHOCOOH dehydrogenize to form COCOOH, after that COCOOH react with OH to get COOHCOOH.

Keywords: Pt (111) surface, acetylene, oxalic acid, mechanism, density functional theory.

1. INTRODUCTION

Oxalic acid, as one of the simplest binary carboxylic acid, is widely used in rare earth element refining industry, textile industry, organic synthesis, and metal purification equipment and so on [1, 2]. Its dosage increases with the development of related industries [3]. Thus, its production method attracted much attention. The method of acetylene catalytic oxidation to oxalic acid was proposed as a new method to obtain oxalic acid.

There existed abundant researches on acetylene catalytic oxidation to form oxalic acid. Kearns et al. [4] found that oxalic acid could be quantificationally obtained by reaction of acetylene and nitric acid with argentum nitricum as catalyst. Li et al. [5] studied acetylene oxidation to generate oxalate through a bubbling reactor device. Menor-Salvan et al. [6] found that acetylene can transform into

glyoxal under water ice system and high vacuum ultraviolet radiation. The produced glyoxal is easily oxidized by hydroxyl radicals to form oxalate. Our group [7, 8] put forward prepared oxalic acid from acetylene by electrochemical method. The results show that this approach indeed can produce oxalic acid from acetylene, which yield a positive result but with a low production rate. Meanwhile, we obtained the reaction mechanism through polarization curves and electrochemical theory. The intermediates are mainly CHOHCHOH and CHOCHO . Increasing the acetylene concentration or reducing the acidity of the electrolytic system can improve the yield of oxalic acid. Herein we use the first principles calculation to study the reaction mechanism of acetylene oxidation to produce oxalic acid on Pt electrode surface and determine the best reaction path, which can provide theoretical guidance for the experiment through comparing the experimental and theoretical results.

With the rapid development of the computer technology, first principles have been widely applied in the actual simulation of chemical reactions. It not only can predict the configuration and energy of adsorbed molecules [9], but also can predict intermediates and determine the transition state [10], which are difficult to determine in experiments. So far, only the theoretical adsorption and reaction mechanism for acetylene have been reported. Medlin et al. [11] studied the adsorption mechanism of acetylene on platinum, palladium and other metal (111) surface and obtained the most stable adsorption structure by density functional theory. Lu et al. [12] comprehensively investigated the conversion mechanism of acetylene to ethynylidyne on Pt (111) surface by self-consistent periodic density functional theory. Nevertheless, there is no related report of reaction mechanism of acetylene oxidation to oxalic acid available yet. Thus, this work mainly study the reaction mechanism of the electrochemical synthesis of oxalic acid from acetylene on Pt electrode surface by first principles calculation, which can make people understanding the fundamental mechanisms and reaction pathways controlling acetylene conversion to oxalic acid and then guide future experimental efforts.

2. COMPUTATIONAL DETAILS

2.1. Surface Model.

In the surface calculation, the Pt (111) surface is cleaved from fcc crystal structure and is modeled by a four-atomic layer p (3×3) supercell with nine atoms at each layer. Meanwhile, a 15 Å vacuum slab is employed to separate the periodically repeated slabs. The bottom two layers are constrained at the bulk position to simulate the presence of a larger number of layers in real metal particles, whereas the upper two layers together with the adsorbed species are allowed to relax. The Pt (111)– (3×3) surface model are shown in Figure 1. There are four different adsorption sites: top, bridge and two kinds of hollow (namely fcc site and hcp site, where one atom is stacked on the second layer below fcc site whereas on the third layer for hcp site).

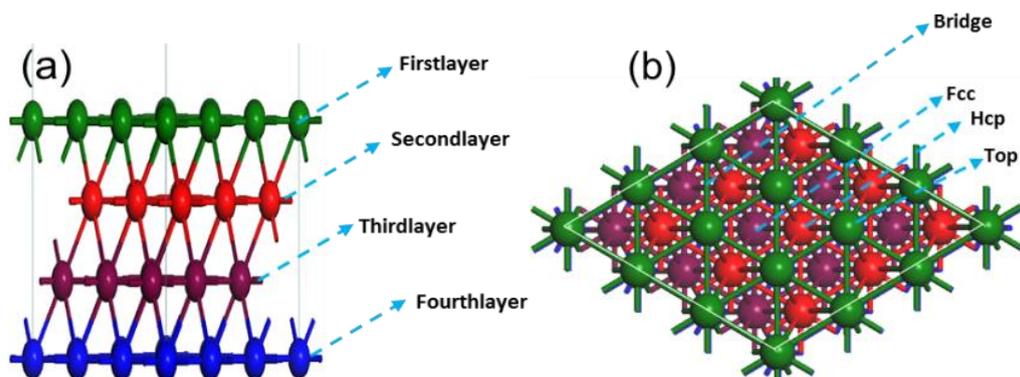


Figure 1. the adsorption configuration and adsorption position on the surface of Pt (111) surface (a: side view, b: top view).

2.2. Calculation Methods.

All of the calculations are performed by DMol³ module [13] in Material Studio developed by Accelrys Company. The geometry optimization, energy optimization are performed and the structural properties are obtained at the Generalized Gradient Approximation (GGA) level with the BLYP/DND method [14, 15]. The Double Numerical plus d-functions (DND) is chosen as the basis set, which is comparable to a Gaussian 6-31G* basis set [16]. The numerical basis set is much more accurate than a Gaussian basis set of the same size [17]. In the geometry optimization process, the convergence tolerance of energy is 1.0×10^{-5} Ha, maximum force is $0.002 \text{ Ha}/\text{\AA}$, and maximum displacement is 0.005 \AA . The smearing of electronic occupations is 0.005 Ha . The LST/QST method [18] is used to search transition states. The atom pairings are defined and 3D trajectory documents are created with Reaction Preview tool. After “transition state searching”, a transition state was found for each reaction, and harmonic vibration frequencies are calculated at the same level to insure that there is only one imaginary frequency in each transition state. Finally, the minimum energy paths (MEP) are calculated on the intrinsic reaction coordinates (IRC) theory. For purpose of proving the reliability of the selected adsorption model and calculation parameters, we calculate the parameters of bulk Pt and optimized acetylene molecule firstly. Calculation results show that the calculated parameter of bulk Pt is 3.958 \AA , which agrees well with the experimentally values (3.891 \AA) [19]. For the acetylene molecule, it is planar configuration with the C-C bond length of 1.21 \AA and C-H bond length of 1.09 \AA , which are in accordance with experimental results [20].

The adsorption energy of an adsorbate on the metallic surfaces (E_{ads}) was calculated according to the following equation:

$$E_{\text{ads}} = E_{\text{adsorbate/surface}} - (E_{\text{adsorbate}} + E_{\text{surface}})$$

Where $E_{\text{adsorbate/surface}}$ is the total energy of the system containing the metal surface with interacted adsorbate; $E_{\text{adsorbate}}$ and E_{surface} are the total energies of the adsorbates in vacuum and bare metal surface, respectively. A negative E_{ads} represents an exothermic process.

3. RESULTS AND DISCUSSION

3.1. The determination of calculation model

According to related reports, when acetylene adsorbed on Pt (111) surface at different coverage, all related parameters are quite closed despite the size of the slab model. In our calculation, the (1 x1), (2 x2), (3 x3), and (3 x4) surface models are considered. These four adsorption models are optimized and the corresponding adsorption energies are shown in Table 1.

Table 1. Adsorption energies of acetylene on different size of Pt (111) surface.

P(unit cell)	(1x1)	(2x2)	(3x3)	(3x4)
E_{ads} (eV)	0.773484	-2.42373	-2.48602	-2.47901

Table 1 shows the adsorption energies of acetylene on four slab models. Comparing the adsorption energy of the four slab models, we can conclude that slab model (2x2) is suitable in theory. However, the slab model (2x2) is too small for the calculation of adsorption mechanism of macromolecular system such as CHOCOOH, COOHCOOH. Therefore, considering both the feasibility and efficiency of the calculation, we choose the slab model (3x3) in the following calculations.

3.2 Adsorptions of Reactants and Possible Intermediates.

The adsorption energies and the key geometric parameters of various relevant species involved in the formation of COOHCOOH on Pt (111) surface are shown in Table 2.

Table 2. Adsorption energies and key geometric parameters for various relevant species involved in the formation of COOHCOOH on the Pt (111) surface

Species	E_{ads} (eV)	Adsorption Configuration	D_{Pt-x} (Å) Configuration	Bond	Length(Å)
CHCH	-2.381	parallel to surface	2.004	C-C C-H	1.396 1.092
OH	-0.079	O -bridge	2.204	O-H	0.985
O	-0.143	O- fcc	2.054	-	-
H ₂ O	-0.035	O-top	2.464	O-H	0.978
CHOCH	-0.135	parallel to surface	Pt-C:2.026 Pt-O:2.446	C-C C-O C-H	1.474 1.456 1.092
CHCHO	-0.165	O-bridge C-top	Pt-C:2.093 Pt-O:2.170	C-C C-O C-H	1.438 1.264 1.104

CHCHOH	-0.126	C-bridge	Pt-C:2.119/2.078 Pt-O:2.975	C-C C-O C-H	1.479 1.388 1.101
CHOCHO	-3.587	parallel to surface	Pt-C:2.625 Pt-O:2.232	C-C C-O C-H	1.450 1.280 1.101
CHOCO	-0.482	perpendicular to surface	Pt-C:1.986 Pt-O:2.228	C-C C-O C-H	1.500 1.238 1.105
CHOCHOH	-2.071	parallel to surface	Pt-C:2.162 Pt-O:2.961	C-C C-O O-H C-H	1.488 1.373/1.229 0.985 1.096
CHOCHOO	-2.022	parallel to surface O-bridge H-bridge	Pt-H:1.873 Pt-O:2.081	C-C C-O C-H	1.669 1.192/1.269 1.232/1.108
CHOCHOOH	-0.056	parallel to surface O-bridge H-bridge	Pt-H:1.946 Pt-O:2.123/3.333	C-C C-O C-H	1.542 1.380/1.215 1.111
CHOCOOH	-0.156	parallel to surface	Pt-C:3.248	C-C C-O O-H	1.538 1.222/1.357 0.982
COCOOH	-0.092	parallel to surface C-top O-top	Pt-C:2.021 Pt-H:2.237	C-C C-O O-H	1.561 1.321/1.224 0.997
CHOOCOHOH	-2.524	parallel to surface through O	Pt-O:2.124	C-C C-O O-H	1.616 1.385/1.207 0.998
CHOOHCOO H	-2.629	parallel to surface through O	Pt-C:3.102 Pt-O:2.113	C-C C-O C-H	1.580 1.213/1.337 0.988
COOHCOOH	-2.578	parallel to surface	3.738	C-C C-O O-H	1.539 1.218/1.333 0.987

(1) CHCH

According to Song et al. [7], there are four kinds of possible configurations for adsorbed acetylene on Pt (111): di- σ , parallel-bridge, perpendicular-bridge and top. The calculated adsorption energies of the four configurations calculated here are -1.935 eV, -2.381 eV, -2.136 eV and -0.737 eV. The results show that parallel-bridge configuration is the most stable configuration owing to its minimum adsorption energy, which also agree with a previous theoretical study [21]. The C-C bond of acetylene is stretched to 1.396 Å from 1.210 Å, indicating that acetylene is activated after adsorption on Pt (111) surface. At the same time, two hydrogen atoms distorted outside with C-H bond of 1.092 Å and C-C-H angle of 125°. Each C atom interacts with two Pt atoms, and the bond lengths of C1-Pt1/C2-Pt2 and C-Pt3 are 2.020 Å and 2.220 Å respectively.

second is reacting with OH to form CHCHO and H₂O (R1-5), and the last is CHCHOH directly dissociates into CHCHO and H atom (R1-6). The potential energy diagram of these reaction pathways together with the structures of the initial states, transition states, and final states are shown in Figure 3 and Figure 4.

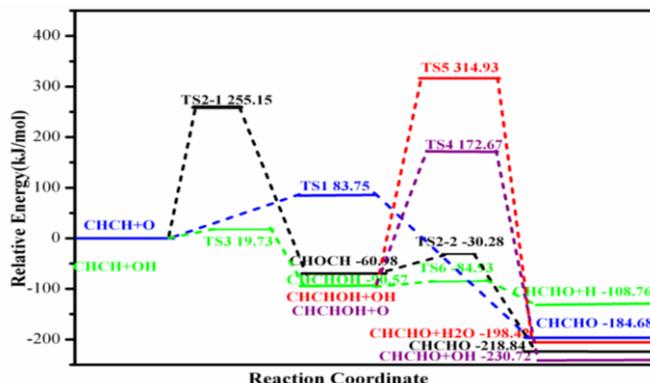
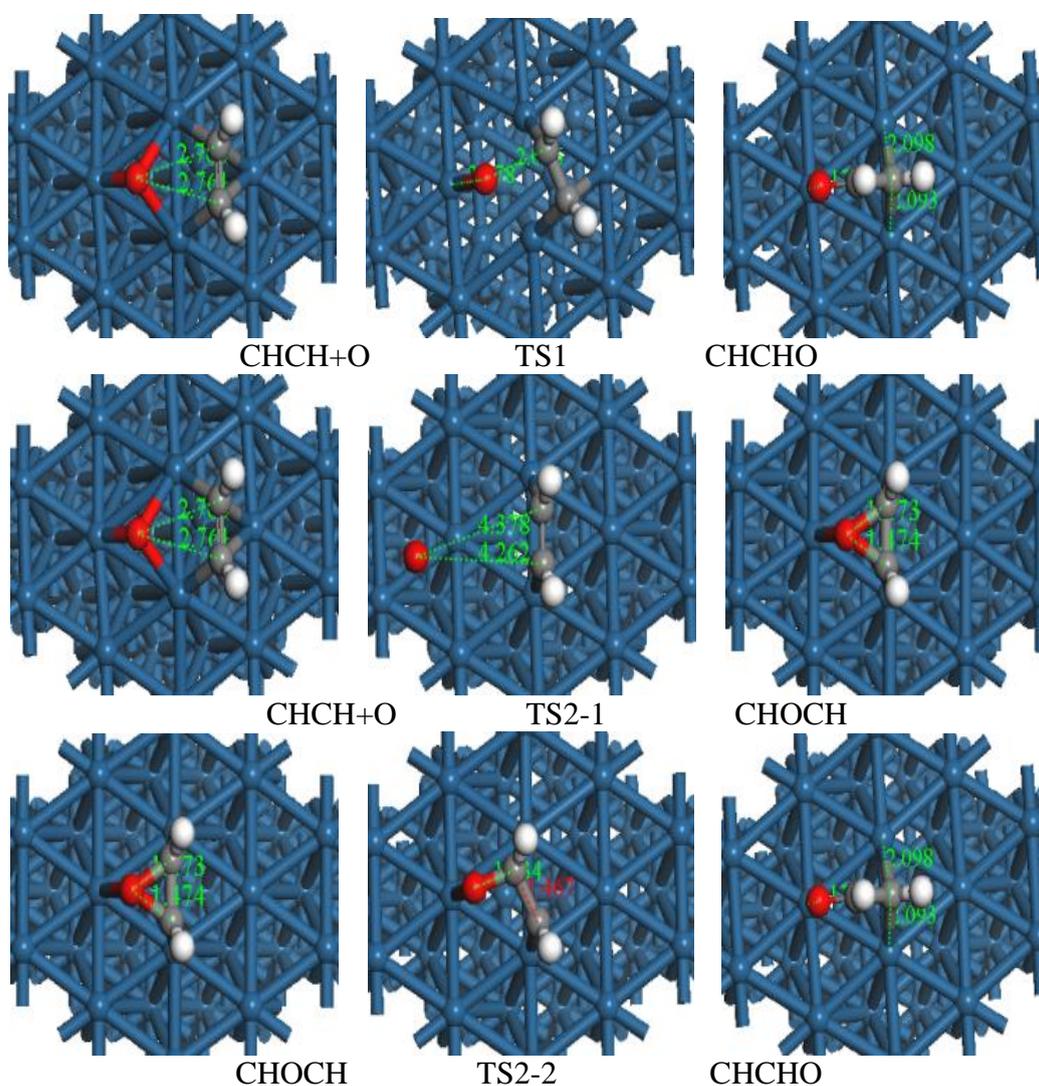


Figure 3. Potential energy diagram of CHCHO formation.



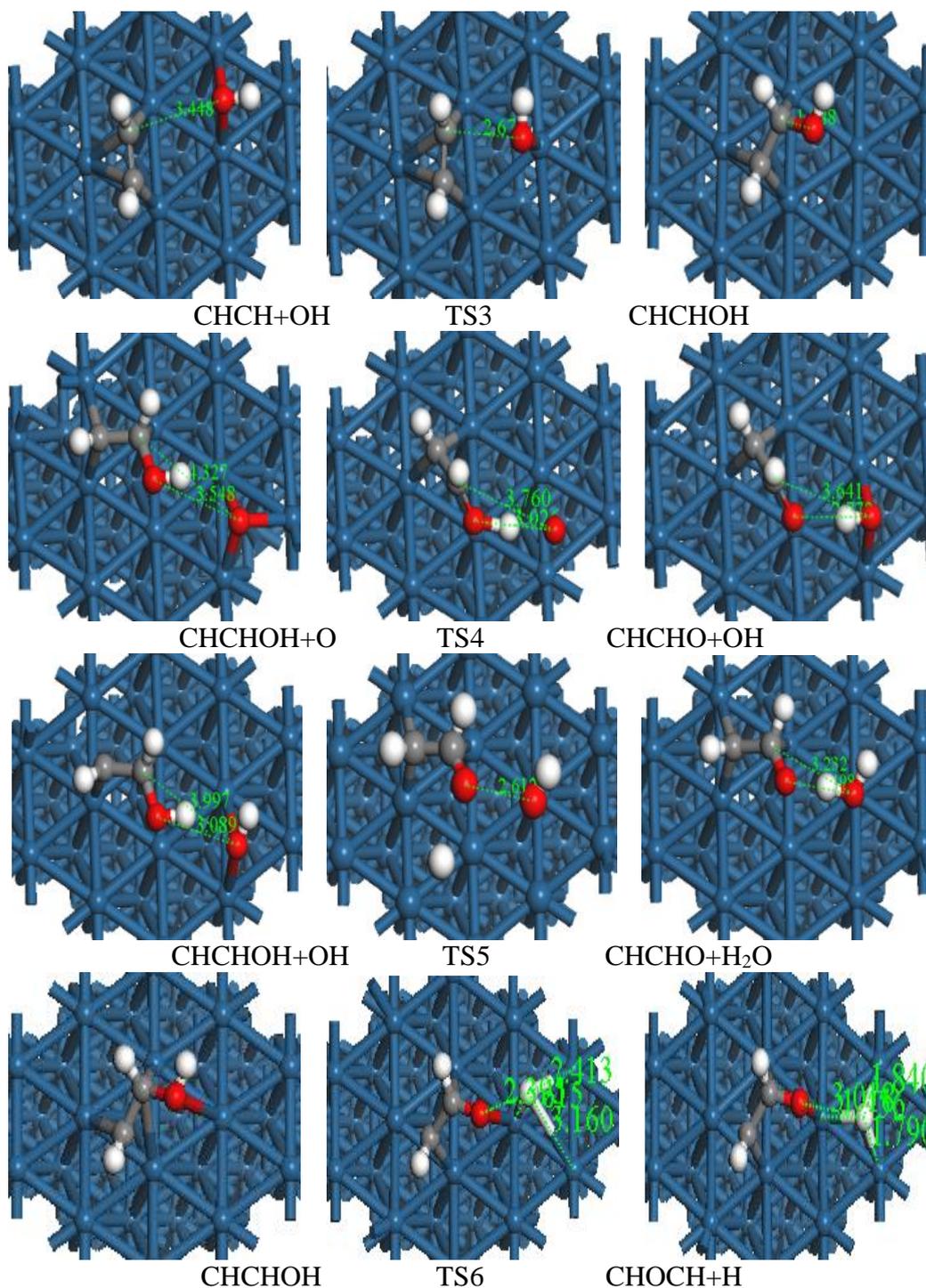
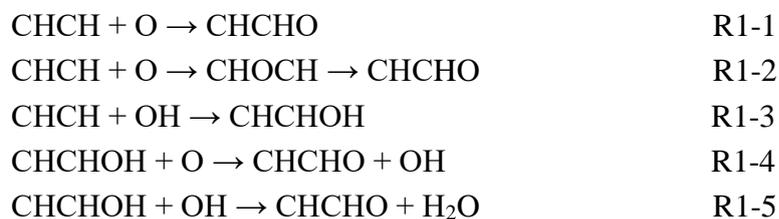


Figure 4. The structures of partial initial states, transition states, final states of CHCHO formation on Pt (111) surface.





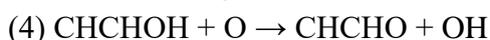
For the CHCHO (R1-1) formation, starting from its initial state, CHCH+O, CHCH is parallel to the surface bridge bond and O atom binds at the adjacent fcc site, both are the most stable configurations for CHCH and O species on the Pt (111) surface. The C atom of adsorbed CHCH moves toward the O atom by transition state TS1. In TS1, the distance between the C and O atoms decreases to 1.28 Å from 3.01 Å. Finally the O and C atoms of CHCHO adsorb at the top and bridge site respectively. This elementary reaction needs to overcome an activation barrier of 83.75 kJ·mol⁻¹, and the reaction is exothermic by -184.68 kJ·mol⁻¹.



For the CHCHO (R1-2) formation, the annular CHOCH is formed via the transition state TS2-1. In TS2-1, CHOCH is parallel to the surface and the C-O distance is stretched from 2.764 Å to 4.318 Å. Then the C-O bond continues to deform and finally breaks with the formation of CHCHO by transition state TS2-2. Finally the C and O atoms of CHCHO adsorb at top and bridge site respectively. For the first step, the activation barrier and reaction energy are 255.15 and -60.98 kJ·mol⁻¹, respectively. For the second step, they are 30.7 and -157.86 kJ·mol⁻¹ respectively.



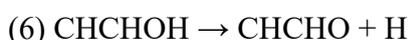
For the CHCHOH (R1-3) formation, starting from the initial state, CHCH+OH, CHCH is parallel to the surface bridge site and OH binds at the adjacent fcc site through a O atom, both are the most stable configuration for the CHCH and OH species on the Pt (111) surface. The C atom of the adsorbed CHCH moves towards the O atom of OH by transition state TS3. In TS3, the distance between the C atom and O decreases to 2.673 Å from 3.448 Å, finally CHCHOH adsorbs at the bridge site through C atom with C-O bond of 1.428 Å. The activation barrier for this elementary reaction is 19.73 kJ·mol⁻¹, and the reaction is exothermic by -90.57 kJ·mol⁻¹.



For R1-4, CHCHOH oxidizes through a transition state TS4 to form CHCHO. In TS4, the distance between H atom and the adsorbed O atom shortens from 3.548 Å to 1.236 Å. In the final state, the C and O atoms of CHCHO adsorb at the top and bridge site respectively, and OH adsorbs at adjacent bridge site. The activation barrier for this elementary reaction is 263.24 kJ·mol⁻¹, and the reaction is exothermic by -140.15 kJ·mol⁻¹.



For R1-5, CHCHOH dehydrogenated to form CHCHO and the stripped H atom combines with OH to form H₂O by transition state TS5. In TS5, the distance between stripped H atom and O atom of the adsorbed OH shortens from 3.048 Å to 2.619 Å. Finally, the C and O atoms of CHCHO adsorb at the top and bridge site respectively, and H₂O adsorbs at adjacent top site through O atom. The activation barrier for this elementary reaction is 405.50 kJ·mol⁻¹, and the reaction is exothermic by -107.85 kJ·mol⁻¹.



For R1-6, CHCHOH is directly dehydrogenated by a transition state TS6 to form CHCHO and H atom. In TS6, the O-H bond of CHCHOH is elongated to 3.082 Å from 2.391 Å. Finally, the C and O

atoms of CHCHO adsorb at the top and bridge site respectively. The activation barrier and reaction energy for this elementary reaction are 5.64 and $-18.19 \text{ kJ}\cdot\text{mol}^{-1}$, respectively.

Based on these results, we find that the CHCH first oxidizes with O atom or OH during the process of CHCHO formation. The barriers for R1-1, R1-2 and R1-3 are 83.75, 225.15 and $19.37 \text{ kJ}\cdot\text{mol}^{-1}$ with the corresponding reaction energies of 184.68, -218.84 , and $-108.76 \text{ kJ}\cdot\text{mol}^{-1}$ respectively, suggesting that the formation of CHCHOH is more favorable both kinetically and thermodynamically than CHCHO. In the experiments, similarly, acetylene also reacts with hydroxyl groups [7], which is consistent with the theoretical results. For CHCHOH, it is more easily dissociates into CHCHO and H than oxidize with O to form CHCHO and OH.

3.3.2 Formation of CHOCHO

On the basis of the above study of CHCHO formation mechanism, we further discuss the formation mechanism of CHOCHO on Pt (111) surface. On this step, CHCHO selectively reacts with hydroxyl or oxygen, and reacting with oxygen can directly generate CHOCHO (R2-1). In addition, reacting with hydroxyl can also form CHOHCHO (R2-2), then the CHOHCHO can be transferred into CHOCHO via three pathways: In the first pathway, CHOHCHO react with OH to form CHOCHO and H_2O (R2-3). In the second pathway, CHOHCHO dehydrogenized to form CHOCHO and OH (R2-4). In the third pathway, CHOHCHO directly dissociate into CHOCHO and H atom (R2-5). The potential energy diagram of these reaction pathways together with the structures of the initial states, transition states, and final states are shown in Figure 5 and Figure 6.

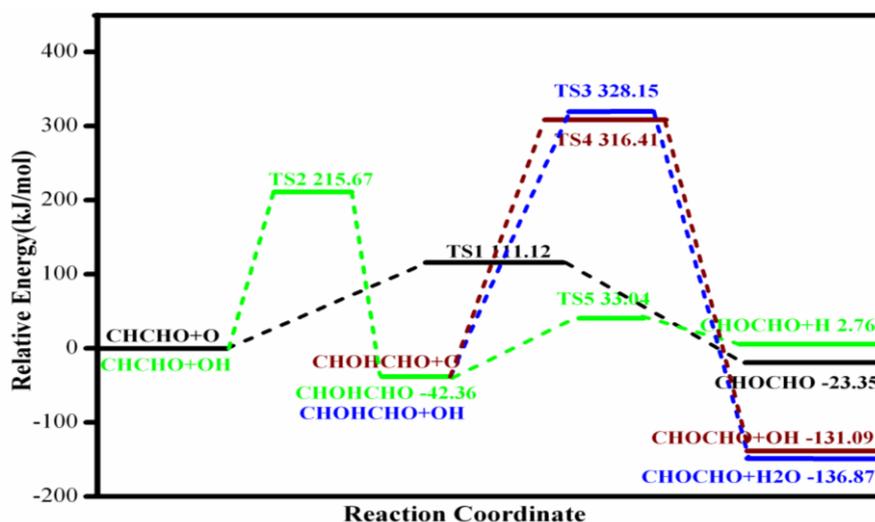
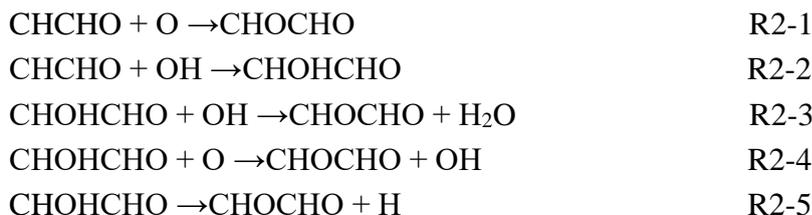
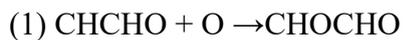
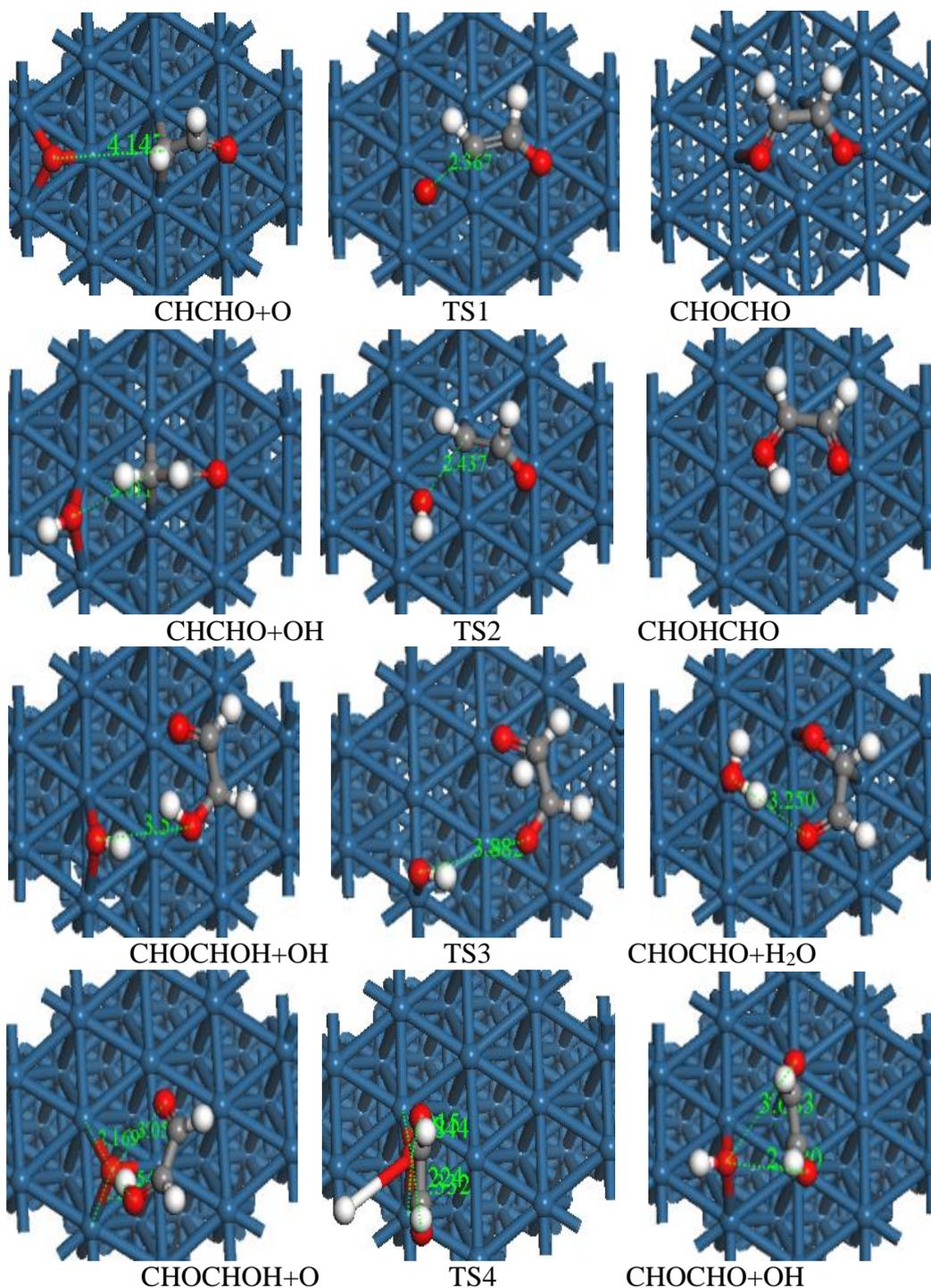


Figure 5. Potential energy diagram of CHOCHO formation.



For R2-1, CHOCHO is produced through the oxygenation of CHCHO by transition state TS1. In TS1, the O atom adsorbed at fcc site moves towards the C atom of CHCHO adsorbed at bridge site, and the distance between the two atoms shortens from the initial state of 4.142 Å to 2.627 Å. Finally, the produced CHOCHO is parallel to the surface. The activation barrier and reaction energy for this reaction are $111.12 \text{ kJ}\cdot\text{mol}^{-1}$ and $-23.35 \text{ kJ}\cdot\text{mol}^{-1}$ respectively.



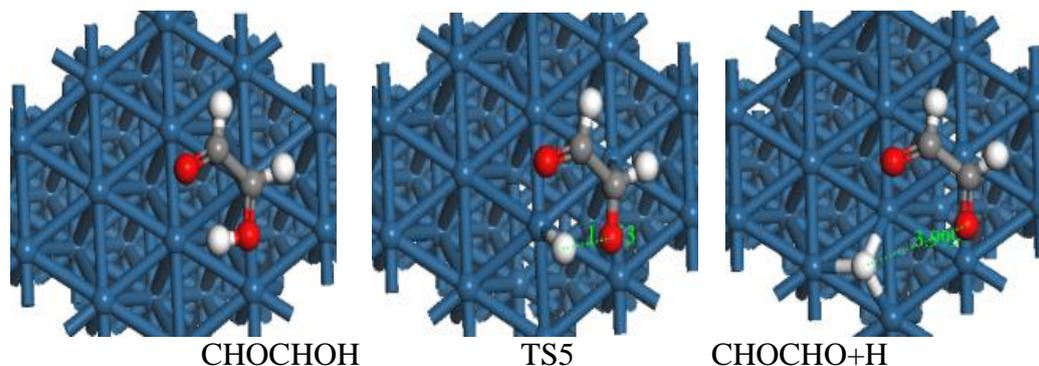


Figure 6. The structures of partial initial states, transition states, final states of CHOCHO formation on Pt (111) surface.



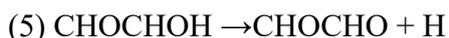
For R2-2, CHCHO reacts with OH to form CHOCHOH by transition state TS2. In the transition state TS2, CHCHO is still adsorbed at the bridge site, and the OH adsorbed at the adjacent bridge site by O atom with a short C–O distance of 2.437 Å. Finally, CHOCHOH is parallel to the surface. This elementary reaction needs to overcome an activation barrier of 215.67 kJ·mol⁻¹, and the reaction is exothermic by -42.36 kJ·mol⁻¹.



For R2-3, starting from CHOCHOH + OH, CHOCHOH adsorbs on the surface with the C–C bond parallel to the surface, while OH adsorbs at fcc site through the O atom. The O atom moves to the H atom of CHOCHOH to form CHOCHO and H₂O by transition state TS3. In TS3, the distance between the O and H atoms shortens from 3.011 Å to 2.437 Å. Finally, CHOCHO adsorbs on the surface with the C–C bond parallel to the surface and H₂O adsorbs at top site through O atom. This elementary reaction needs to overcome an activation barrier of 370.51 kJ·mol⁻¹, and the reaction is exothermic by -94.51 kJ·mol⁻¹.



For R2-4, beginning from CHOCHOH + O, CHOCHOH is adsorbed on the surface with the C–C bond parallel to the surface, O atom adsorbs at the adjacent fcc site. The H atom of CHOCHOH moves to the adsorbed O to form OH and CHOCHO by transition state TS4. In TS4, the distance between the H and O atoms shortens to 1.328 Å. This elementary reaction has an activation barrier of 358.77 kJ·mol⁻¹, and the reaction is exothermic by -88.73 kJ·mol⁻¹.



For R2-5, CHOCHOH dissociates into CHOCHO and H by transition state TS5. In TS5, the distance between the H atom and O atom of CHOCHOH stretches from the initial state of the 1.013 Å to 3.990 Å. In the final state, CHOCHO adsorbs on the surface with the C–C bond parallel to the surface, whereas H atom is adsorbed at the adjacent fcc site. This elementary reaction needs to overcome an activation barrier of 75.4 kJ·mol⁻¹, and the reaction is endothermic by 39.60 kJ·mol⁻¹.

According to the comparison on activation barriers and reaction energies, we concluded that the reaction of CHCHO and O is more favorable to occur both kinetically and thermodynamically. However, the reaction CHCHO + OH → CHOCHOH may partially occur due to the competition of oxidations. In

the experiment on the acetylene oxidation to oxalic acid, it also generates CHOCHO intermediate, which shows that the experimental results agree well with the theoretical calculation [22].

3.3.3 Formation of CHOCOOH

On the basis of the above formation mechanism of CHOCHO, we further discuss the formation mechanism of CHOCOOH on Pt (111) surface. CHOCHO may interact with OH or O atom. For O atom, it directly forms CHOCHOO (R3-1), followed by the formation of CHOCOOH (R3-2). In addition, it can also form CHOCHOOH with OH (R3-3). For CHOCOOH, it can be generated from CHOCHOOH via two pathways. On the one hand, it can interact with OH to form CHOCOOH and H₂O (R3-4). On the other hand, it can interact with O to form CHOCOOH and OH (R3-5). However, CHOCHO can also directly dissociate into CHOCO and H atom (R3-6), then, CHOCO interact with OH to form CHOCHOOH (R3-7). The potential energy diagram of these reaction pathways together with the structures of the initial states, transition states, and final states are shown in Figure 7 and Figure 8.

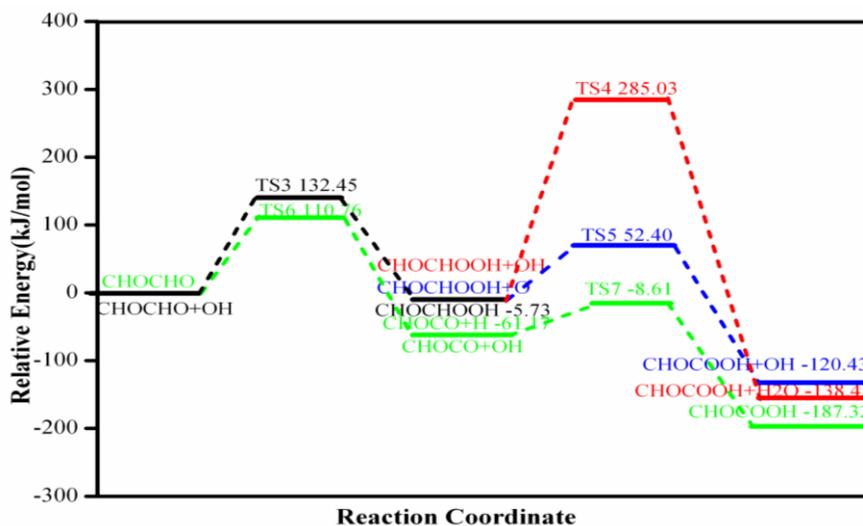
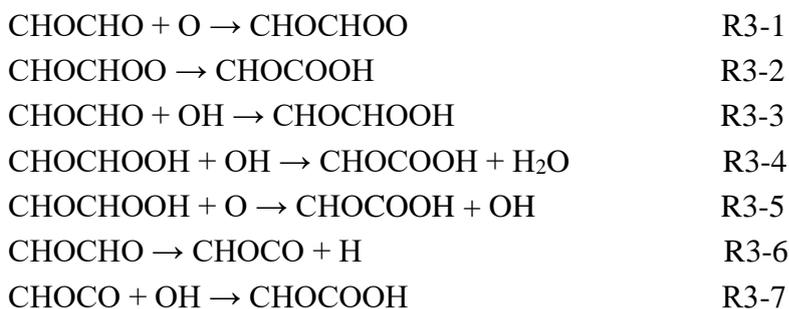
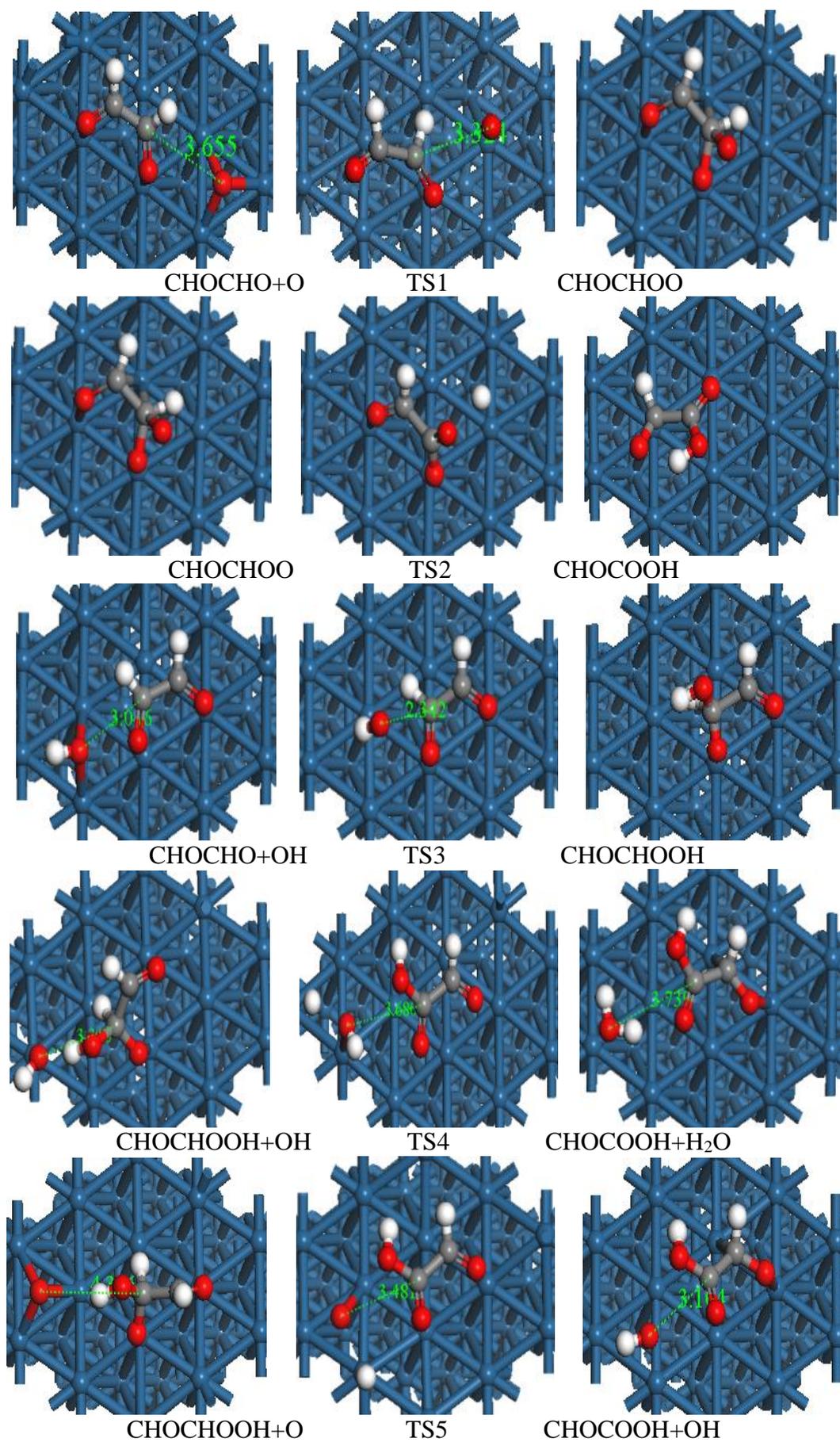


Figure 7. Potential energy diagram of CHOCOOH formation.



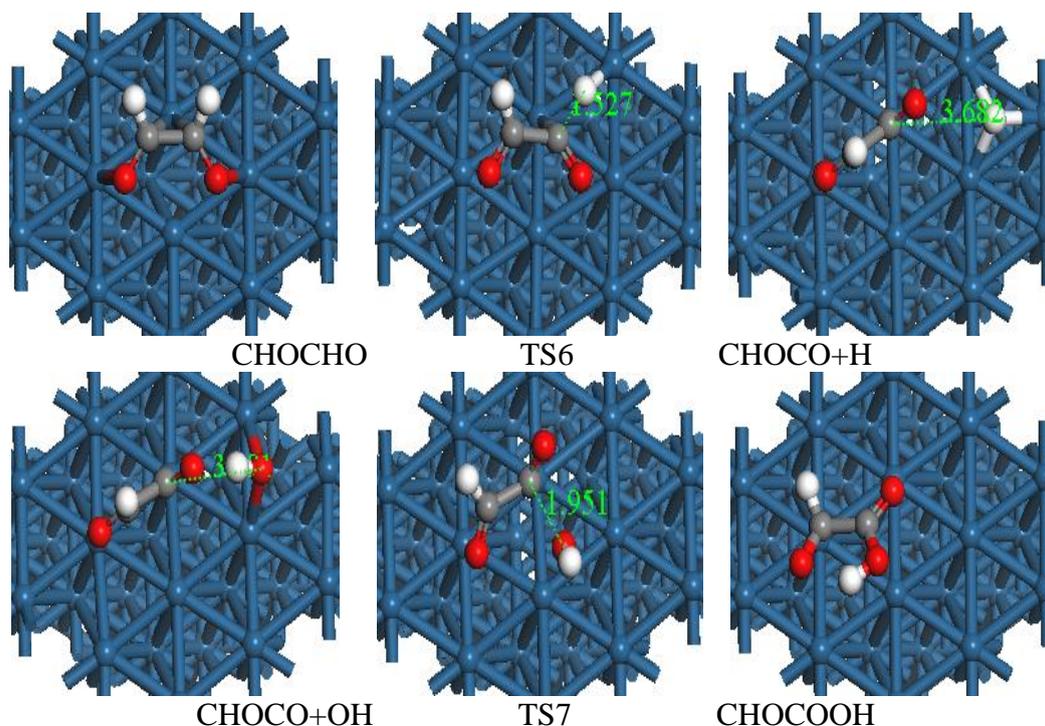


Figure 8. The structures of partial initial states, transition states, final states of CHOCOOH formation on Pt (111) surface.



For R3-1, starting from CHOCHO+O, CHOCHO adsorb on the surface with the C-C bond parallel to the surface, whereas O atom is adsorbed at the adjacent fcc site. The O atom moves from fcc site to the C atom of CHOCHO to form CHOCHOO by transition state TS1. In TS1, the distance between the O and C atoms shortens from 3.655 Å to 3.321 Å. This elementary reaction needs to overcome an activation barrier of 844.76 kJ·mol⁻¹, and the reaction is endothermic by 39166.05 kJ·mol⁻¹. Next, for R3-2, the C-H bond of CHOCHOO breaks. Then the single H atom combines with the adjacent O atom to form CHOCOOH by transition state TS2. The activation barrier and reaction energy for this reaction are 251.54 kJ·mol⁻¹ and -61.83 kJ·mol⁻¹ respectively. However, for this reaction, it cannot occur due to high energy needed.

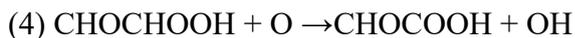


For R3-3, beginning from CHOCHO+OH, CHOCHO adsorb on the surface with the C-C bond parallel to the surface, whereas OH is adsorbed at the adjacent bridge site. OH attacks the C atom of CHOCHO to form CHOCHOOH by transition state TS3. In TS3, OH moves towards CHOCHO with shortened distance between O and C atoms of 2.312 Å. The activation barrier for this elementary reaction is 132.45 kJ·mol⁻¹, and the reaction is exothermic by -5.73 kJ·mol⁻¹.

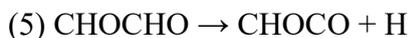


For R3-4, starting from CHOCHOOH + OH, CHOCHOOH adsorb on the surface with the C-C bond parallel to the surface, whereas OH is adsorbed at the adjacent bridge site. CHOCHOOH interacts with OH to form CHOCOOH and H₂O by transition state TS4. In TS4, OH moves to H atom of CHOCHOOH with shortened H-O bond of 1.328 Å. In the final state, CHOCOOH adsorbs on the surface

with the C-C bond parallel to the surface, H₂O adsorbed at top site. This elementary reaction needs to overcome an activation barrier of 290.76 kJ·mol⁻¹, and the reaction is exothermic by -132.72 kJ·mol⁻¹.



In the initial state of R3-5, CHOCHOH adsorbs on surface with the C-C bond parallel to the surface, O atom adsorbed at the adjacent fcc site, and CHOCHOH dehydrogenizes to form CHOCOOH and OH by transition state TS5. In TS5, the distance between the O and H atoms shortens to 1.094 Å. Finally, OH formed and adsorbs at bridge site. The activation barrier and reaction energy for this reaction are 58.13 kJ·mol⁻¹ and -126.16 kJ·mol⁻¹ respectively.



For R3-6, the C-H bond scission of CHOCHO leads to the formations of CHOCO and H atom by transition state TS6. In TS6, C-H bond of CHOCHO is stretched to 1.526 Å. Finally, CHOCO adsorbs on surface with the C-C bond parallel to the surface and the single H atom adsorbs at fcc site. The activation barrier for this elementary reaction is 110.76 kJ·mol⁻¹, and the reaction is found to be exothermic by -61.17 kJ·mol⁻¹.



For R3-7, starting from CHOCO+OH, CHOCO adsorb on the surface with the C-C bond parallel to the surface, whereas OH is adsorbed at the bridge site. The CHOCOOH is generated by transition state TS7. In TS7, the distance between the H atom of OH and the C atom of CHOCO shortens 1.951 Å. In the final state, CHOCOOH adsorbs on surface with C-C bond parallel to the surface. This elementary reaction needs to overcome an activation barrier of 52.56 kJ·mol⁻¹, and the reaction is exothermic by -126.15 kJ·mol⁻¹.

During the process of CHOCOOH formation, the reaction activation energy of R3-1 is too much bigger than the highest boundary of usual chemical reaction, which makes it impossible to occur. The activation energy difference between reactions R3-3 and R3-6 are small, so these two reactions may occur in parallel. In the next step, reaction CHOCHOH + O is easier to occur than CHOCHOH + OH. For the activation barriers and reaction energies of reactions CHOCHOH + O → CHOCOOH + OH and CHOCO+OH → CHOCOOH are similar. Thus, they may occur in parallel.

3.3.4 Formation of COOHCOOH

Based on the above formation mechanism of CHOCOOH, we further discuss the formation mechanism of COOHCOOH on Pt (111) surface. For CHOCOOH, it can interact with O atom or OH. CHOOCO (R4-1) is produced through oxygenation, following by the transformation of CHOOCO to COOHCOOH (R4-2). In addition, hydroxylation of CHOCOOH can form CHOOHCOOH (R4-3). Then, CHOOHCOOH can form COOHCOOH via two pathways. One is interacting with OH to form COOHCOOH and H₂O (R4-4). The other is reacting with O atom to form COOHCOOH and OH (R4-5). However, for CHOCOOH, it can also dissociate into COCOOH and H (R4-6). Then COCOOH can further interact with OH to form COOHCOOH (R4-7). Thus, the formation of COOHCOOH is discussed in this part. The potential energy diagram of these reaction pathways

together with the structures of the initial states, transition states, and final states are shown in Figure 9 and Figure 10.

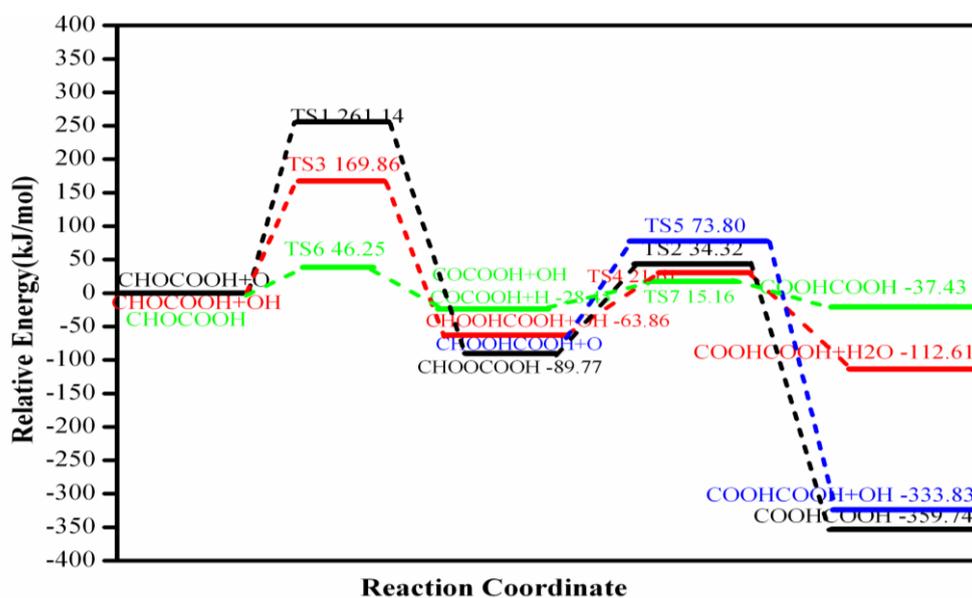
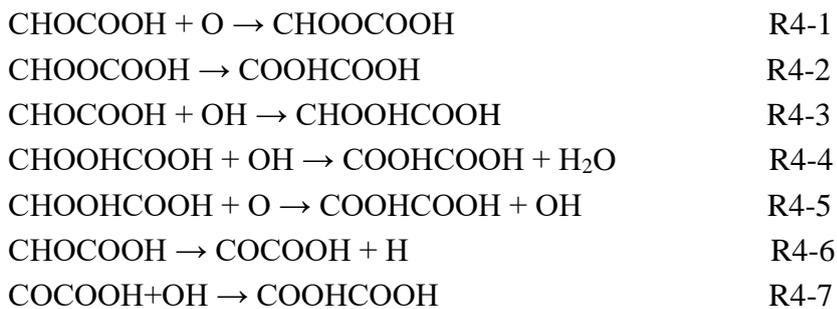
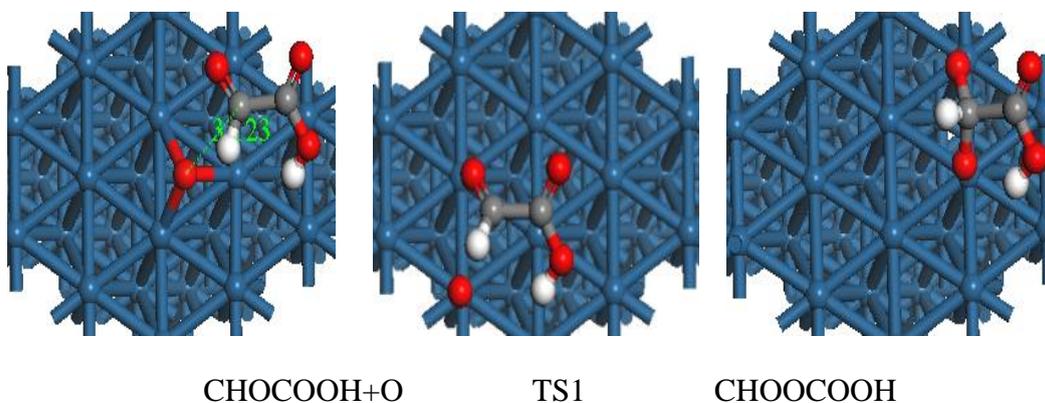
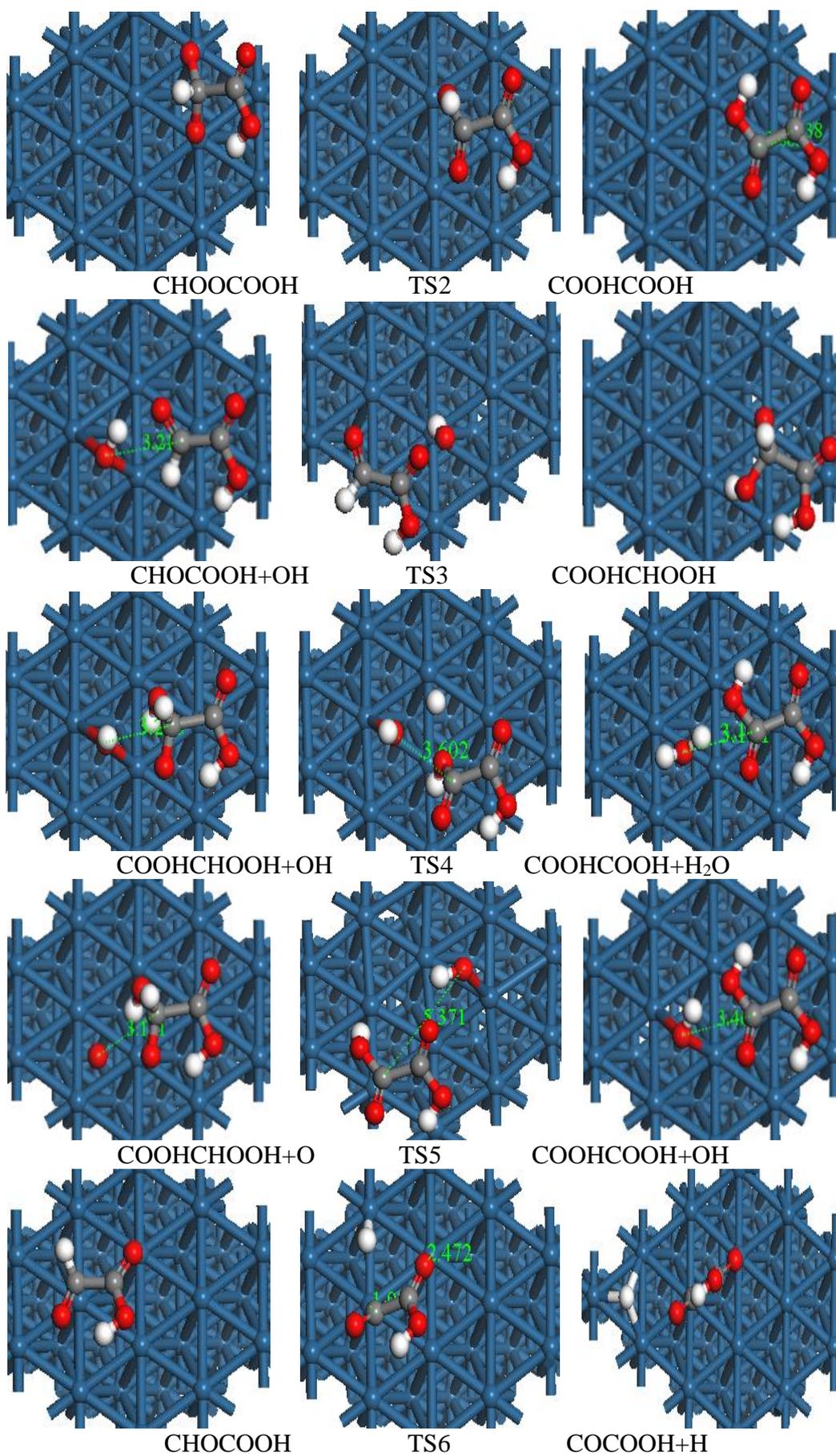


Figure 9. Potential energy diagram of COOHCOOH formation.





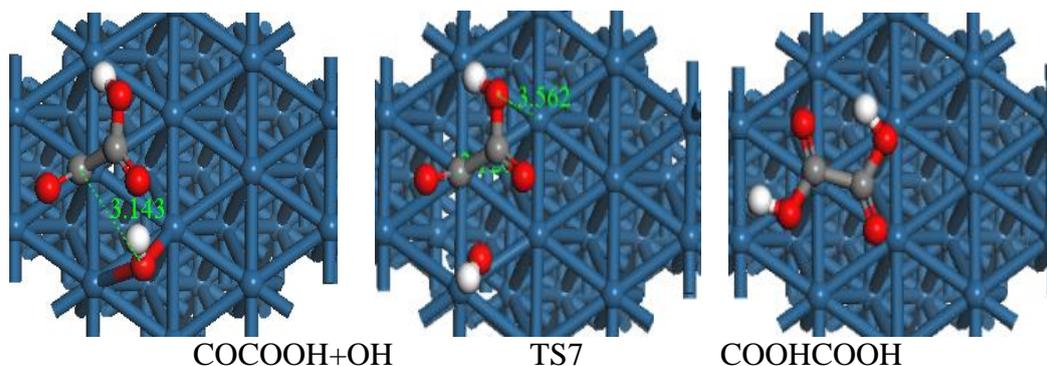


Figure 10. The structures of partial initial states, transition states, final states of COOHCOOH formation on Pt (111) surface.



For R4-1, starting from CHOCO OH+O, CHOCO OH adsorb on the surface with the C-C bond parallel to the surface and the O atom is adsorbed at adjacent fcc site, both of which are the most stable configuration on the Pt (111) surface. CHOOCO OH is formed by transition state TS1. In TS1, the O atom moves towards the C atom of CHOCHO with shortened distance of 1.625 Å. In the final state, generated CHOOCO OH adsorbs on the surface with the C-C bond parallel to the surface. The activation barrier and reaction energy for this reaction are 261.14 kJ·mol⁻¹ and -89.77 kJ·mol⁻¹ respectively.



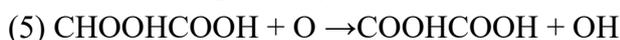
For R4-2, in the beginning, CHOOCO OH adsorbs on the surface with the C-C bond parallel to the surface. The CHOOCO OH turns into COOHCO OH by transition state TS2. In TS2, the distance between the C atom and the H atom is elongated to 3.427 Å. Finally, COOHCO OH adsorbs on the surface with the C-C bond parallel to the surface. The activation barrier for this elementary reaction is 124.09 kJ·mol⁻¹, and the reaction is exothermic by -269.97 kJ·mol⁻¹.



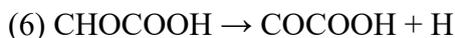
For R4-3, starting with CHOCO OH+OH, CHOCO OH adsorb on the surface with the C-C bond parallel to the surface, OH is adsorbed at the adjacent bridge site. The CHOOHCO OH is generated by transition state TS3. In TS3, the O atom of OH at bridge site moves to the C atom of CHOCO OH with shortened C-O bond of 1.628 Å. In the final state, COOHCO OH adsorbs on the surface with the C-C bond parallel to the surface. This elementary reaction needs to overcome an activation barrier of 169.86 kJ·mol⁻¹, and the reaction is exothermic by -63.86 kJ·mol⁻¹.



For R4-4, beginning with CHOOHCO OH +OH, CHOOHCO OH adsorb on the surface with the C-C bond parallel to the surface and the OH is adsorbed at adjacent bridge site. CHOOHCO OH reacts with OH to form COOHCO OH and H₂O by transition state TS4. In TS4, the distance between the O atom of OH and the C atom of CHOOHCO OH gradually shortens. Finally, OH changes to H₂O, which adsorbed at the top site. The activation barrier and reaction energy for this reaction are 42.25 kJ·mol⁻¹ and -48.75 kJ·mol⁻¹ respectively.



For R4-5, beginning with $\text{CHOOHCOOH} + \text{O}$, CHOOHCOOH adsorb on the surface with the C-C bond parallel to the surface and the O atom is adsorbed at the adjacent fcc site, both of which are the most stable configurations on the Pt (111) surface. The O atom attacks the H atom of CHOOHCOOH to form OH and CHOOHCOOH loses H atom to form COOHCOOH by transition state TS5. In TS5, the distance between the C atom and the H atom is elongated to 3.824 Å. The activation barrier for this elementary reaction is $137.66 \text{ kJ}\cdot\text{mol}^{-1}$, and the reaction is exothermic by $-269.97 \text{ kJ}\cdot\text{mol}^{-1}$.



For R4-6, CHOCOOH dissociates into COCOOH and a H atom by transition state TS6. In TS6, H atom desorbs from CHOCOOH with elongated distance of 2.013 Å. In the final state, COCOOH adsorbs on surface with the C-C bond parallel to the surface and the H atom adsorbs at adjacent fcc site. This elementary reaction needs to overcome an activation barrier of $46.25 \text{ kJ}\cdot\text{mol}^{-1}$, and the reaction is exothermic by $-28.45 \text{ kJ}\cdot\text{mol}^{-1}$.



For R4-7, starting with $\text{COCOOH} + \text{OH}$, COCOOH adsorb on surface with the C-C bond parallel to the surface and the OH is adsorbed at the adjacent bridge site. The COOHCOOH is formed by transition state TS7. In TS7, the O atom of OH moves to the C atom of COCOOH with shortened distance of 1.837 Å. The activation barrier and reaction energy for this reaction are $12.84 \text{ kJ}\cdot\text{mol}^{-1}$ and $-8.98 \text{ kJ}\cdot\text{mol}^{-1}$ respectively.

Based on the analysis of the above formation of COOHCOOH species, it is easier for CHOCOOH to interact with OH than that with O atom either on kinetics or thermodynamics. However, for reaction $\text{CHOCOOH} \rightarrow \text{COCOOH} + \text{H}$, its activation energy is smaller than the above two, the activation energy for COCOOH to form COOHCOOH is also small, as a consequence it is easier to occur. The main reactions in this part are as follows: $\text{CHOCOOH} \rightarrow \text{COCOOH} + \text{H}$, $\text{COCOOH} + \text{OH} \rightarrow \text{COOHCOOH}$.

4. CONCLUSION

The mechanism of electrochemical synthesis to oxalic acid from acetylene on Pt (111) has been comprehensively investigated using first-principles method based on density functional theory (DFT). Geometries and energies for all of the intermediates involved as well as the conversion mechanism are investigated. We mainly discuss four key steps: first, the formation of CHCHO species; Second, the formation of CHOCHO species; Third, the formation of CHOCOOH species; Fourth, the forming of COOHCOOH species. All the results are shown as follows:

In the formation of CHCHO species, the main reaction is the reaction $\text{CHCH} + \text{OH} \rightarrow \text{CHCHOH} \rightarrow \text{CHCHO} + \text{H}$, and it is most likely to occur, followed by $\text{CHCH} + \text{OH} \rightarrow \text{CHCHOH} + \text{O} \rightarrow \text{CHCHO} + \text{OH}$.

In the formation of CHOCHO species, the chemical reaction occurs mainly is $\text{CHCHO} + \text{O} \rightarrow \text{CHOCHO}$.

In the formation of CHOCOOH species, the main step is $\text{CHOCHO} \rightarrow \text{CHOCO} + \text{OH} \rightarrow \text{CHOCOOH}$ followed by $\text{CHOCHO} + \text{OH} \rightarrow \text{CHOCHOH} + \text{O} \rightarrow \text{CHOCOOH} + \text{OH}$.

In the formation of CHCHO species, the main process is $\text{CHOCOOH} \rightarrow \text{COCOOH} + \text{OH} \rightarrow \text{COOHCOOH}$.

In conclusion, the main process of generating oxalic acid by acetylene oxidation is $\text{CHCH} + \text{OH} \rightarrow \text{CHCHOH} \rightarrow \text{CHCHO} + \text{O} \rightarrow \text{CHOCHO} \rightarrow \text{CHOCO} + \text{OH} \rightarrow \text{CHOCOOH} \rightarrow \text{COCOOH} + \text{OH} \rightarrow \text{COOHCOOH}$.

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