Dear Reviewers:

We wish to thank you for the time and effort you have spent reviewing our paper. We are pleased to note that you have found our research work interesting and also pointed out some problems to help us improve the quality of our work.

Motivated by your comments, we have deeply reconsidered the architecture of our work and tried to fix all the problems you mentioned. In particular, this revised paper of our resubmitted letter has significantly been improved mainly as follows: (The improvements are in yellow in the revised paper for your convenience).

Our itemized response to your questions, comments and suggestions is as follows:

Reviewer #1

Reviewer comment:

1. The major computational results could be summarized in a table.
2. The authors might include a comparison between the current results and existing works if there is any.

Our response:

1. The single point energies are already shown in the Figure 1 and 2, we will put the other major results in the supplementary information.
2. We calculate the potential energy surface for the reactions so far. We could include a comparison with experimental results when we continue to get the rate constants results.

Thank you for your comments.

Reviewer #2

Reviewer comment:

1. The details in Figs. 1 (scheme 3), 2 and 4 can be hardly seen.
2. The energy unit is missing in Fig. 3.

Our response:

1. We revise these figures to more clear edition. These new figures will not lose clarity when they are zoomed in.
2. We add the energy unit for Fig. 3.

Thank you for your comments.

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Kinetics of $\dot{\text{O}}\text{H}$ Radical Addition to 1,3-Butadiene and Related Reactions on the $\dot{\text{C}}_4\text{H}_7\text{O}$ Potential Energy Surface

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ABSTRACT

The chemical reaction kinetics of 1,3-butadiene is significant to understand the role of polyunsaturated hydrocarbons in combustion and soot formation. The important reactions of 1,3-butadiene and $\dot{\text{O}}\text{H}$ radical and their subsequent reactions have been investigated in this work. The geometry optimizations and vibrational frequency are calculated at BH&HLYP/6-311++G(d,p) level of theory. Electronic energy for stationary points on the potential energy surface related to the primary reactions are calculated at ROCCSD(T)/CBS and G4 level of theory. Discussion of the different configurations of trans and cis structures for reactants and intermediates are also given. Based on the comparison of barrier heights, terminal addition is the dominating pathway, $\text{CH}_2=\text{CHCH}_2\text{CH}_2\dot{\text{O}}$ and $\text{CH}_2=\text{CHCH}\dot{\text{O}}\text{CH}_3$ are two important intermediates, and $\text{CH}_2=\text{CHCHO} + \dot{\text{C}}\text{H}_3$, $\text{CH}_2=\text{CH}\dot{\text{C}}\text{H}_2 + \text{HCHO}$ are important bimolecular products. A significant three-membered ring intermediate (IT7) is found in both terminal and central addition. Pressure- and temperature-dependent rate constants and thermodynamic properties for the $\dot{\text{O}}\text{H}$ radical addition to 1,3-butadiene will also be investigated. The calculated kinetics and thermodynamics properties of the title reaction will be helpful to understand the 1,3-butadiene oxidation in their model development.

1 INTRODUCTION

1,3-butadiene is a significant intermediate which involves the soot formation and benzene formation.[1] Therefore, the correct understanding of the oxidation chemistry is the basis of the development of kinetic model. The importance of the reaction of 1,3-butadiene at the low temperature have been investigated by Zhou et al [2]. According to the Brute-force sensitivity analysis of 1,3-butadiene, the addition reaction of 1,3-butadiene and $\dot{\text{O}}\text{H}$ plays a very important role when temperature is lower than 870K. Thus, a comprehensive investigation on the key addition reaction of $\dot{\text{O}}\text{H}$ radical to 1,3-butadiene is important to have a better understanding of the oxidation chemistry of 1,3-butadiene at low temperatures.

Rate constants for the reaction of 1,3-butadiene and $\dot{\text{O}}\text{H}$ has been investigated mainly by experiments. Llyod et al.[3] carried out irradiations of the HC- NO_x -air system in an all-glass (Pyrex) chamber and measured the rate constant to be $(7.45 \pm 1.45) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 305 K. Atkinson et al.[4] measured the rate constant at 100 Torr in Ar over a temperature range of 299-424 K employing a flash photolysis-resonance fluorescence technique, derived an Arrhenius expression of $k_1^{\text{II}}(T) = 1.45 \times 10^{-11} \exp[(930 \pm 300)/RT] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 50 Torr in argon between 299 and 424 K. Liu et al.[5] also measured the rate constant at 1 atm in Ar at 305-1173 K using resonance fluorescence technique, obtaining an

Arrhenius expression of $k_1^{\text{II}}(T) = (1.4 \pm 0.1) \times 10^{-11} \exp[(440 \pm 40)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ between 313 and 623 K and a rate constant of $(6.1 \pm 0.6) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 313 K. The kinetics of the reaction of hydroxyl radical with 1,3-butadiene at 240-340 K and a total pressure of 1 Torr has been studied employing the discharge flow and mass spectrometer technique by Li et al. [6]. They also obtained an Arrhenius expression of $k_1^{\text{II}}(T) = (1.58 \pm 0.07) \times 10^{-11} \exp[(436 \pm 13)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 1 Torr between 240 and 340 K. The rate constants for the reaction of the $\dot{\text{O}}\text{H}$ radical with 1,3-butadiene and its deuterated isotopomer has been measured at 1-6 Torr total pressure at 263-423 K using the discharge flow system coupled with resonance fluorescence/laser-induced fluorescence detection of $\dot{\text{O}}\text{H}$ by Vimal et al. [7]. An Arrhenius expression for this reaction was determined to be $k_1^{\text{II}}(T) = (7.23 \pm 1.2) \times 10^{-11} \exp[(664 \pm 49)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 263-423 K. The reaction was studied behind reflected shock waves over the temperature range of 1011-1406 K and at pressures near 2.2 atm by Vasu et al. [8].

There are few theoretical work for the reaction of 1,3-butadiene and $\dot{\text{O}}\text{H}$. Li et al. [6] investigated title entrance reaction including terminal addition and central addition pathways using MP2/6-311++G(d,p) method. Optimized geometry of reactants, products and transition states are given. Total electronic energy, ZPE and vibrational frequencies of title entrance species involved in reactions are also calculated. However, rate constants based on their potential energy surface has not been provided in their work. Vasu et al. [8] calculated a series of rate coefficients of part of reactions applying variational transition state theory based on QCISD(T)/cc-pV ∞ Z//B3LYP/6-311++G(d,p).

The comprehensive reaction kinetics of $\dot{\text{O}}\text{H}$ radical addition to 1,3-butadiene and related reactions have not been investigated extensively. Moreover, the important intermediates and bimolecular products of this reaction have not been verified as well. Thus, further theoretical investigation on the title reaction kinetics is important to understand the chemical kinetics of 1,3-butadiene oxidation especially at low temperatures. This work provides all the possible pathways in the reaction system and completed potential energy surface employing high level ab initio calculations.

2 METHODOLOGY

The BH&HLYP [9] method with the 6-311++G(d,p) [10, 11] basis set is employed to fully optimize the geometries of the van der Waals complex, reactants, intermediates, transition states, and products. The zero-point vibrational energy corrections (ZPE) were calculated at the same level of theory. In addition,

vibration frequency calculations are also carried out to verify the existence of transition states with one and only one imaginary frequency. The intrinsic reaction coordinate (IRC) calculations are employed to guarantee that the transition states are connecting the right minima between a specific pair of stationary points. Single-point energies of all species are obtained by the ROCCSD(T) method with basis set cc-PVQZ [12]. ROCCSD(T) with cc-pVTZ is also used to complete the basis set limit (CBS) [13].

$$E_{\text{CBS}} = E_{\text{ROCCSD(T)/cc-pVQZ}} + (E_{\text{ROCCSD(T)/cc-pVQZ}} - E_{\text{ROCCSD(T)/cc-pVTZ}}) * 4^4 / (5^4 - 4^4)$$

Comparing with ROCCSD(T) method, G4 [14] method is much less expensive when dealing with single point energies. Thus, in this work, G4 method is also used in the single point energies calculation for all stationary points for comparison. All of the geometries optimization and single point energies are performed with Molpro program [15] and Gaussian 09 [16].

3 RESULT

Schematic diagram of $\dot{\text{O}}\text{H}$ radical addition to 1,3-butadiene and related reactions are shown in Scheme 1, Scheme 2 and Scheme 3. Potential energy surface (PES) of $\dot{\text{O}}\text{H}$ and 1,3-butadiene is shown in Figure 1 and Figure 2. The PES is very complex for the reaction system, including all possible pathways for association, abstraction, β -division, H-transfer and cyclization, which finally lead to bimolecular products. All the electronic energies for the reaction system are given, which include all the reactants, intermediates, transition states and products. Employing the results of scan of every stationary point, single point energy for each stationary point (SPE) is calculated based on the lowest energy conformer.

For the addition reactions, $\dot{\text{O}}\text{H}$ radical first may form a van der Waals complex (COM) with 1,3-butadiene, before it inserts into the C-C double bond to form either the intermediate $\text{CH}_2=\text{CH}\dot{\text{C}}\text{HCH}_2\text{OH}$ (IT1) or $\text{CH}_2=\text{CHCH}(\text{OH})\dot{\text{C}}\text{H}_2$ (IC1). The optimized geometrical parameters of the complex COM using BH&HLYP/6-311++G(d,p) method is given in Figure 3. The distance and angle performed in the Figure 3 is consistent with the result of the reaction between propene and $\dot{\text{O}}\text{H}$ investigated by Huynh et al. [17]. The SPE of complex COM is 1.9 kcal/mol lower than $\text{C}_4\text{H}_6 + \dot{\text{O}}\text{H}$. This could explain SPE for the TS of terminal addition is 1.6 kcal/mol lower than $\text{C}_4\text{H}_6 + \dot{\text{O}}\text{H}$. The existence of van der Waals complex COM may decline the barrier height for both terminal addition and central addition.

Scheme 1. OH radical terminal addition to 1,3-butadiene and related reactions

Scheme 2. OH radical central addition to 1,3-butadiene and related reactions

Scheme 3. Isomerization of C₄H₇O in terminal addition and central addition

Figure 1. The C₄H₇O potential energy surface (including ZPE) for the terminal addition of the OH radical

radical. Energies are calculated using ROCCSD(T)/CBS and G4 method (in brackets), important reactions marked by bold lines.

Figure 2. The C₄H₇O potential energy surface (including ZPE) for the central addition of the OH radical. Energies are calculated using ROCCSD(T)/CBS and G4 method (in brackets), important reactions marked by bold lines.

Figure 3. The optimized geometry of the van der Waals complex COM (the unit for distance are Å and for angle is degree)

Figure 4. Internal rotor potential of the CC-CC dihedral angle for 1,3-butadiene. The energy is in kcal/mol.

Note that for all the C₄H₆ and C₄H₇O species in this paper involve two main structure, trans and cis. Trans-structure is normally lower in SPE, as shown in Figure 4. So we focus on the trans-structure mainly, nevertheless, there are some situations that cis-structure

have lower SPE than Trans-structure. Moreover, there are other special occasions that in one pathway, the structure of reactant and product are trans, however the transition state is cis, such as the reaction from $\text{CH}_2=\text{CHCH}_2\dot{\text{C}}\text{HOH}$ (IT2) to $\text{CH}_2=\text{CHCH}=\text{CHOH}+\dot{\text{H}}$ (PT3). These situations are all observed by the scanned calculations of every stationary point. According to the internal rotation potential of the CC-CC dihedral angles, the lowest energy conformer was used in the high level SPE calculation. When the species involves more than one possible conformers, both of the cis and trans structures will be generally included implicitly in the kinetic analysis through torsional treatments.

There are two initial reaction pathways of $\dot{\text{O}}\text{H}$ addition to 1,3-butadiene involving terminal addition and central addition, based on the symmetry of 1,3-butadiene.

The PES of these two pathways and subsequent reactions are given separately (Figure 1 and Figure 2). All the electronic energies are zero-point-corrected and relative energies to the primal reactants, the sum energies of 1,3-butadiene and $\dot{\text{O}}\text{H}$ radical. The PES for terminal addition includes 10 intermediates, 28 transition states, 8 bimolecular products, and it includes 11 intermediates, 31 transition states, 14 bimolecular products for the central addition. From the potential energy surface comparison shown in Figure 1 and Figure 2, we can get that the barrier for central addition is 3.0 kcal/mol higher than the terminal addition, which means the terminal addition is much more favored.

Subsequent β -scission/Isomerization and cyclization reactions for the two adducts formed from terminal and central addition will be discussed in the following section.

3.1 Terminal addition

β -scission/Isomerization. After the reaction of the terminal addition, the most dominating reaction will be bimolecular reaction to $\text{CH}_2=\text{CHCH}=\text{CHOH}+\dot{\text{H}}$ (PT3) from $\text{CH}_2=\text{CH}\dot{\text{C}}\text{HCH}_2\text{OH}$ (IT1), whose barrier height is 41.4 kcal/mol. Every intermediate of the terminal addition could isomerize to each other by H-transfer. The H-transfer reaction from $\text{CH}_2=\text{CH}\dot{\text{C}}\text{HCH}_2\text{OH}$ (IT1) to $\text{CH}_2=\text{CHCH}_2\dot{\text{C}}\text{HOH}$ (IT2) and $\text{CH}_2=\text{CHCH}_2\text{CH}_2\dot{\text{O}}$ (IT3) (barrier height: 46.8 kcal/mol and 43.6 kcal/mol) is also important. The reactions from $\text{CH}_2=\text{CH}\dot{\text{C}}\text{HCH}_2\text{OH}$ (IT1) to $\text{CH}_2=\dot{\text{C}}\text{CH}_2\text{CH}_2\text{OH}$ (IT4), $\dot{\text{C}}\text{H}=\text{CHCH}_2\text{CH}_2\text{OH}$ (IT5) and $\text{CH}\equiv\text{CCH}_2\text{CH}_2\text{OH}+\dot{\text{H}}$ (PT7) tend to be ignored with a barrier of more than 60 kcal/mol. The dominating reaction from $\text{CH}_2=\text{CHCH}_2\dot{\text{C}}\text{HOH}$ (IT2) is the H-transfer reaction to $\dot{\text{C}}\text{H}=\text{CHCH}_2\text{CH}_2\text{OH}$ (IT5) (barrier

height: 32.3 kcal/mol), the reaction from $\text{CH}_2=\text{CHCH}_2\dot{\text{C}}\text{HOH}$ (IT2) to $\text{CH}_2=\text{CHCH}_2\text{CH}_2\dot{\text{O}}$ (IT3), $\text{CH}_2=\text{CHCH}_2\text{CHO}+\dot{\text{H}}$ (PT2), $\text{CH}_2=\text{CHCH}=\text{CHOH}+\dot{\text{H}}$ (PT3) and $\text{CH}_2=\dot{\text{C}}\text{H}+\text{CH}_2=\text{CHOH}$ (PT5) are also important for barrier heights of 35.3 to 39.0 kcal/mol. The dominating reaction from $\text{CH}_2=\text{CHCH}_2\text{CH}_2\dot{\text{O}}$ (IT3) is the bimolecular reaction to $\text{CH}_2=\text{CH}\dot{\text{C}}\text{H}_2+\text{HCHO}$ (PT1) for barrier heights of only 9.3 kcal/mol. The other reaction from $\text{CH}_2=\text{CHCH}_2\text{CH}_2\dot{\text{O}}$ (IT3) are also important for barrier heights of 13.8 to 22.5 kcal/mol, relatively lower comparing to other intermediates, which means $\text{CH}_2=\text{CHCH}_2\text{CH}_2\dot{\text{O}}$ (IT3) is a significant intermediate in the reaction system. The dominating reaction from $\text{CH}_2=\dot{\text{C}}\text{CH}_2\text{CH}_2\text{OH}$ (IT4) is the bimolecular reaction to $\text{CH}_2=\text{C}=\text{CH}_2+\dot{\text{C}}\text{H}_2\text{OH}$ (PT4) (barrier height: 31.3kcal/mol). The dominating reaction from $\dot{\text{C}}\text{H}=\text{CHCH}_2\text{CH}_2\text{OH}$ (IT5) is the formation of the bimolecular products of $\text{CH}\equiv\text{CH}+\dot{\text{C}}\text{H}_2\text{CH}_2\text{OH}$ (PT6) (barrier height: 32.5kcal/mol).

Cyclization reactions. Cyclization reactions from $\text{CH}_2=\text{CH}\dot{\text{C}}\text{HCH}_2\text{OH}$ (IT1) and $\text{CH}_2=\text{CHCH}_2\text{CH}_2\dot{\text{O}}$ (IT3) tend to be unimportant. Barrier height for the reaction from $\text{CH}_2=\text{CH}\dot{\text{C}}\text{HCH}_2\text{OH}$ (IT1) to IT6 (barrier height: 50.3kcal/mol) is 8.9 kcal/mol higher than the most dominating reaction, which involves the formation of the bimolecular products of $\text{CH}_2=\text{CHCH}=\text{CHOH}+\dot{\text{H}}$ (PT3) from $\text{CH}_2=\text{CH}\dot{\text{C}}\text{HCH}_2\text{OH}$ (IT1). The reaction from $\text{CH}_2=\text{CHCH}_2\text{CH}_2\dot{\text{O}}$ (IT3) to IT9 (barrier height: 15.9kcal/mol) and IT10 (barrier height: 16.6kcal/mol) is 6.6 and 7.3 kcal/mol higher than the most dominating reaction, involving the formation of the bimolecular products from $\text{CH}_2=\text{CHCH}_2\text{CH}_2\dot{\text{O}}$ (IT3) to $\text{CH}_2=\text{CH}\dot{\text{C}}\text{H}_2+\text{HCHO}$ (PT1) with a barrier of only 9.3 kcal/mol. However, the cyclization reaction from $\text{CH}_2=\text{CHCH}_2\dot{\text{C}}\text{HOH}$ (IT2) to IT7 is rather important with a barrier of only 17 kcal/mol, which is 15.3 kcal/mol lower than the most dominating reaction, the H-transfer reaction from $\text{CH}_2=\text{CHCH}_2\dot{\text{C}}\text{HOH}$ (IT2) to $\dot{\text{C}}\text{H}=\text{CHCH}_2\text{CH}_2\text{OH}$ (IT5). More importantly, IT7 is also a significant intermediate for cyclization reactions in central addition of $\dot{\text{O}}\text{H}$ to 1,3-butadiene. It should be considered as an important intermediate connecting two entrance channels. The subsequent reaction of IT7 will be discussed in the central addition part. Finally, the reaction from $\text{CH}_2=\text{CHCH}_2\dot{\text{C}}\text{HOH}$ (IT2) to IT8 (barrier height: 33.6 kcal/mol) is 16.6 kcal/mol higher than the cyclization reaction from $\text{CH}_2=\text{CHCH}_2\dot{\text{C}}\text{HOH}$ (IT2) to IT7. According to the barrier height, the subsequent decomposition reactions for IT6, IT8, IT9, IT10 are not considered for their relatively higher barrier.

3.2 Central addition

β -scission/Isomerization. Regarding to the central addition, the most dominating reaction will be H-transfer

reaction to $\dot{\text{C}}\text{H}=\text{CHCH}(\text{OH})\text{CH}_3$ (IC5) from $\text{CH}_2=\text{CHCH}(\text{OH})\dot{\text{C}}\text{H}_2$ (IC1), whose barrier height is 27.4 kcal/mol, which means $\dot{\text{C}}\text{H}=\text{CHCH}(\text{OH})\text{CH}_3$ (IC5) is an important intermediate. The reactions from $\text{CH}_2=\text{CHCH}(\text{OH})\dot{\text{C}}\text{H}_2$ (IC1) to $\text{CH}_2=\text{CH}\dot{\text{C}}(\text{OH})\text{CH}_3$ (IC2), $\text{CH}_2=\text{CHCH}\dot{\text{O}}\text{CH}_3$ (IC3) and $\text{CH}_2=\text{CHC}(\text{OH})=\text{CH}_2+\dot{\text{H}}$ (PC4) (barrier height: from 30.6 to 31.0 kcal/mol) are also important. The SPE for $\text{CH}_2=\text{CH}\dot{\text{C}}(\text{OH})\text{CH}_3$ (IC2) is rather low, which means $\text{CH}_2=\text{CH}\dot{\text{C}}(\text{OH})\text{CH}_3$ (IC2) is a more stable intermediate. The barrier heights for reactions from $\text{CH}_2=\text{CH}\dot{\text{C}}(\text{OH})\text{CH}_3$ (IC2) to $\text{CH}_2=\dot{\text{C}}\text{H}+\text{CH}_3\text{CHO}$ (PC2), $\text{CH}_2=\text{CHCH}\dot{\text{O}}\text{CH}_3$ (IC3) and $\text{CH}_2=\text{CHC}(\text{OH})=\text{CH}_2+\dot{\text{H}}$ (PC4) (barrier height: 45.1, 46.3 and 49.1 kcal/mol) is relatively lower, comparing the other reactions which are even higher. The dominating reaction from $\text{CH}_2=\text{CHCH}\dot{\text{O}}\text{CH}_3$ (IC3) is the bimolecular reaction to $\text{CH}_2=\text{CHCHO} + \dot{\text{C}}\text{H}_3$ (PC1) for barrier heights of only 12.8 kcal/mol. The other reaction from $\text{CH}_2=\text{CHCH}\dot{\text{O}}\text{CH}_3$ (IC3) are also important for barrier heights of 17.3 to 23.1 kcal/mol, relatively lower comparing to other intermediate, which means $\text{CH}_2=\text{CHCH}\dot{\text{O}}\text{CH}_3$ (IC3) is a significant intermediate in the reaction system, just like the discussion in the terminal addition part. The dominating reaction from $\text{CH}_2=\dot{\text{C}}\text{HCH}(\text{OH})\text{CH}_3$ (IC4) is the bimolecular reaction to $\text{CH}_2=\text{C}=\text{CHOH}+\dot{\text{C}}\text{H}_3$ (PC7) (barrier height: 34.8 kcal/mol). The dominating reaction from $\dot{\text{C}}\text{H}=\text{CHCH}(\text{OH})\text{CH}_3$ (IC5) is the bimolecular reaction to $\text{CH}\equiv\text{CH}+\text{CH}_3\dot{\text{C}}\text{HOH}$ (PC5) (barrier height: 29.0 kcal/mol). In addition, it should be mentioned that M062X[18] method is employed for one reaction channel, from $\text{CH}_2=\text{CH}\dot{\text{C}}(\text{OH})\text{CH}_3$ (IC2) to $\text{CH}_2=\text{CHC}(\text{OH})=\text{CH}_2+\dot{\text{H}}$ (PC4), which could not converge using BH&HLYP. The reaction using M062X is marked by *.

Cyclization reactions. The cyclization reactions from $\text{CH}_2=\text{CHCH}(\text{OH})\dot{\text{C}}\text{H}_2$ (IC1) to IT7 (barrier height: 10.8 kcal/mol) is rather important, as it is mentioned in the terminal addition part. It is 16.6 kcal/mol lower than the most dominating reaction, H-transfer reaction to $\dot{\text{C}}\text{H}=\text{CHCH}(\text{OH})\text{CH}_3$ (IC5) from $\text{CH}_2=\text{CHCH}(\text{OH})\dot{\text{C}}\text{H}_2$ (IC1), whose barrier height is 27.4 kcal/mol. About the reaction from IT7, the reaction from IT7 to PT71 has a rather high barrier for 50.9 kcal/mol. The cyclization reactions from $\text{CH}_2=\text{CH}\dot{\text{C}}(\text{OH})\text{CH}_3$ (IC2) to IC8 (barrier height: 50.6 kcal/mol) has a relatively low barrier, whose barrier height is 5.5 kcal/mol higher than the most dominating reaction $\text{CH}_2=\text{CH}\dot{\text{C}}(\text{OH})\text{CH}_3$ (IC2) to $\text{CH}_2=\dot{\text{C}}\text{H}+\text{CH}_3\text{CHO}$ (PC2). About the subsequent reaction from IC8, the reaction from IC8 to PC81, PC82, PC83 all have a rather high barrier for 43.0, 46.2, 46.3 kcal/mol. Note that the reactions from IT7 to PT71, IC8 to PC81, PC82, PC83 have similar reaction type, which

is $\dot{\text{H}}$, $\dot{\text{O}}\text{H}$, or $\dot{\text{C}}\text{H}_3$ dissociated from three-membered ring to form unsaturated three-membered ring. According to their similar reaction process and similar high barrier heights, we could draw the conclusion that these types of reactions could be ignored in the subsequent chemical reaction kinetics calculations.

However, the ring opening reaction is a relatively important reaction type according to our work. The cyclization reactions from $\text{CH}_2=\text{CHCH}\dot{\text{O}}\text{CH}_3$ (IC3) to IC9 (barrier height: 5.0 kcal/mol) is rather important, it is 7.8 kcal/mol lower than the most dominating reaction, the bimolecular reaction to $\text{CH}_2=\text{CHCHO}+\dot{\text{C}}\text{H}_3$ (PC1) for 12.8 kcal/mol. About the subsequent reaction from IC9, the ring opening reaction from IC9 to IC11 has a relatively low barrier for 13.3 kcal/mol. The bimolecular reaction from IC11 to PC92 and PC2 has a barrier for 38.8 and 31.1 kcal/mol. According to the barrier height, the subsequent reactions for IC7, IC10 are not considered for their relatively higher barrier.

In addition, the four-membered ring and five-membered ring formation are relatively unimportant comparing to three-membered ring formation for both terminal addition and central addition, according to their relatively higher barrier.

4 CONCLUSION

The important reactions of 1,3-butadiene and $\dot{\text{O}}\text{H}$ radical and their subsequent reactions have been investigated in this work. The geometry optimizations and vibrational frequency are calculated at BH&HLYP/6-311++G(d,p) level of theory. Stationary points on the potential energy surface of $\text{C}_4\text{H}_7\text{O}$ which is related to the primary reactions are calculated using ROCCSD(T)/ CBS and G4 methods.

A van der Waals complex (COM) formed by $\dot{\text{O}}\text{H}$ radical with 1,3-butadiene is found, which is 1.9 kcal/mol lower than $\text{C}_4\text{H}_6+\dot{\text{O}}\text{H}$ in SPE. According to the results internal rotation treatment of the CC-CC dihedral angle, SPE in this work are calculated based on the lowest energy conformer when it involves more than one possible conformer.

Based on the comparison of barrier heights, terminal addition is the dominating pathway, $\text{CH}_2=\text{CHCH}_2\text{CH}_2\dot{\text{O}}$ (IT3) and $\text{CH}_2=\text{CHCH}\dot{\text{O}}\text{CH}_3$ (IC3) are two important intermediates, and $\text{CH}_2=\text{CHCHO}+\dot{\text{C}}\text{H}_3$, $\text{CH}_2=\text{CH}\dot{\text{C}}\text{H}_2+\text{HCHO}$ are important bimolecular products, and $\text{CH}_2=\text{CH}\dot{\text{C}}(\text{OH})\text{CH}_3$ (IC2) is the most stable intermediate for rather low barrier height.

A significant three-membered ring intermediate (IT7) is found in both terminal and central addition. The cyclization reactions from $\text{CH}_2=\text{CHCH}\dot{\text{O}}\text{CH}_3$ (IC3) to IC9 is rather important. The ring opening reaction is also

a relatively important reaction type, the reaction from IC9 to IC11 has a relatively low barrier.

The calculated kinetics of the title reaction will provide better understanding of the 1,3-butadiene oxidation in their model development.

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Kinetics of $\dot{\text{O}}\text{H}$ Radical Addition to 1,3-Butadiene and Related Reactions on the $\dot{\text{C}}_4\text{H}_7\text{O}$ Potential Energy Surface

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ABSTRACT

The chemical reaction kinetics of 1,3-butadiene is significant to understand the role of polyunsaturated hydrocarbons in combustion and soot formation. The important reactions of 1,3-butadiene and $\dot{\text{O}}\text{H}$ radical and their subsequent reactions have been investigated in this work. The geometry optimizations and vibrational frequency are calculated at BH&HLYP/6-311++G(d,p) level of theory. Electronic energy for stationary points on the potential energy surface related to the primary reactions are calculated at ROCCSD(T)/CBS and G4 level of theory. Discussion of the different configurations of trans and cis structures for reactants and intermediates are also given. Based on the comparison of barrier heights, terminal addition is the dominating pathway, $\text{CH}_2=\text{CHCH}_2\text{CH}_2\dot{\text{O}}$ and $\text{CH}_2=\text{CHCH}\dot{\text{O}}\text{CH}_3$ are two important intermediates, and $\text{CH}_2=\text{CHCHO} + \dot{\text{C}}\text{H}_3$, $\text{CH}_2=\text{CH}\dot{\text{C}}\text{H}_2 + \text{HCHO}$ are important bimolecular products. A significant three-membered ring intermediate (IT7) is found in both terminal and central addition. Pressure- and temperature-dependent rate constants and thermodynamic properties for the $\dot{\text{O}}\text{H}$ radical addition to 1,3-butadiene will also be investigated. The calculated kinetics and thermodynamics properties of the title reaction will be helpful to understand the 1,3-butadiene oxidation in their model development.

1 INTRODUCTION

1,3-butadiene is a significant intermediate which involves the soot formation and benzene formation.[1] Therefore, the correct understanding of the oxidation chemistry is the basis of the development of kinetic model. The importance of the reaction of 1,3-butadiene at the low temperature have been investigated by Zhou et al [2]. According to the Brute-force sensitivity analysis of 1,3-butadiene, the addition reaction of 1,3-butadiene and $\dot{\text{O}}\text{H}$ plays a very important role when temperature is lower than 870K. Thus, a comprehensive investigation on the key addition reaction of $\dot{\text{O}}\text{H}$ radical to 1,3-butadiene is important to have a better understanding of the oxidation chemistry of 1,3-butadiene at low temperatures.

Rate constants for the reaction of 1,3-butadiene and $\dot{\text{O}}\text{H}$ has been investigated mainly by experiments. Llyod et al.[3] carried out irradiations of the HC- NO_x -air system in an all-glass (Pyrex) chamber and measured the rate constant to be $(7.45 \pm 1.45) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 305 K. Atkinson et al.[4] measured the rate constant at 100 Torr in Ar over a temperature range of 299-424 K employing a flash photolysis-resonance fluorescence technique, derived an Arrhenius expression of $k_1^{\text{II}}(T) = 1.45 \times 10^{-11} \exp[(930 \pm 300)/RT] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 50 Torr in argon between 299 and 424 K. Liu et al.[5] also measured the rate constant at 1 atm in Ar at 305-1173 K using resonance fluorescence technique, obtaining an

Arrhenius expression of $k_1^{\text{II}}(T) = (1.4 \pm 0.1) \times 10^{-11} \exp[(440 \pm 40)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ between 313 and 623 K and a rate constant of $(6.1 \pm 0.6) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 313 K. The kinetics of the reaction of hydroxyl radical with 1,3-butadiene at 240-340 K and a total pressure of 1 Torr has been studied employing the discharge flow and mass spectrometer technique by Li et al. [6]. They also obtained an Arrhenius expression of $k_1^{\text{II}}(T) = (1.58 \pm 0.07) \times 10^{-11} \exp[(436 \pm 13)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 1 Torr between 240 and 340 K. The rate constants for the reaction of the $\dot{\text{O}}\text{H}$ radical with 1,3-butadiene and its deuterated isotopomer has been measured at 1-6 Torr total pressure at 263-423 K using the discharge flow system coupled with resonance fluorescence/laser-induced fluorescence detection of $\dot{\text{O}}\text{H}$ by Vimal et al. [7]. An Arrhenius expression for this reaction was determined to be $k_1^{\text{II}}(T) = (7.23 \pm 1.2) \times 10^{-11} \exp[(664 \pm 49)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 263-423 K. The reaction was studied behind reflected shock waves over the temperature range of 1011-1406 K and at pressures near 2.2 atm by Vasu et al. [8].

There are few theoretical work for the reaction of 1,3-butadiene and $\dot{\text{O}}\text{H}$. Li et al. [6] investigated title entrance reaction including terminal addition and central addition pathways using MP2/6-311++G(d,p) method. Optimized geometry of reactants, products and transition states are given. Total electronic energy, ZPE and vibrational frequencies of title entrance species involved in reactions are also calculated. However, rate constants based on their potential energy surface has not been provided in their work. Vasu et al. [8] calculated a series of rate coefficients of part of reactions applying variational transition state theory based on QCISD(T)/cc-pV ∞ Z//B3LYP/6-311++G(d,p).

The comprehensive reaction kinetics of $\dot{\text{O}}\text{H}$ radical addition to 1,3-butadiene and related reactions have not been investigated extensively. Moreover, the important intermediates and bimolecular products of this reaction have not been verified as well. Thus, further theoretical investigation on the title reaction kinetics is important to understand the chemical kinetics of 1,3-butadiene oxidation especially at low temperatures. This work provides all the possible pathways in the reaction system and completed potential energy surface employing high level ab initio calculations.

2 METHODOLOGY

The BH&HLYP [9] method with the 6-311++G(d,p) [10, 11] basis set is employed to fully optimize the geometries of the van der Waals complex, reactants, intermediates, transition states, and products. The zero-point vibrational energy corrections (ZPE) were calculated at the same level of theory. In addition,

vibration frequency calculations are also carried out to verify the existence of transition states with one and only one imaginary frequency. The intrinsic reaction coordinate (IRC) calculations are employed to guarantee that the transition states are connecting the right minima between a specific pair of stationary points. Single-point energies of all species are obtained by the ROCCSD(T) method with basis set cc-PVQZ [12]. ROCCSD(T) with cc-pVTZ is also used to complete the basis set limit (CBS) [13].

$$E_{\text{CBS}} = E_{\text{ROCCSD(T)/cc-pVQZ}} + (E_{\text{ROCCSD(T)/cc-pVQZ}} - E_{\text{ROCCSD(T)/cc-pVTZ}}) * 4^4 / (5^4 - 4^4)$$

Comparing with ROCCSD(T) method, G4 [14] method is much less expensive when dealing with single point energies. Thus, in this work, G4 method is also used in the single point energies calculation for all stationary points for comparison. All of the geometries optimization and single point energies are performed with Molpro program [15] and Gaussian 09 [16].

3 RESULT

Schematic diagram of $\dot{\text{O}}\text{H}$ radical addition to 1,3-butadiene and related reactions are shown in Scheme 1, Scheme 2 and Scheme 3. Potential energy surface (PES) of $\dot{\text{O}}\text{H}$ and 1,3-butadiene is shown in Figure 1 and Figure 2. The PES is very complex for the reaction system, including all possible pathways for association, abstraction, β -division, H-transfer and cyclization, which finally lead to bimolecular products. All the electronic energies for the reaction system are given, which include all the reactants, intermediates, transition states and products. Employing the results of scan of every stationary point, single point energy for each stationary point (SPE) is calculated based on the lowest energy conformer.

For the addition reactions, $\dot{\text{O}}\text{H}$ radical first may form a van der Waals complex (COM) with 1,3-butadiene, before it inserts into the C-C double bond to form either the intermediate $\text{CH}_2=\text{CH}\dot{\text{C}}\text{HCH}_2\text{OH}$ (IT1) or $\text{CH}_2=\text{CHCH}(\text{OH})\dot{\text{C}}\text{H}_2$ (IC1). The optimized geometrical parameters of the complex COM using BH&HLYP/6-311++G(d,p) method is given in Figure 3. The distance and angle performed in the Figure 3 is consistent with the result of the reaction between propene and $\dot{\text{O}}\text{H}$ investigated by Huynh et al. [17]. The SPE of complex COM is 1.9 kcal/mol lower than $\text{C}_4\text{H}_6 + \dot{\text{O}}\text{H}$. This could explain SPE for the TS of terminal addition is 1.6 kcal/mol lower than $\text{C}_4\text{H}_6 + \dot{\text{O}}\text{H}$. The existence of van der Waals complex COM may decline the barrier height for both terminal addition and central addition.

Scheme 1. $\dot{\text{O}}\text{H}$ radical terminal addition to 1,3-butadiene and related reactions

Scheme 2. $\dot{\text{O}}\text{H}$ radical central addition to 1,3-butadiene and related reactions

Scheme 3. Isomerization of $\dot{\text{C}}_4\text{H}_7\text{O}$ in terminal addition and central addition

Figure 1. The $\dot{\text{C}}_4\text{H}_7\text{O}$ potential energy surface (including ZPE) for the terminal addition of the $\dot{\text{O}}\text{H}$

radical. Energies are calculated using ROCCSD(T)/CBS and G4 method (in brackets), important reactions marked by bold lines.

Figure 2. The $\dot{\text{C}}_4\text{H}_7\text{O}$ potential energy surface (including ZPE) for the central addition of the $\dot{\text{O}}\text{H}$ radical. Energies are calculated using ROCCSD(T)/CBS and G4 method (in brackets), important reactions marked by bold lines.

Figure 3. The optimized geometry of the van der Waals complex COM (the unit for distance are Å and for angle is degree)

Figure 4. Internal rotor potential of the CC-CC dihedral angle for 1,3-butadiene. The energy is in kcal/mol.

Note that for all the C_4H_6 and $\dot{\text{C}}_4\text{H}_7\text{O}$ species in this paper involve two main structure, trans and cis. Trans-structure is normally lower in SPE, as shown in Figure 4. So we focus on the trans-structure mainly, nevertheless, there are some situations that cis-structure

have lower SPE than Trans-structure. Moreover, there are other special occasions that in one pathway, the structure of reactant and product are trans, however the transition state is cis, such as the reaction from $\text{CH}_2=\text{CHCH}_2\dot{\text{C}}\text{HOH}$ (IT2) to $\text{CH}_2=\text{CHCH}=\text{CHOH}+\dot{\text{H}}$ (PT3). These situations are all observed by the scanned calculations of every stationary point. According to the internal rotation potential of the CC-CC dihedral angles, the lowest energy conformer was used in the high level SPE calculation. When the species involves more than one possible conformers, both of the cis and trans structures will be generally included implicitly in the kinetic analysis through torsional treatments.

There are two initial reaction pathways of $\dot{\text{O}}\text{H}$ addition to 1,3-butadiene involving terminal addition and central addition, based on the symmetry of 1,3-butadiene.

The PES of these two pathways and subsequent reactions are given separately (Figure 1 and Figure 2). All the electronic energies are zero-point-corrected and relative energies to the primal reactants, the sum energies of 1,3-butadiene and $\dot{\text{O}}\text{H}$ radical. The PES for terminal addition includes 10 intermediates, 28 transition states, 8 bimolecular products, and it includes 11 intermediates, 31 transition states, 14 bimolecular products for the central addition. From the potential energy surface comparison shown in Figure 1 and Figure 2, we can get that the barrier for central addition is 3.0 kcal/mol higher than the terminal addition, which means the terminal addition is much more favored.

Subsequent β -scission/Isomerization and cyclization reactions for the two adducts formed from terminal and central addition will be discussed in the following section.

3.1 Terminal addition

β -scission/Isomerization. After the reaction of the terminal addition, the most dominating reaction will be bimolecular reaction to $\text{CH}_2=\text{CHCH}=\text{CHOH}+\dot{\text{H}}$ (PT3) from $\text{CH}_2=\text{CH}\dot{\text{C}}\text{HCH}_2\text{OH}$ (IT1), whose barrier height is 41.4 kcal/mol. Every intermediate of the terminal addition could isomerize to each other by H-transfer. The H-transfer reaction from $\text{CH}_2=\text{CH}\dot{\text{C}}\text{HCH}_2\text{OH}$ (IT1) to $\text{CH}_2=\text{CHCH}_2\dot{\text{C}}\text{HOH}$ (IT2) and $\text{CH}_2=\text{CHCH}_2\text{CH}_2\dot{\text{O}}$ (IT3) (barrier height: 46.8 kcal/mol and 43.6 kcal/mol) is also important. The reactions from $\text{CH}_2=\text{CH}\dot{\text{C}}\text{HCH}_2\text{OH}$ (IT1) to $\text{CH}_2=\dot{\text{C}}\text{CH}_2\text{CH}_2\text{OH}$ (IT4), $\dot{\text{C}}\text{H}=\text{CHCH}_2\text{CH}_2\text{OH}$ (IT5) and $\text{CH}\equiv\text{CCH}_2\text{CH}_2\text{OH}+\dot{\text{H}}$ (PT7) tend to be ignored with a barrier of more than 60 kcal/mol. The dominating reaction from $\text{CH}_2=\text{CHCH}_2\dot{\text{C}}\text{HOH}$ (IT2) is the H-transfer reaction to $\dot{\text{C}}\text{H}=\text{CHCH}_2\text{CH}_2\text{OH}$ (IT5) (barrier

height: 32.3 kcal/mol), the reaction from $\text{CH}_2=\text{CHCH}_2\dot{\text{C}}\text{HOH}$ (IT2) to $\text{CH}_2=\text{CHCH}_2\text{CH}_2\dot{\text{O}}$ (IT3), $\text{CH}_2=\text{CHCH}_2\text{CHO}+\dot{\text{H}}$ (PT2), $\text{CH}_2=\text{CHCH}=\text{CHOH}+\dot{\text{H}}$ (PT3) and $\text{CH}_2=\dot{\text{C}}\text{H}+\text{CH}_2=\text{CHOH}$ (PT5) are also important for barrier heights of 35.3 to 39.0 kcal/mol. The dominating reaction from $\text{CH}_2=\text{CHCH}_2\text{CH}_2\dot{\text{O}}$ (IT3) is the bimolecular reaction to $\text{CH}_2=\text{CH}\dot{\text{C}}\text{H}_2+\text{HCHO}$ (PT1) for barrier heights of only 9.3 kcal/mol. The other reaction from $\text{CH}_2=\text{CHCH}_2\text{CH}_2\dot{\text{O}}$ (IT3) are also important for barrier heights of 13.8 to 22.5 kcal/mol, relatively lower comparing to other intermediates, which means $\text{CH}_2=\text{CHCH}_2\text{CH}_2\dot{\text{O}}$ (IT3) is a significant intermediate in the reaction system. The dominating reaction from $\text{CH}_2=\dot{\text{C}}\text{CH}_2\text{CH}_2\text{OH}$ (IT4) is the bimolecular reaction to $\text{CH}_2=\text{C}=\text{CH}_2+\dot{\text{C}}\text{H}_2\text{OH}$ (PT4) (barrier height: 31.3kcal/mol). The dominating reaction from $\dot{\text{C}}\text{H}=\text{CHCH}_2\text{CH}_2\text{OH}$ (IT5) is the formation of the bimolecular products of $\text{CH}\equiv\text{CH}+\dot{\text{C}}\text{H}_2\text{CH}_2\text{OH}$ (PT6) (barrier height: 32.5kcal/mol).

Cyclization reactions. Cyclization reactions from $\text{CH}_2=\text{CH}\dot{\text{C}}\text{HCH}_2\text{OH}$ (IT1) and $\text{CH}_2=\text{CHCH}_2\text{CH}_2\dot{\text{O}}$ (IT3) tend to be unimportant. Barrier height for the reaction from $\text{CH}_2=\text{CH}\dot{\text{C}}\text{HCH}_2\text{OH}$ (IT1) to IT6 (barrier height: 50.3kcal/mol) is 8.9 kcal/mol higher than the most dominating reaction, which involves the formation of the bimolecular products of $\text{CH}_2=\text{CHCH}=\text{CHOH}+\dot{\text{H}}$ (PT3) from $\text{CH}_2=\text{CH}\dot{\text{C}}\text{HCH}_2\text{OH}$ (IT1). The reaction from $\text{CH}_2=\text{CHCH}_2\text{CH}_2\dot{\text{O}}$ (IT3) to IT9 (barrier height: 15.9kcal/mol) and IT10 (barrier height: 16.6kcal/mol) is 6.6 and 7.3 kcal/mol higher than the most dominating reaction, involving the formation of the bimolecular products from $\text{CH}_2=\text{CHCH}_2\text{CH}_2\dot{\text{O}}$ (IT3) to $\text{CH}_2=\text{CH}\dot{\text{C}}\text{H}_2+\text{HCHO}$ (PT1) with a barrier of only 9.3 kcal/mol. However, the cyclization reaction from $\text{CH}_2=\text{CHCH}_2\dot{\text{C}}\text{HOH}$ (IT2) to IT7 is rather important with a barrier of only 17 kcal/mol, which is 15.3 kcal/mol lower than the most dominating reaction, the H-transfer reaction from $\text{CH}_2=\text{CHCH}_2\dot{\text{C}}\text{HOH}$ (IT2) to $\dot{\text{C}}\text{H}=\text{CHCH}_2\text{CH}_2\text{OH}$ (IT5). More importantly, IT7 is also a significant intermediate for cyclization reactions in central addition of $\dot{\text{O}}\text{H}$ to 1,3-butadiene. It should be considered as an important intermediate connecting two entrance channels. The subsequent reaction of IT7 will be discussed in the central addition part. Finally, the reaction from $\text{CH}_2=\text{CHCH}_2\dot{\text{C}}\text{HOH}$ (IT2) to IT8 (barrier height: 33.6 kcal/mol) is 16.6 kcal/mol higher than the cyclization reaction from $\text{CH}_2=\text{CHCH}_2\dot{\text{C}}\text{HOH}$ (IT2) to IT7. According to the barrier height, the subsequent decomposition reactions for IT6, IT8, IT9, IT10 are not considered for their relatively higher barrier.

3.2 Central addition

β -scission/Isomerization. Regarding to the central addition, the most dominating reaction will be H-transfer

reaction to $\dot{\text{C}}\text{H}=\text{CHCH}(\text{OH})\text{CH}_3$ (IC5) from $\text{CH}_2=\text{CHCH}(\text{OH})\dot{\text{C}}\text{H}_2$ (IC1), whose barrier height is 27.4 kcal/mol, which means $\dot{\text{C}}\text{H}=\text{CHCH}(\text{OH})\text{CH}_3$ (IC5) is an important intermediate. The reactions from $\text{CH}_2=\text{CHCH}(\text{OH})\dot{\text{C}}\text{H}_2$ (IC1) to $\text{CH}_2=\text{CH}\dot{\text{C}}(\text{OH})\text{CH}_3$ (IC2), $\text{CH}_2=\text{CHCH}\dot{\text{O}}\text{CH}_3$ (IC3) and $\text{CH}_2=\text{CHC}(\text{OH})=\text{CH}_2+\dot{\text{H}}$ (PC4) (barrier height: from 30.6 to 31.0 kcal/mol) are also important. The SPE for $\text{CH}_2=\text{CH}\dot{\text{C}}(\text{OH})\text{CH}_3$ (IC2) is rather low, which means $\text{CH}_2=\text{CH}\dot{\text{C}}(\text{OH})\text{CH}_3$ (IC2) is a more stable intermediate. The barrier heights for reactions from $\text{CH}_2=\text{CH}\dot{\text{C}}(\text{OH})\text{CH}_3$ (IC2) to $\text{CH}_2=\dot{\text{C}}\text{H}+\text{CH}_3\text{CHO}$ (PC2), $\text{CH}_2=\text{CHCH}\dot{\text{O}}\text{CH}_3$ (IC3) and $\text{CH}_2=\text{CHC}(\text{OH})=\text{CH}_2+\dot{\text{H}}$ (PC4) (barrier height: 45.1, 46.3 and 49.1 kcal/mol) is relatively lower, comparing the other reactions which are even higher. The dominating reaction from $\text{CH}_2=\text{CHCH}\dot{\text{O}}\text{CH}_3$ (IC3) is the bimolecular reaction to $\text{CH}_2=\text{CHCHO} + \dot{\text{C}}\text{H}_3$ (PC1) for barrier heights of only 12.8 kcal/mol. The other reaction from $\text{CH}_2=\text{CHCH}\dot{\text{O}}\text{CH}_3$ (IC3) are also important for barrier heights of 17.3 to 23.1 kcal/mol, relatively lower comparing to other intermediate, which means $\text{CH}_2=\text{CHCH}\dot{\text{O}}\text{CH}_3$ (IC3) is a significant intermediate in the reaction system, just like the discussion in the terminal addition part. The dominating reaction from $\text{CH}_2=\dot{\text{C}}\text{HCH}(\text{OH})\text{CH}_3$ (IC4) is the bimolecular reaction to $\text{CH}_2=\text{C}=\text{CHOH}+\dot{\text{C}}\text{H}_3$ (PC7) (barrier height: 34.8 kcal/mol). The dominating reaction from $\dot{\text{C}}\text{H}=\text{CHCH}(\text{OH})\text{CH}_3$ (IC5) is the bimolecular reaction to $\text{CH}\equiv\text{CH}+\text{CH}_3\dot{\text{C}}\text{HOH}$ (PC5) (barrier height: 29.0 kcal/mol). In addition, it should be mentioned that M062X[18] method is employed for one reaction channel, from $\text{CH}_2=\text{CH}\dot{\text{C}}(\text{OH})\text{CH}_3$ (IC2) to $\text{CH}_2=\text{CHC}(\text{OH})=\text{CH}_2+\dot{\text{H}}$ (PC4), which could not converge using BH&HLYP. The reaction using M062X is marked by *.

Cyclization reactions. The cyclization reactions from $\text{CH}_2=\text{CHCH}(\text{OH})\dot{\text{C}}\text{H}_2$ (IC1) to IT7 (barrier height: 10.8 kcal/mol) is rather important, as it is mentioned in the terminal addition part. It is 16.6 kcal/mol lower than the most dominating reaction, H-transfer reaction to $\dot{\text{C}}\text{H}=\text{CHCH}(\text{OH})\text{CH}_3$ (IC5) from $\text{CH}_2=\text{CHCH}(\text{OH})\dot{\text{C}}\text{H}_2$ (IC1), whose barrier height is 27.4 kcal/mol. About the reaction from IT7, the reaction from IT7 to PT71 has a rather high barrier for 50.9 kcal/mol. The cyclization reactions from $\text{CH}_2=\text{CH}\dot{\text{C}}(\text{OH})\text{CH}_3$ (IC2) to IC8 (barrier height: 50.6 kcal/mol) has a relatively low barrier, whose barrier height is 5.5 kcal/mol higher than the most dominating reaction $\text{CH}_2=\text{CH}\dot{\text{C}}(\text{OH})\text{CH}_3$ (IC2) to $\text{CH}_2=\dot{\text{C}}\text{H}+\text{CH}_3\text{CHO}$ (PC2). About the subsequent reaction from IC8, the reaction from IC8 to PC81, PC82, PC83 all have a rather high barrier for 43.0, 46.2, 46.3 kcal/mol. Note that the reactions from IT7 to PT71, IC8 to PC81, PC82, PC83 have similar reaction type, which

is $\dot{\text{H}}$, $\dot{\text{O}}\text{H}$, or $\dot{\text{C}}\text{H}_3$ dissociated from three-membered ring to form unsaturated three-membered ring. According to their similar reaction process and similar high barrier heights, we could draw the conclusion that these types of reactions could be ignored in the subsequent chemical reaction kinetics calculations.

However, the ring opening reaction is a relatively important reaction type according to our work. The cyclization reactions from $\text{CH}_2=\text{CHCH}\dot{\text{O}}\text{CH}_3$ (IC3) to IC9 (barrier height: 5.0 kcal/mol) is rather important, it is 7.8 kcal/mol lower than the most dominating reaction, the bimolecular reaction to $\text{CH}_2=\text{CHCHO}+\dot{\text{C}}\text{H}_3$ (PC1) for 12.8 kcal/mol. About the subsequent reaction from IC9, the ring opening reaction from IC9 to IC11 has a relatively low barrier for 13.3 kcal/mol. The bimolecular reaction from IC11 to PC92 and PC2 has a barrier for 38.8 and 31.1 kcal/mol. According to the barrier height, the subsequent reactions for IC7, IC10 are not considered for their relatively higher barrier.

In addition, the four-membered ring and five-membered ring formation are relatively unimportant comparing to three-membered ring formation for both terminal addition and central addition, according to their relatively higher barrier.

4 CONCLUSION

The important reactions of 1,3-butadiene and $\dot{\text{O}}\text{H}$ radical and their subsequent reactions have been investigated in this work. The geometry optimizations and vibrational frequency are calculated at BH&HLYP/6-311++G(d,p) level of theory. Stationary points on the potential energy surface of $\text{C}_4\text{H}_7\text{O}$ which is related to the primary reactions are calculated using ROCCSD(T)/ CBS and G4 methods.

A van der Waals complex (COM) formed by $\dot{\text{O}}\text{H}$ radical with 1,3-butadiene is found, which is 1.9 kcal/mol lower than $\text{C}_4\text{H}_6+\dot{\text{O}}\text{H}$ in SPE. According to the results internal rotation treatment of the CC-CC dihedral angle, SPE in this work are calculated based on the lowest energy conformer when it involves more than one possible conformer.

Based on the comparison of barrier heights, terminal addition is the dominating pathway, $\text{CH}_2=\text{CHCH}_2\text{CH}_2\dot{\text{O}}$ (IT3) and $\text{CH}_2=\text{CHCH}\dot{\text{O}}\text{CH}_3$ (IC3) are two important intermediates, and $\text{CH}_2=\text{CHCHO}+\dot{\text{C}}\text{H}_3$, $\text{CH}_2=\text{CH}\dot{\text{C}}\text{H}_2+\text{HCHO}$ are important bimolecular products, and $\text{CH}_2=\text{CH}\dot{\text{C}}(\text{OH})\text{CH}_3$ (IC2) is the most stable intermediate for rather low barrier height.

A significant three-membered ring intermediate (IT7) is found in both terminal and central addition. The cyclization reactions from $\text{CH}_2=\text{CHCH}\dot{\text{O}}\text{CH}_3$ (IC3) to IC9 is rather important. The ring opening reaction is also

a relatively important reaction type, the reaction from IC9 to IC11 has a relatively low barrier.

The calculated kinetics of the title reaction will provide better understanding of the 1,3-butadiene oxidation in their model development.

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