Theoretical Kinetics Analysis for **OH** Radical Addition to 1,3-Butadiene and Related Reaction on the C₄H₇O 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 $\dot{O}H$ 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, CH₂=CHCH₂CH₂O and CH₂=CHCHOCH₃ are two important intermediates, and CH₂=CHCHO + $\dot{C}H_3$, CH₂=CHCH $\dot{C}H_2$ + HCHO are important bimolecular products. A significant three-membered ring intermediate (IT7) is found to be important in both terminal and central addition reactions. Pressure- and temperature-dependent rate constants and thermodynamic properties for the $\dot{O}H$ radical addition to 1,3-butadiene are also investigated using the Master Equation System Solver (MESS). 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]. According to the Brute-force sensitivity analysis of 1,3-butadiene, the addition reaction of 1,3-butadiene and OH plays a very important role when temperature is lower than 870K. Thus, a comprehensive investigation on the key addition reaction of OH radical to 1,3-butadien is important to have a better understanding of the oxidation chemistry of 1,3-butadiene at low temperatures[2].

Rate constants for the reaction of 1,3-butadiene and $\dot{O}H$ has been investigated mainly by experiments. 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. [3] They also obtained an Arrhenius expression of $k_1^{II}(T)=(1.58\pm0.07)\times10^{-11}\exp[(436\pm13)/T]$ cm³ molecule⁻¹ s⁻¹ at 1 Torr between 240 and 340 K. The rate constants for the reaction of the $\dot{O}H$ 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 $\dot{O}H$ by Vimal et al. [4]

There are few theoretical work for the reaction of 1,3-butadiene and $\dot{O}H$. Li et al.[3] 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. However, rate constants based on their potential energy surface has not been provided in their work.

The comprehensive reaction kinetics of OH 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

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is important to understand the chemical kinetics of 1,3-butadiene oxidation especially at low temperatures.

2. Computational methods

The BH&HLYP [5] method with the 6-311++G(d,p) [6] 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[7]. ROCCSD(T) with cc-pVTZ is also used to complete the basis set limit (CBS)[8].

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

Comparing with ROCCSD(T) method, G4 [9] 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 [10] and Gaussian 09 [11].

The Master Equation System Solver (MESS) was used to calculate temperature and pressure-dependent rate constants [12]. Rate constants for the reactions are obtained at temperatures ranging from 500 to 2000 K, and at pressures ranging from 0.01 to 100 atm. The interaction between the reactant and N₂ bath gas was modeled employing the Lennard-Jones (L-J) potential [13]. For N₂, $\sigma = 3.6$ Å and $\varepsilon = 68$ cm⁻¹ were used, while for \dot{C}_4H_7O , $\sigma = 5.916$ Å and $\varepsilon = 308.3$ cm⁻¹ were used [14]. A single-parameter exponential down model with $<\Delta E > down = 200 \times (T/300)^{0.75}$ cm⁻¹ was used to represent the collisional energy transfer function, which has served as a fairly good model for C3, C4 hydrocarbons [15].The calculated rate constants will be fitted to a modified Arrhenius expression as a function of temperature: k=ATⁿ exp(-E/RT).

3. Result and discussion

Potential energy surface (PES) of $\dot{O}H$ and 1,3-butadiene is shown in Figure 1 and Figure 3. 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. 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, $\dot{O}H$ 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 CH₂=CHĊHCH₂OH (IT1) or CH₂=CHCH(OH)ĊH₂ (IC1). The optimized geometrical parameters of the complex COM using BH&HLYP/6-311++G(d,p) method is given in Figure 2. The distance and angle performed in the Figure 2 is consistent with the result of the reaction between propene and $\dot{O}H$ investigated by Huynh et al. [16] The SPE of complex COM is 1.9 kcal/mol lower than C₄H₆+ $\dot{O}H$. This could explain SPE for the TS of terminal addition is 1.6 kcal/mol lower than C₄H₆+ $\dot{O}H$. The existence of van der Waals complex COM may decline the barrier height for both terminal addition and central addition.



Figure 1. The \dot{C}_4H_7O potential energy surface (including ZPE) for the terminal addition of the $\dot{O}H$ radical. Energies are calculated using ROCCSD(T)/CBS and G4 method (in brackets), important reactions marked in bold (unit kcal/mol).



Figure 3. The \dot{C}_4H_7O potential energy surface (including ZPE) for the central addition of the $\dot{O}H$ radical. Energies are calculated using ROCCSD(T)/CBS and G4 method (in brackets), important reactions marked in bold (unit kcal/mol).



Figure 2. The optimized geometry of the van der Waals complex COM

Figure 4. Internal rotor potential of the CC–CC dihedral angle for 1,3-butadiene.

It should be noted that for all the C₄H₆ and \dot{C}_4 H₇O 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. 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. It also should be noted that some H-transfer and cyclization reactions are feasible starting from cis isomers that are not feasible for the trans isomers, such as the reaction from CH₂=CHCH₂ĊHOH (IT2) to CH=CHCH₂CH₂OH (IT5). In these cases, only cis-structure is considered.

There are two initial reaction pathways of OH addition to 1,3-butadiene involving terminal addition and central addition, based on the symmetry of 1,3-butadiene.

 $CH_2=CHCH=CH_2+\dot{O}H\longleftrightarrow CH_2=CH\dot{C}HCH_2OH$

 $CH_2=CHCH=CH_2+\dot{O}H \leftrightarrow CH_2=CHCH(OH)\dot{C}H_2$

The PES of these two pathways and subsequent reactions are given separately (Figure 1 and Figure 3). All the electronic energies are zero-point-corrected and relative energies to the primal reactants, the sum energies of 1,3-butadiene and OH 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 3, 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 CH₂=CHCH=CHOH+H (PT3) from CH₂=CHCHCH₂OH (IT1), whose barrier height is 41.4 kcal/mol. Every intermediate of the terminal addition could isomerize to each other by H-

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transfer. The H-transfer reaction from CH2=CHCH2OH (IT1) to CH2=CHCH2CHOH (IT2) and CH₂=CHCH₂CH₂O (IT3) (barrier height: 46.8 kcal/mol and 43.6 kcal/mol) is also important. The reactions from CH₂=CHCHCH₂OH (IT1) to CH₂=CCH₂CH₂OH (IT4), CH=CHCH₂CH₂OH (IT5) and CH=CCH₂CH₂OH+H (PT7) tend to be ignored with a barrier of more than 60 kcal/mol. Cyclization reactions. Cyclization reactions from CH₂=CHCHCH₂OH (IT1) and CH₂=CHCH₂CH₂O (IT3) tend to be unimportant. Barrier height for the reaction from CH₂=CHCHCH₂OH (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 CH₂=CHCH=CHOH+H (PT3) from CH₂=CHCHCH₂OH (IT1). The reaction from CH₂=CHCH₂CH₂O (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 CH₂=CHCH₂CH₂O (IT3) to CH₂=CHCH₂+HCHO (PT1) with a barrier of only 9.3 kcal/mol. However, the cyclization reaction from CH₂=CHCH₂CHOH (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 CH₂=CHCH₂CHOH (IT2) to CH=CHCH₂CH₂OH (IT5). More importantly, IT7 is also a significant intermediate for cyclization reactions in central addition of OH to 1,3-butadiene, hence 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 CH₂=CHCH₂CHOH (IT2) to IT8 (barrier height: 33.6 kcal/mol) is 16.6 kcal/mol higher than the cyclization reaction from CH₂=CHCH₂CHOH (IT2) to IT7. The subsequent decomposition reactions for IT6, IT8, IT9, IT10 are not considered because of 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 CH=CHCH(OH)CH₃ (IC5) from CH₂=CHCH(OH)CH₂ (IC1), whose barrier height is 27.4 kcal/mol, which means CH=CHCH(OH)CH3 (IC5) is an important intermediate. The reactions from $CH_2 = CH\dot{C}(OH)CH_3$ CH₂=CHCHOCH₃ CH₂=CHCH(OH)CH₂ (IC1) to (IC2), (IC3)and CH₂=CHC(OH)=CH₂+H (PC4) (barrier height: from 30.6 to 31.0 kcal/mol) are also important. The SPE for $CH_2=CH\dot{C}(OH)CH_3$ (IC2) is rather low, which means $CH_2=CH\dot{C}(OH)CH_3$ (IC2) is a more stable intermediate. The dominating reaction from CH2=CHCHOCH3 (IC3) is the bimolecular reaction to CH₂=CHCHO + CH₃ (PC1) for barrier heights of only 12.8 kcal/mol. In addition, it should be mentioned that M062X[17] method is employed for one reaction channel, from CH₂=CHC(OH)CH₃ (IC2) to $CH_2=CHC(OH)=CH_2+\dot{H}(PC4)$, which could not converge using BH&HLYP. The reaction using M062X is marked by *.

Cyclization reactions. The cyclization reactions from CH₂=CHCH(OH)CH₂(IC1) to IT7 with barrier height of 10.8 kcal/mol is rather important, as has been mentioned in the terminal addition part. Its barrier is 16.6 kcal/mol lower than the important reaction which is H-transfer reaction to CH=CHCH(OH)CH₃(IC5) from CH₂=CHCH(OH)ĊH₂ (IC1) with barrier height of 27.4 kcal/mol. For the reaction from IT7, the reaction from IT7 to PT71 has a rather high barrier for 50.9 kcal/mol. The cyclization reactions from CH₂=CHĊ(OH)CH₃ (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 from CH₂=CHC(OH)CH₃ (IC2) to CH_2 =CH+CH₃CHO (PC2). The subsequent reaction from IC8 to PC81, PC82, PC83 all have rather high barriers of 43.0, 46.2, 46.3 kcal/mol. It should be noted that the reactions from IT7 to PT71, IC8 to PC81, PC82, PC83 have similar reaction process, which is H, $\dot{O}H$, or $\dot{C}H_3$ 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 CH₂=CHCHOCH₃ (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 CH₂=CHCHO+CH₃ (PC1) for 12.8 kcal/mol. 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

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for 38.8 and 31.1 kcal/mol. 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.

Temperature and pressure-dependent rate constants will be calculated using the Master Equation System Solver (MESS). The calculated rate constants will be fitted to a modified Arrhenius expression as a function of temperature: $k=AT^n \exp(-E/RT)$. We will further determine the title reaction pathways and title products in different pressure and temperature by the results of Temperature and pressure-dependent rate constants. The parameters A, n and E determined by fit results will be provided. Then we will include parameters A, n and E of these channels in models and make comparison between the models with and without these channels. We will also compare the models with these channels with the experimental results. The calculated kinetics of the title reactions will improve the prediction ability of the models.

4. CONCLUSION

The important reactions of 1,3-butadiene and $\dot{O}H$ 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 \dot{C}_4H_7O which is related to the primary reactions are calculated using ROCCSD(T)/ CBS and G4 methods.

A van der Waals complex (COM) formed by $\dot{O}H$ radical with 1,3-butadiene is found, which is 1.9 kcal/mol lower than C₄H₆+ $\dot{O}H$ 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, $CH_2=CHCH_2CH_2\dot{O}$ (IT3) and $CH_2=CHCH\dot{O}CH_3$ (IC3) are two important intermediates, and $CH_2=CHCHO+\dot{C}H_3$, $CH_2=CH\dot{C}H_2+HCHO$ are important bimolecular products, and $CH_2=CH\dot{C}(OH)CH_3$ (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 with a low barrier height. The cyclization reactions from CH_2 =CHCHOCH₃ (IC3) to IC9 is rather important. The ring opening reaction is also a relatively important reaction process, the reaction from IC9 to IC11 has a relatively low barrier. Temperature and pressure-dependent rate constants will be calculated using the Master Equation System Solver (MESS). The parameters A, n and E determined by fit results will be provided. By including the rate constants results in models, the calculated kinetics of the title reactions will provide better understanding of the 1,3-butadiene oxidation in their model development.

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