Theoretical Kinetics Study on the Reactions of 1,3-butadiene + HO₂

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Abstract

The reaction system of 1,3-butadiene + $\dot{HO_2}$ was investigated in this study. Electronic chemical calculations were carried out on possible entrance channels and subsequent reaction paths for 1,3-butadiene + $\dot{HO_2}$, at ROCCSD(T)/CBS//BHandHLYP/6-311++G(d,p) level of theory. Potential energy surfaces (PES) were obtained based on the zero-point corrected relative energies. It was found that $\dot{HO_2}$ addition to 1,3-butadiene forming C₄H₇1-OO3 and C₄H₆1-3OOH4 are two energetically favoured entrance channels. C₄H₇1-OO3 undergoes β -scission reaction to the formation of the bimolecular products C₄H₇1-3 and O₂, and C₄H₆1-3OOH4 undergoes the ring closure reaction to form the bimolecular products of C=C(CYCO) and \dot{O} H radical are the most important reaction pathways. Whilst, C₄H₆1-4OOH3 undergoing the cyclization reaction to form HOO(CYCC)C•, and C₄H₇1-OO4 cyclizing to (CYCOOC)C• and CYCOOCC• are the important products channels. The calculations of the rate constants for all reaction channels studied are underway.

1. Introduction

1,3-butadiene is an important unsaturated intermediate in the pyrolysis and oxidation of higher-order hydrocarbons, its oxidation chemistry plays a significant part in predicting poly-aromatic hydrocarbons (PAH) and soot formation in combustion process of hydrocarbons.

A number of experimental and modeling studies have been conducted on 1,3-butadiene chemistry. Laskin et al. [1] measured concentration profiles for some C_1 – C_4 species in 1,3-butadiene pyrolysis and oxidation over temperatures in the range of 1035–1185 K at 1 atm, using turbulent flow reactor. Libby et al. [2] carried out shock tube study on 1,3-butadiene oxidation. They conducted $\dot{O}H$ radical time history measurement while measuring ignition delay time at 1390–1810 K and 1.4–3.9 atm with equivalence ratio at 0.25, 0.5 and 1.0. Recently, Zhou et al. [3] measured ignition delay time in shock tube and rapid compression machine under temperature in 650–1780 K and pressure in 1–40 atm, which are engine-relevant conditions, and flame speeds at 1 and 5 atm at 295 K, 359 K and 399 K over a broad range of equivalence ratios. As concluded by Zhou et al. [3], the current model predicts most of the high-temperature 1,3-butadiene combustion characteristics well, however, model accuracy in capturing its low-temperature combustion chemistry still has room for improvement. Quantitative studies on low-temperature chemical kinetics for 1,3-butadiene oxidation are needed for developing a more applicable model. It was found that hydroperoxyl (H \dot{O}_2) radical addition to 1,3-butadiene and their subsequent reactions are sensitive at low to intermediate temperature range (600-900 K) [3], and are important in determining the fuel reactivity at such conditions.

Quite limited studies have been carried out in the literature directly focusing on the reaction system of 1,3butadiene + $H\dot{O}_2$. Miyoshi et al. [4] performed theoretical calculation to study 3-butenylperoxy (C₄H₇1-OO4) unimolecular reactions. They explored the 3-butenylperoxy potential energy surfaces, which are also

Zhu Y.

a part of the full potential energy surfaces for 1,3-butadiene + HO₂, at the CBS-QB3 level of theory, and conducted transition-state theory (TST) calculations to analyze the kinetics. The intramolecular reactions that forming five- or six-membered peroxide rings on the 3-butenylperoxy potential energy surfaces were found to be dominant based on their theoretical analyses. You et al. [5] studied the kinetics of heptenylperoxy radical, which is a bit larger yet similar to butenylperoxy radical, since they both are unsaturated alkenylperoxy radicals. Their results indicated the importance of intramolecular addition channel of heptenylperoxy radical, which forming five- or six-membered peroxide rings, at low temperatures. Theoretical studies on other alkene + HO₂ reaction systems can also give insight into the possible reaction channels between 1,3-butadiene and HO_2 radical and for the subsequent reaction pathways. Zador et al. [6] performed theoretical analyses on HO₂ addition to six alkenes including ethylene, propene, 1-butene, trans-2-butene, isobutene and cyclohexene. They suggested that, HO₂ addition to alkenes could lead to hydroperoxyalkyl ('QOOH) radicals and alkylperoxy (ROO') radicals. And the formation of alkylperoxy radical was concluded to be important at low temperatures. Note that alkenyl + O_2 were connected with the corresponding alkene $+ H\dot{O}_2$ on the same potential energy surfaces, the studies on alkenyl $+ O_2$ may provide inspirations for us. Lee et al. [7] reported the potential energy surfaces of allyl $+ O_2$ at the CBSQ//B3LYP/6-31G(d,p) level, with possible unimolecular reaction channels for the two adducts of allene + HO₂, C=CCOO' and C=C'COOH, illustrated as well. The subsequent unimolecular reaction channels for C=CCOO' and C=C'COOH were analogous to those for the adducts of 1.3-butadiene $+ H\dot{O}_2$.

In this study, we performed high-level ab initio calculations to investigate the reaction system of 1,3butadiene + $H\dot{O}_2$. Detailed reaction pathways were proposed, the geometries of reactants, transition states, intermediates and bimolecular products included were determined using electronic structure method. The electronic energies of these single-point geometries were calculated, and potential energy surfaces (PES) have been given, based on the calculated values, for $H\dot{O}_2$ addition to 1,3-butadiene and subsequent reaction paths. Rate coefficients for all reaction paths on the C₄H₇O₂ PES will be calculated via ab initio Transition State Theory (TST) method.

2 Computational Method

The BHandHLYP/6-311++G(d,p) method was used for geometry optimizations, vibrational frequency calculations and zero-point energy (ZPE) calculations, for all reactants, intermediates and bimolecular products involved. In order to ensure that each transition state (TS) was connected to the reactants and products desired, intrinsic reaction coordinate (IRC) calculations were also carried out at the BHandHLYP/6-311++G(d,p) level of theory. Internal rotations of molecules and TSs that correspond to low-frequency torsional modes were treated as hindered rotors. Such rotations were scanned in 5-degree increments at the BHandHLYP/6-31G(d) level of theory, to obtain relaxed potential energies as a function of dihedral angle. The global minima geometry located on the scanned potentials was used in single-point energy (SPE) calculations for each joint-structure TSs and species. The SPE from the ROCCSD(T)/cc-pVQZ and ROCCSD(T)/cc-pVTZ methodologies were obtained, and extrapolated to the complete basis set (CBS) SPE via formula: [8, 9]

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

 T_1 diagnostic [10] for all transition states and species were carried out at the ROCCSD(T)/cc-pVQZ level of theory. T_1 diagnostic ≤ 0.025 for reactant species and ≤ 0.03 for transition states indicate that single-reference methods are reliable in describing the wave function [11]. Additionally, for evaluating the effects of calculation method on the predicted single-point energy values, the methodologies of G4, G3, CBS-QB3

Zhu Y.

and CBS-APNO were also used to calculate the SPEs for reactants and some chosen stationary points of TSs and intermediates. Programs of Gaussian 09 [12] and Molpro 2015 [13] were used to carry out the electronic chemical calculations.

Master Equation System Solver (MESS) of the PAPR [14] program suite was used in rate constant calculations for $H\dot{O}_2$ addition to 1,3-butadiene and subsequent reaction channels. Rate constants for all reaction pathways were obtained at temperatures in the range of 298.15 to 2000 K, and at pressures in the range of 0.01 to 100 atm. Torsional modes at stationary points were treated as one-dimensional hindered rotors, with rotational potentials obtained at the BHandHLYP/6-31G(d) level of theory. For Lennard-Jones well depth ε and minimal interacting distance σ in the collisional model, $\varepsilon = 406.4980$ cm⁻¹ and $\sigma = 5.5471$ for C₄H₇O₂ from ref [15], and $\varepsilon = 68.0015$ cm⁻¹ and $\sigma = 3.610$ for bath gas N₂ from ref [16] were used. Temperature dependence of the average downward energy transferred per collision, $\langle \Delta E_d \rangle = 200 \times (T/300)^{0.75}$ [16].

3 Results and Discussion

3.1 Potential Energy Surfaces

Potential energy surfaces were given based on the calculation results we got, for entrance channels of $H\dot{O}_2$ addition to 1,3-butadiene and subsequent reaction paths. The PES from the ROCCSD(T)/CBS// BHandHLYP/6-311++G(d,p) electronic chemical calculations are depicted in Figure 1 Figure 2. Energies relative to reactants $C_4H_6 + H\dot{O}_2$ for all stationary points are illustrated.

Four entrance channels for $C_4H_6 + H\dot{O}_2$ were considered, namely, central $H\dot{O}_2$ directed addition channel, central $H\dot{O}_2$ concerted addition channel, terminal $H\dot{O}_2$ directed addition channel and terminal $H\dot{O}_2$ concerted addition channel. Among the four channels, terminal $H\dot{O}_2$ directed addition channel forming hydroperoxyalkenyl radical C_4H_6 1-300H4, and central $H\dot{O}_2$ concerted addition channel forming alkenylperoxy radical C_4H_7 1-0O3 were energetical favoured, while the energy barriers are 9.05 kcal/mol and 9.80 kcal/mol, respectively. And they were found to be the two competitive reaction pathways, since the energy barrier for the latter is only 0.75 kcal/mol higher.

PES for $H\dot{O}_2$ central addition channels and subsequent reaction pathways were illustrated in Figure 1, which contains 16 species and 11 transition states. The concerted $H\dot{O}_2$ adduct C_4H_71 -OO3 stays 16.07 kcal/mol below the reactants, it can then undergo β -scission reactions to bimolecular products C_4H_71 -3 and O_2 , the binding energy is 19.29 kcal/mol and is the lowest among those for subsequent reaction channels for C_4H_71 -OO3. C_4H_71 -OO3 can undergo H-atom transfer reactions and intramolecular peroxyl addition to C=C bond as well, yet these channels are of minor importance, since the most energetically favoured one of them still has an ~10 kcal/mol higher barrier than the β -scission one does. Barrier for the isomerization reaction between C_4H_71 -OO3 and C_4H_61 -4OOH3 from the C_4H_71OO3 side is 6.58 kcal/mol higher the barrier for the β -scission one. For the adduct C_4H_61 -4OOH3, the intramolecular methyl addition to C=C bond forming HOO(CYCC)C⁺, and the ring closure reaction forming (CYOC)C=C and $\dot{O}H$ radical are the two competitive channels. They are more important compared to the other reaction paths for C_4H_61 -4OOH3.



Figure 1. ZPE corrected Potential energy surfaces at the ROCCSD(T)/CBS//BHandHLYP/6-311++G(d,p) level of theory for $C_4H_6 + H\dot{O}_2$ central addition channels and subsequent reactions (relative energies in units of kcal/mol)

PES containing 16 species and 12 transition states for $H\dot{O}_2$ terminal addition channels and subsequent reaction pathways were depicted in Figure 2. C_4H_61 -300H4 can undergo cyclization reactions to (C•YCC)COOH, bimolecular products C=C(CYCO) and $\dot{O}H$ radical, and bimolecular products CY=CCOC and $\dot{O}H$, respectively. It can also isomerize to C_4H_71 -OO4 and C_4H_71 -OO4, respectively. The ring closure reaction pathway leading to C=C(CYCO) and $\dot{O}H$ radical has the lowest barrier (19.23 kcal/mol). For concerted H \dot{O}_2 adduct C_4H_71 -OO4, the cyclization reactions forming (CYCOOC)C[•] and CYCOOCC[•] were found to be important, compare to other reaction channels for C_4H_61 -300H4.



Figure 2 ZPE corrected Potential energy surfaces at the ROCCSD(T)/CBS//BHandHLYP/6-311++G(d,p) level of theory for $C_4H_6 + H\dot{O}_2$ terminal addition channels and subsequent reactions (relative energies in units of kcal/mol)

3.2 Relative Energy Comparison

The calculated results for some chosen stationary points on the PES from the ROCCSD(T)/CBS level of theory were compared to those from the other methods in Table 1. Generally, among the energies obtained from the five different methods for the 7 stationary points, some of the energies are not consistent with each other, which need to be further investigated. The ROCCSD(T)/CBS level of theory always obtained the highest value, while the CBS-QB3 and CBS-APNO methods often produced a lower value and those calculated from G4 and G3 were in the middle. Miyoshi et al. [4] obtained the energies at the CBS-QB3 level of theory, their results were illustrated in Table 1 as well. We obtained similar results as they provided in the paper when using the same method of CBS-QB3.

Table 1 Comparison of the calculated zero-point corrected electronic energies (relative to $C_4H_6 + H\dot{O}_2$) (in the unit of kcal/mol) for the chosen TSs and species.

Zhu Y.

1,3-butadiene + HO₂

TSs $C_4H_6+H\dot{O}_2 \leftrightarrow C_4H_71-OO3$ $C_4H_6+H\dot{O}_2 \leftrightarrow C_4H_61-4OOH3$ $C_4H_6+H\dot{O}_2 \leftrightarrow C_4H_6+H\dot{O}_2 $	C ₄ H ₇ 1-OO4
ROCCSD(T)/CBS 9.80 13.79 15.1 G4 9.34 12.95 12.95	2
G4 9.34 12.95 12.9	
3. 1200	96
G3 \ 13.26	
CBS-QB3 9.56 10.80 13	35
CBS-APNO 5.69 12.23 12.5	93
Miyoshi et al. \ 13.1	4
TSs $C_4H_6+H\dot{O}_2 \leftrightarrow C_4H_61-300H4$ $C_4H_71-004 \leftrightarrow C_4H_61-300H4$	
ROCCSD(T)/CBS 9.05 17.19	
G4 8.66 15.27	
G3 8.12 16.66	
CBS-QB3 5.94 12.77	
CBS-APNO 6.83	
Miyoshi et al. 5.73 11.95	
Species C ₄ H ₇ 1-OO4 C ₄ H ₆ 1-3OOH4	
ROCCSD(T)/CBS -12.93 -13.76	
G4 -14.62 -14.94	
G3 -14.05 -14.45	
CBS-QB3 -14.43 -15.76	
CBS-APNO -14.54 -14.59	
Miyoshi et al14.57 -15.77	

The computations of rate coefficients for all reaction channels studied are ongoing, and kinetically important pathways will be determined through branching ratio analyses. The detailed reaction mechanism and the PES for 1,3-butadiene+ $H\dot{O}_2$ will be refined based on the kinetics data we obtain, and the study on subsequent reaction paths for important intermediates will be fulfilled. And the model applications of the rate constants calculated will be discussed.

4 Conclusions

This was a first systematic investigation on the reaction system of 1,3-butadiene + H \dot{O}_2 . Through high-level ab initio calculations for H \dot{O}_2 addition to 1,3-butadiene and subsequent unimolecular reactions, potential energy surfaces at ROCCSD(T)/CBS// BHandHLYP/6-311++G(d,p) level of theory were obtained. It is concluded that, the H \dot{O}_2 directed addition to 1,3-butadiene forming C₄H₆1-3OOH4, and the H \dot{O}_2 concerted addition to 1,3-butadiene forming C₄H₆1-3OOH4, and the H \dot{O}_2 concerted addition to 1,3-butadiene forming C₄H₇1-OO3 are two energetically favoured entrance channels. They compete with each other. For central H \dot{O}_2 addition reactions and subsequent unimolecular reactions, C₄H₇1-OO3 undergoes β-scission reaction forming bimolecular products C₄H₇1-3 and O₂, and C₄H₆1-4OOH3 undergoes cyclization forming hydroperoxycycloalkyl radical HOO(CYCC)C• are energetically favoured. For terminal H \dot{O}_2 addition reactions and subsequent unimolecular reactions (CYCOOC)C• and CYCOOCC• are important.

The results we obtained here may provide a good implication for modellers who study 1,3-butadiene oxidation. Kinetics calculations based on the PES of 1,3-butadiene + $H\dot{O}_2$ will be performed, and kinetically favoured reaction pathways for 1,3-butadiene + $H\dot{O}_2$ will be determined.

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