

We thank all reviewers for the comments.

We received no revision requirements from the Reviewer 1.

Comments of the Reviewer 2:

1. The different channels in Figs. 1 and 2 can be hardly distinguished if the paper is printed in white and black.
2. A citation to the work of Miyoshi et al should be added in Table 1.
3. The language of the paper can be improved.

In order to address these comments, following changes were made in our revised paper:

1. Different reaction channels in Figures 1 and 2 were distinguished by the newly added texts in both figures, instead of colors.
2. Citation to the work of Miyoshi et al. in Table 1 was added.
3. The language of the paper was reviewed and polished.

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Theoretical Kinetics Study on HO₂ addition to 1,3-butadiene

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ABSTRACT

The reaction system of 1,3-butadiene + HO₂ was investigated in this study. Electronic chemical calculations were carried out on the entrance channels and subsequent reaction pathways for 1,3-butadiene + HO₂, at the 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 HO₂ addition to 1,3-butadiene forming C₄H₇1-OO3 and C₄H₆1-3OOH4 are two energetically favoured entrance channels. C₄H₇1-OO3 undergoing β-scission reaction to the formation of the bimolecular products C₄H₇1-3 and O₂, and C₄H₆1-3OOH4 undergoing the ring closure reaction to form the bimolecular products of C=C(CYCO) and OH radical are the most important reaction pathways. Whilst, C₄H₆1-4OOH3 undergoing the cyclization reaction to form (CYCC)C•, and C₄H₇1-OO4 cyclizing to (CYCOOC)C• and CYCOOCC•, are energetically favoured reaction channels.

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. (Laskin, et al., 2000) measured concentration profiles for some C1–C4 species in 1,3-butadiene pyrolysis and oxidation over temperature in the range of 1035–1185 K at 1 atm, using turbulent flow reactor. Libby et al. (Libby, et al., 2004) carried out shock tube study on 1,3-butadiene oxidation. They conducted OH 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. (Zhou, et al., 2018) 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., 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 (HO₂) radical addition to 1,3-butadiene and their subsequent reactions are sensitive at low to intermediate temperature range (600–900 K) (Zhou, et al., 2018), 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 1,3-butadiene + HO₂. Miyoshi et al. (Miyoshi, 2010) performed theoretical calculation to study 3-butenylperoxy (C₄H₇1-OO4) unimolecular reactions. They explored the 3-butenylperoxy potential energy surfaces, which are also 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. (You, et al., 2016) 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 HO₂ radical and for the subsequent reaction pathways. Zador et al. (Zador, et al., 2011) 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 hydroperoxyalkenyl (•QOOH) radicals and alkenylperoxy (ROO•) radicals. And the formation of alkenylperoxy radical was concluded to be important at low temperatures. Note that alkenyl + O₂ were connected with the corresponding alkene + HO₂ on the same potential energy surfaces, the studies on alkenyl + O₂ may provide inspirations for us. Lee et al. (Lee and Bozzelli, 2005) reported the potential energy surfaces of allyl + O₂ 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 + HO₂.

In this study, we performed high-level ab initio calculations to investigate the reaction system of 1,3-butadiene + HO₂. A detailed mechanism for this system has been proposed, the geometries of reactants, transition states, intermediates and bimolecular products included in the mechanism have been 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 1,3-butadiene plus HO₂ and subsequent reaction paths.

METHODOLOGY

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: (Momro, 1996; Feller and Dixon, 2001)

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

T1 diagnostic (Lee and Taylor, 1989) for all transition states and species were carried out at the ROCCSD(T)/cc-pVQZ level of theory. T1 diagnostic ≤ 0.025 for reactant species and ≤ 0.03 for transition states indicate that single-reference methods are reliable in describing the wave function (Klippenstein and Harding, 2009).

Additionally, for evaluating the effects of calculation method on the predicted single-point energy values, the methodologies of G4, G3, CBS-QB3 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 (Frisch, et al.) and Molpro 2015 (Werner, et al., et al., 2015) were used to carry out the electronic chemical calculations.

Reaction Paths for 1,3-butadiene + HO₂

Detailed reaction pathways for the reaction system of C₄H₆ + HO₂ have been illustrated in Figures 1 and 2. For entrance channels, two types of addition reactions between 1,3-butadiene and HO₂ radical have been taken into consideration. Hydroperoxyl (HO₂) radicals can add to the central or terminal carbon atom in 1,3-butadiene directly, forming 2-hydroperoxy-3-buten-1-yl (C₄H₆1-4OOH3) and resonantly stabilized 1-hydroperoxy-3-buten-2-yl (C₄H₆1-3OOH4) radicals. Alternatively, the concerted addition reaction can also happen, in which the H atom and O-O group in the HO₂ radicals add to the two carbon atoms of C-C double bond separately with O-H bond cleavage in HO₂ radicals, forming 3-butenyl-2-peroxy (C₄H₇1-OO3) radicals as the O-O group adds to the central carbon atom, and 3-butenyl-1-peroxy (C₄H₇1-OO4) radicals as the O-O group adds to the terminal carbon atom.

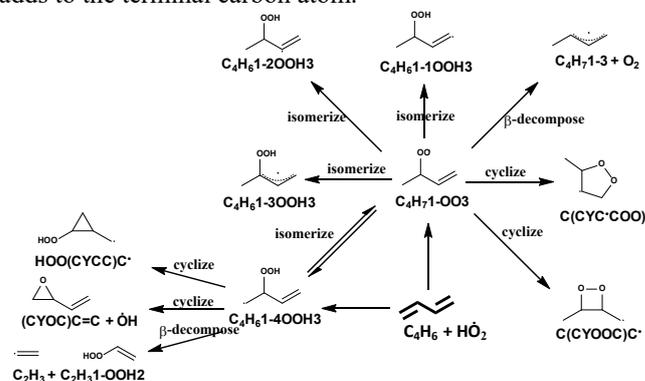


Figure 1. Central carbon addition channels and sub-mechanism for the adducts

In general, three possible reaction types have been taken into consideration for the sub-mechanisms of the initial adducts as depicted in Figures 1 and 2, which are:

- H-atom transfer reactions (isomerization) within molecules. For the C₄H₇1-OO3 radical, H atoms from the α site, two β sites and γ site can be abstracted by the peroxy radical forming hydroperoxyalkenyl radicals. For the C₄H₇1-OO4 radical, H atoms from the α site, β site, γ site and δ site can be abstracted by the peroxy radical forming hydroperoxyalkenyl radicals.

- Cyclization reactions. Hydroperoxyalkenyl radicals can undergo ring closure reaction, with O-O bond dissociation and C-O bond formation happened simultaneously, forming cyclic ether and $\dot{\text{O}}\text{H}$ radical. Besides, the methyl in hydroperoxyalkenyl radical can add to its C-C double bond, forming cycloalkyl radicals. The alkenylperoxy radicals can also undergo intramolecular addition reaction, in which the peroxy radical adds to the C-C double bond, forming cyclic peroxidealkyl radicals.
- β -scission reactions. β site C-C or C-O bonds of the species can break via β -scission.

Central addition reaction channels

As shown in Figure 1, the direct $\text{H}\dot{\text{O}}_2$ addition product $\text{C}_4\text{H}_6\text{1-4OOH3}$ can undergo two types of ring closure reactions forming cyclic ether $(\text{CYOC})\text{C}=\text{C}$ and $\dot{\text{O}}\text{H}$ radical, and hydroperoxycycloalkyl radical $\text{HOO}(\text{CYCC})\text{C}\cdot$, respectively. The concerted central addition product $\text{C}_4\text{H}_7\text{1-OO3}$ can isomerize to hydroperoxyalkenyl radicals, namely, $\text{C}_4\text{H}_6\text{1-1OOH3}$, $\text{C}_4\text{H}_6\text{1-2OOH3}$, $\text{C}_4\text{H}_6\text{1-3OOH3}$ and $\text{C}_4\text{H}_6\text{1-4OOH3}$, via H-atom transfer reactions. The concerted adduct $\text{C}_4\text{H}_7\text{1-OO3}$ can also dissociate directly to bimolecular products $\text{C}_4\text{H}_7\text{1-3}$ and O_2 . Moreover, $\text{C}_4\text{H}_7\text{1-OO3}$ can undergo intramolecular addition, forming cyclic peroxidealkyl radicals $\text{C}(\text{CYOOC}\cdot)$ and $\text{C}(\text{CYOOC})\text{C}\cdot$ ($\text{Y}=\text{cyclic}$).

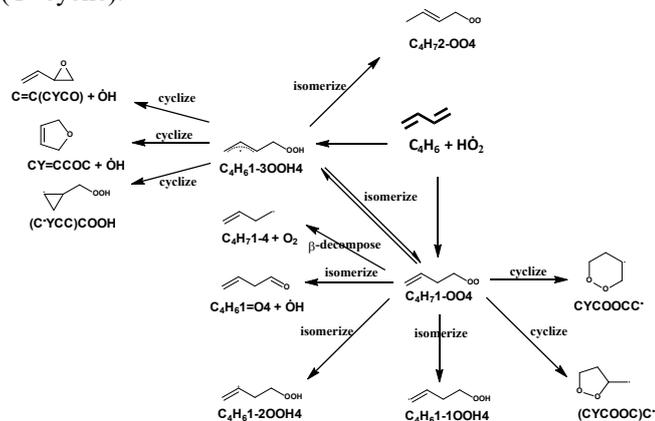


Figure 2. Terminal carbon addition channels and sub-mechanism for the adducts

Terminal addition reaction channels

As depicted in Figure 2, the resonantly stabilized direct $\text{H}\dot{\text{O}}_2$ addition product $\text{C}_4\text{H}_6\text{1-3OOH4}$ can form cyclic ethers $\text{C}=\text{C}(\text{CYCO})$ and $\text{CY}=\text{CCOC}$, respectively, and $\dot{\text{O}}\text{H}$ radicals via ring closure, and hydroperoxycycloalkyl radical $(\text{C}\cdot\text{YCC})\text{COOH}$ via intramolecular addition reaction. It can also undergo H-atom transfer to form alkenylperoxy radical 2-butenyl-1-peroxy ($\text{C}_4\text{H}_7\text{2-OO4}$). Similar to the central concerted $\text{H}\dot{\text{O}}_2$ adduct $\text{C}_4\text{H}_7\text{1-OO3}$, $\text{C}_4\text{H}_7\text{1-OO4}$ can undergo H-atom transfer reactions that forming $\text{C}_4\text{H}_6\text{1-1OOH4}$ and $\text{C}_4\text{H}_6\text{1-2OOH4}$, and bimolecular products $\text{C}_4\text{H}_6\text{1}=\text{O4}$ and $\dot{\text{O}}\text{H}$ radical, while the β O-O bond resulted from α site H atom abstraction by the peroxy in $\text{C}_4\text{H}_7\text{1-OO4}$ are too weak

to sustain. In addition, the peroxy radical in $\text{C}_4\text{H}_7\text{1-OO4}$ can add to both carbon atoms of the C-C double bond, forming cyclic peroxidealkyl radicals $\text{CYCOOC}\cdot$ and $(\text{CYOOC})\text{C}\cdot$.

RESULTS AND DISCUSSION

Relative Energy Comparison

Relative energies to the reactants of $\text{C}_4\text{H}_6 + \text{H}\dot{\text{O}}_2$ for some chosen stationary points on the PES were calculated using four other methods apart from ROCCSD(T)/CBS, namely, G4, G3, CBS-QB3 and CBS-APNO. The stationary points included: TSs for the four addition channels of $\text{C}_4\text{H}_6 + \text{H}\dot{\text{O}}_2$, TS for the isomerization reaction between $\text{C}_4\text{H}_7\text{1-OO4}$ and $\text{C}_4\text{H}_6\text{1-3OOH4}$ and the two wells $\text{C}_4\text{H}_7\text{1-OO4}$ and $\text{C}_4\text{H}_6\text{1-3OOH4}$.

The calculated results 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. (Miyoshi, 2010) obtained the energies at the CBS-QB3 level of theory, their results were also illustrated in Table 1. 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 $\text{C}_4\text{H}_6 + \text{H}\dot{\text{O}}_2$) (in the units of kcal/mol) for the chosen TSs and species.

TSs	$\text{C}_4\text{H}_6 + \text{H}\dot{\text{O}}_2 \rightarrow \text{C}_4\text{H}_7\text{1-OO3}$	$\text{C}_4\text{H}_6 + \text{H}\dot{\text{O}}_2 \rightarrow \text{C}_4\text{H}_6\text{1-4OOH3}$
ROCCSD(T)/CBS	9.80	13.79
G4	9.34	12.95
G3	\	13.26
CBS-QB3	9.56	10.80
CBS-APNO	5.69	12.23
(Miyoshi, 2010)	\	\
TSs	$\text{C}_4\text{H}_6 + \text{H}\dot{\text{O}}_2 \rightarrow \text{C}_4\text{H}_7\text{1-OO4}$	$\text{C}_4\text{H}_6 + \text{H}\dot{\text{O}}_2 \rightarrow \text{C}_4\text{H}_6\text{1-3OOH4}$
ROCCSD(T)/CBS	15.12	9.05
G4	12.96	8.66
G3	\	8.12
CBS-QB3	13.35	5.94
CBS-APNO	12.93	6.83
(Miyoshi, 2010)	13.14	5.73
TSs	$\text{C}_4\text{H}_7\text{1-OO4} \rightarrow \text{C}_4\text{H}_6\text{1-3OOH4}$	
ROCCSD(T)/CBS	17.19	
G4	15.27	
G3	16.66	
CBS-QB3	12.77	
CBS-APNO	\	
(Miyoshi, 2010)	11.95	
Species	$\text{C}_4\text{H}_7\text{1-OO4}$	$\text{C}_4\text{H}_6\text{1-3OOH4}$
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, 2010)	-14.57	-15.77

Potential Energy Surfaces

Potential energy surfaces were given based on the calculation results we got, for entrance channels of HO_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 Figures 3 and 4. Zero-point corrected energies relative to reactants $\text{C}_4\text{H}_6 + \text{HO}_2$ for all stationary points are illustrated.

Four entrance channels for $\text{C}_4\text{H}_6 + \text{HO}_2$ were considered, namely, central HO_2 directed addition channel, central HO_2 concerted addition channel, terminal HO_2 directed addition channel and terminal HO_2 concerted addition channel. Among the four channels, terminal HO_2 directed addition channel forming hydroperoxyalkenyl radical $\text{C}_4\text{H}_6\text{-1-3OOH4}$, and central HO_2 concerted addition channel forming alkenylperoxy radical $\text{C}_4\text{H}_7\text{-1-OO3}$ were energetically 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.

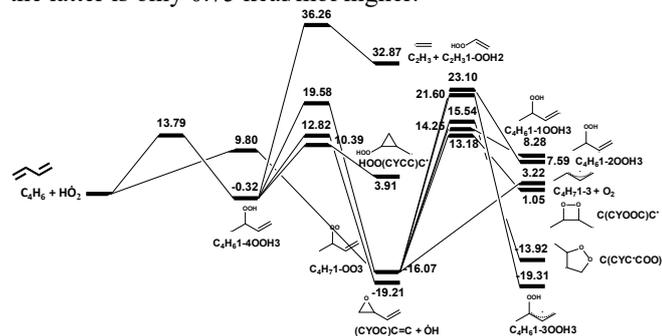


Figure 3. ZPE corrected Potential energy surfaces at the ROCCSD(T)/CBS//BHandHLYP/6-311++G(d,p) level of theory for $\text{C}_4\text{H}_6 + \text{HO}_2$ central addition channels and subsequent reactions (relative energies in units of kcal/mol)

PES for HO_2 central addition channels and subsequent reaction pathways were illustrated in Figure 3, which contains 16 species and 11 transition states. The concerted HO_2 adduct $\text{C}_4\text{H}_7\text{-1-OO3}$ stays 16.07 kcal/mol below the reactants, it can then undergo β -scission reactions to bimolecular products $\text{C}_4\text{H}_7\text{-1-3}$ and O_2 , the binding energy is 19.29 kcal/mol and is the lowest among those for subsequent reaction channels for $\text{C}_4\text{H}_7\text{-1-OO3}$. $\text{C}_4\text{H}_7\text{-1-OO3}$ can undergo H-atom transfer reactions and cyclization reactions, through which the peroxy radical adds to the C-C double bond, yet these channels are of minor importance, since the most energetically favoured one of them still had a 10 kcal/mol higher barrier than the β -scission one did. Barrier for the isomerization reaction between $\text{C}_4\text{H}_7\text{-1-OO3}$ and $\text{C}_4\text{H}_6\text{-1-4OOH3}$ from the $\text{C}_4\text{H}_7\text{-1-OO3}$ side is 6.58 kcal/mol higher the

barrier for the β -scission one. For the directed HO_2 addition product $\text{C}_4\text{H}_6\text{-1-4OOH3}$, the intramolecular methyl radical addition to C-C double bond forming $\text{HOO}(\text{CYCC})\text{C}\cdot$, and the ring closure reaction forming $(\text{CYOC})\text{C}=\text{C}$ and $\dot{\text{O}}\text{H}$ radical are two competitive channels. They are more important compared to the other reaction paths for $\text{C}_4\text{H}_6\text{-1-4OOH3}$.

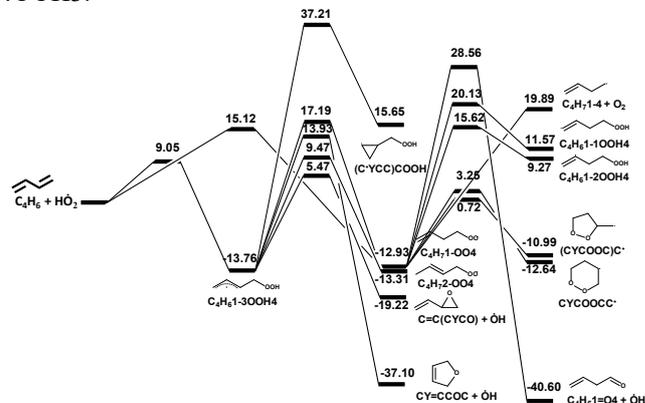


Figure 4. ZPE corrected Potential energy surfaces at the ROCCSD(T)/CBS//BHandHLYP/6-311++G(d,p) level of theory for $\text{C}_4\text{H}_6 + \text{HO}_2$ terminal addition channels and subsequent reactions (relative energies in units of kcal/mol)

PES containing 16 species and 12 transition states for HO_2 terminal addition channels and subsequent reaction pathways were depicted in Figure 4. The directed HO_2 addition product $\text{C}_4\text{H}_6\text{-1-3OOH4}$ can undergo cyclization reactions to $(\text{C}\cdot\text{YCC})\text{COOH}$, bimolecular products $\text{C}=\text{C}(\text{CYCO})$ and $\dot{\text{O}}\text{H}$ radical, and bimolecular products $\text{CY}=\text{CCOC}$ and $\dot{\text{O}}\text{H}$, respectively. It can also isomerize to $\text{C}_4\text{H}_7\text{-1-OO4}$ and $\text{C}_4\text{H}_7\text{-2-OO4}$. The ring closure reaction pathway leading to $\text{C}=\text{C}(\text{CYCO})$ and $\dot{\text{O}}\text{H}$ radical has the lowest barrier (19.23 kcal/mol). For concerted HO_2 adduct $\text{C}_4\text{H}_7\text{-1-OO4}$, the cyclization reactions forming $(\text{CYCOOC})\text{C}\cdot$ and $\text{CYCOOCC}\cdot$ were found to be important, compared to other reaction channels for $\text{C}_4\text{H}_6\text{-1-3OOH4}$.

CONCLUSIONS

This was a first systematic investigation on the reaction system of 1,3-butadiene + HO_2 . Through high-level ab initio calculations for HO_2 addition to 1,3-butadiene and subsequent unimolecular reactions, potential energy surfaces at the ROCCSD(T)/CBS//BHandHLYP/6-311++G(d,p) level of theory were obtained. It was concluded that, HO_2 directly adding to 1,3-butadiene forming $\text{C}_4\text{H}_6\text{-1-3OOH4}$, and HO_2 adding to 1,3-butadiene via concerted addition channel, forming $\text{C}_4\text{H}_7\text{-1-OO3}$, were two energetically favoured entrance channels, and they competed with each other. For central HO_2 addition reactions and subsequent unimolecular reactions, $\text{C}_4\text{H}_7\text{-1-OO3}$ undergoing β -scission reaction to form bimolecular products $\text{C}_4\text{H}_7\text{-1-3}$ and O_2 , and $\text{C}_4\text{H}_6\text{-1-4OOH3}$ undergoing cyclization reaction forming hydroperoxycycloalkyl radical $\text{HOO}(\text{CYCC})\text{C}\cdot$ are energetically favoured. For terminal HO_2 addition reactions and subsequent unimolecular reactions, $\text{C}_4\text{H}_6\text{-1-3OOH4}$ cyclizing to cyclic ether $\text{C}=\text{C}(\text{CYCO})$ and $\dot{\text{O}}\text{H}$ radical and

C₄H₇-OO₄ cyclizing to cyclic peroxidealkyl radicals (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 + HO₂ will be performed, and kinetically favoured reaction pathways for 1,3-butadiene + HO₂ will be determined.

ACKNOWLEDGMENTS

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ABSTRACT

The reaction system of 1,3-butadiene + HO₂ was investigated in this study. Electronic chemical calculations were carried out on the entrance channels and subsequent reaction pathways for 1,3-butadiene + HO₂, at the 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 HO₂ addition to 1,3-butadiene forming C₄H₇1-OO3 and C₄H₆1-3OOH4 are two energetically favoured entrance channels. C₄H₇1-OO3 undergoing β-scission reaction to the formation of the bimolecular products C₄H₇1-3 and O₂, and C₄H₆1-3OOH4 undergoing the ring closure reaction to form the bimolecular products of C=C(CYCO) and OH radical are the most important reaction pathways. Whilst, C₄H₆1-4OOH3 undergoing the cyclization reaction to form (CYCC)C•, and C₄H₇1-OO4 cyclizing to (CYCOOC)C• and CYCOOCC•, are energetically favoured reaction channels.

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. (Laskin, et al., 2000) measured concentration profiles for some C1–C4 species in 1,3-butadiene pyrolysis and oxidation over temperature in the range of 1035–1185 K at 1 atm, using turbulent flow reactor. Libby et al. (Libby, et al., 2004) carried out shock tube study on 1,3-butadiene oxidation. They conducted OH 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. (Zhou, et al., 2018) 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., 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 (HO₂) radical addition to 1,3-butadiene and their subsequent reactions are sensitive at low to intermediate temperature range (600–900 K) (Zhou, et al., 2018), 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 1,3-butadiene + HO₂. Miyoshi et al. (Miyoshi, 2010) performed theoretical calculation to study 3-butenylperoxy (C₄H₇1-OO4) unimolecular reactions. They explored the 3-butenylperoxy potential energy surfaces, which are also 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. (You, et al., 2016) 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 HO₂ radical and for the subsequent reaction pathways. Zador et al. (Zador, et al., 2011) 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 hydroperoxyalkenyl (•QOOH) radicals and alkenylperoxy (ROO•) radicals. And the formation of alkenylperoxy radical was concluded to be important at low temperatures. Note that alkenyl + O₂ were connected with the corresponding alkene + HO₂ on the same potential energy surfaces, the studies on alkenyl + O₂ may provide inspirations for us. Lee et al. (Lee and Bozzelli, 2005) reported the potential energy surfaces of allyl + O₂ 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 + HO₂.

In this study, we performed high-level ab initio calculations to investigate the reaction system of 1,3-butadiene + HO₂. A detailed mechanism for this system has been proposed, the geometries of reactants, transition states, intermediates and bimolecular products included in the mechanism have been 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 1,3-butadiene plus HO₂ and subsequent reaction paths.

METHODOLOGY

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: (Momro, 1996; Feller and Dixon, 2001)

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

T1 diagnostic (Lee and Taylor, 1989) for all transition states and species were carried out at the ROCCSD(T)/cc-pVQZ level of theory. T1 diagnostic ≤ 0.025 for reactant species and ≤ 0.03 for transition states indicate that single-reference methods are reliable in describing the wave function (Klippenstein and Harding, 2009).

Additionally, for evaluating the effects of calculation method on the predicted single-point energy values, the methodologies of G4, G3, CBS-QB3 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 (Frisch, et al.) and Molpro 2015 (Werner, et al., et al., 2015) were used to carry out the electronic chemical calculations.

Reaction Paths for 1,3-butadiene + HO₂

Detailed reaction pathways for the reaction system of C₄H₆ + HO₂ have been illustrated in Figures 1 and 2. For entrance channels, two types of addition reactions between 1,3-butadiene and HO₂ radical have been taken into consideration. Hydroperoxyl (HO₂) radicals can add to the central or terminal carbon atom in 1,3-butadiene directly, forming 2-hydroperoxy-3-buten-1-yl (C₄H₆1-4OOH3) and resonantly stabilized 1-hydroperoxy-3-buten-2-yl (C₄H₆1-3OOH4) radicals. Alternatively, the concerted addition reaction can also happen, in which the H atom and O-O group in the HO₂ radicals add to the two carbon atoms of C-C double bond separately with O-H bond cleavage in HO₂ radicals, forming 3-butenyl-2-peroxy (C₄H₇1-OO3) radicals as the O-O group adds to the central carbon atom, and 3-butenyl-1-peroxy (C₄H₇1-OO4) radicals as the O-O group adds to the terminal carbon atom.

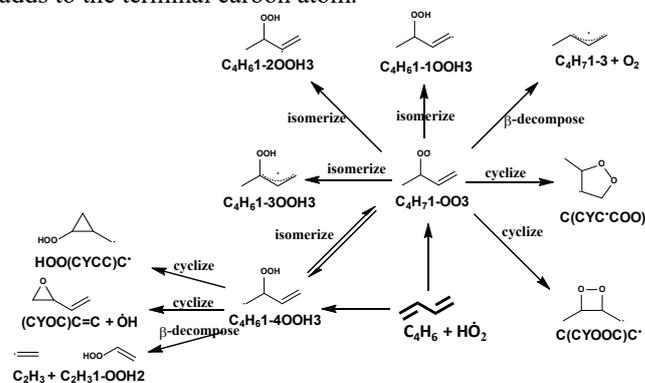


Figure 1. Central carbon addition channels and sub-mechanism for the adducts

In general, three possible reaction types have been taken into consideration for the sub-mechanisms of the initial adducts as depicted in Figures 1 and 2, which are:

- H-atom transfer reactions (isomerization) within molecules. For the C₄H₇1-OO3 radical, H atoms from the α site, two β sites and γ site can be abstracted by the peroxy radical forming hydroperoxyalkenyl radicals. For the C₄H₇1-OO4 radical, H atoms from the α site, β site, γ site and δ site can be abstracted by the peroxy radical forming hydroperoxyalkenyl radicals.

- Cyclization reactions. Hydroperoxyalkenyl radicals can undergo ring closure reaction, with O-O bond dissociation and C-O bond formation happened simultaneously, forming cyclic ether and $\dot{\text{O}}\text{H}$ radical. Besides, the methyl in hydroperoxyalkenyl radical can add to its C-C double bond, forming cycloalkyl radicals. The alkenylperoxy radicals can also undergo intramolecular addition reaction, in which the peroxy radical adds to the C-C double bond, forming cyclic peroxidealkyl radicals.
- β -scission reactions. β site C-C or C-O bonds of the species can break via β -scission.

Central addition reaction channels

As shown in Figure 1, the direct $\text{H}\dot{\text{O}}_2$ addition product $\text{C}_4\text{H}_6\text{1-4OOH3}$ can undergo two types of ring closure reactions forming cyclic ether $(\text{CYOC})\text{C}=\text{C}$ and $\dot{\text{O}}\text{H}$ radical, and hydroperoxycycloalkyl radical $\text{HOO}(\text{CYCC})\text{C}\cdot$, respectively. The concerted central addition product $\text{C}_4\text{H}_7\text{1-OO3}$ can isomerize to hydroperoxyalkenyl radicals, namely, $\text{C}_4\text{H}_6\text{1-1OOH3}$, $\text{C}_4\text{H}_6\text{1-2OOH3}$, $\text{C}_4\text{H}_6\text{1-3OOH3}$ and $\text{C}_4\text{H}_6\text{1-4OOH3}$, via H-atom transfer reactions. The concerted adduct $\text{C}_4\text{H}_7\text{1-OO3}$ can also dissociate directly to bimolecular products $\text{C}_4\text{H}_7\text{1-3}$ and O_2 . Moreover, $\text{C}_4\text{H}_7\text{1-OO3}$ can undergo intramolecular addition, forming cyclic peroxidealkyl radicals $\text{C}(\text{CYOCC})\cdot$ and $\text{C}(\text{CYOC})\text{C}\cdot$ ($\text{Y}=\text{cyclic}$).

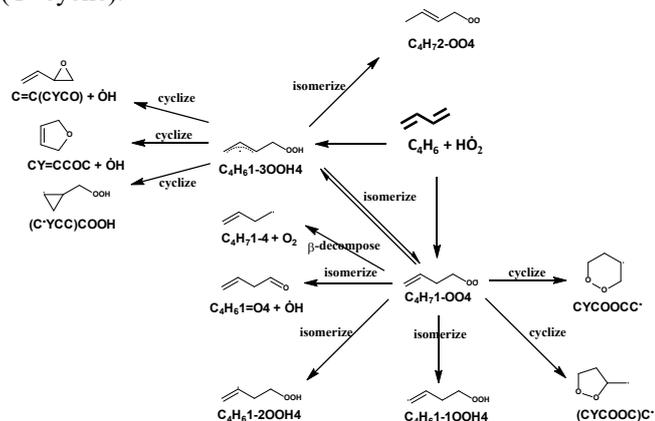


Figure 2. Terminal carbon addition channels and sub-mechanism for the adducts

Terminal addition reaction channels

As depicted in Figure 2, the resonantly stabilized direct $\text{H}\dot{\text{O}}_2$ addition product $\text{C}_4\text{H}_6\text{1-3OOH4}$ can form cyclic ethers $\text{C}=\text{C}(\text{CYCO})$ and $\text{CY}=\text{CCOC}$, respectively, and $\dot{\text{O}}\text{H}$ radicals via ring closure, and hydroperoxycycloalkyl radical $(\text{C}\cdot\text{YCC})\text{COOH}$ via intramolecular addition reaction. It can also undergo H-atom transfer to form alkenylperoxy radical 2-butenyl-1-peroxy ($\text{C}_4\text{H}_7\text{2-OO4}$). Similar to the central concerted $\text{H}\dot{\text{O}}_2$ adduct $\text{C}_4\text{H}_7\text{1-OO3}$, $\text{C}_4\text{H}_7\text{1-OO4}$ can undergo H-atom transfer reactions that forming $\text{C}_4\text{H}_6\text{1-1OOH4}$ and $\text{C}_4\text{H}_6\text{1-2OOH4}$, and bimolecular products $\text{C}_4\text{H}_6\text{1}=\text{O4}$ and $\dot{\text{O}}\text{H}$ radical, while the β O-O bond resulted from α site H atom abstraction by the peroxy in $\text{C}_4\text{H}_7\text{1-OO4}$ are too weak

to sustain. In addition, the peroxy radical in $\text{C}_4\text{H}_7\text{1-OO4}$ can add to both carbon atoms of the C-C double bond, forming cyclic peroxidealkyl radicals $\text{CYCOCC}\cdot$ and $(\text{CYOCC})\text{C}\cdot$.

RESULTS AND DISCUSSION

Relative Energy Comparison

Relative energies to the reactants of $\text{C}_4\text{H}_6 + \text{H}\dot{\text{O}}_2$ for some chosen stationary points on the PES were calculated using four other methods apart from ROCCSD(T)/CBS, namely, G4, G3, CBS-QB3 and CBS-APNO. The stationary points included: TSs for the four addition channels of $\text{C}_4\text{H}_6 + \text{H}\dot{\text{O}}_2$, TS for the isomerization reaction between $\text{C}_4\text{H}_7\text{1-OO4}$ and $\text{C}_4\text{H}_6\text{1-3OOH4}$ and the two wells $\text{C}_4\text{H}_7\text{1-OO4}$ and $\text{C}_4\text{H}_6\text{1-3OOH4}$.

The calculated results 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. (Miyoshi, 2010) obtained the energies at the CBS-QB3 level of theory, their results were also illustrated in Table 1. 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 $\text{C}_4\text{H}_6 + \text{H}\dot{\text{O}}_2$) (in the units of kcal/mol) for the chosen TSs and species.

TSs	$\text{C}_4\text{H}_6 + \text{H}\dot{\text{O}}_2 \rightarrow \text{C}_4\text{H}_7\text{1-OO3}$	$\text{C}_4\text{H}_6 + \text{H}\dot{\text{O}}_2 \rightarrow \text{C}_4\text{H}_6\text{1-4OOH3}$
ROCCSD(T)/CBS	9.80	13.79
G4	9.34	12.95
G3	\	13.26
CBS-QB3	9.56	10.80
CBS-APNO	5.69	12.23
(Miyoshi, 2010)	\	\
TSs	$\text{C}_4\text{H}_6 + \text{H}\dot{\text{O}}_2 \rightarrow \text{C}_4\text{H}_7\text{1-OO4}$	$\text{C}_4\text{H}_6 + \text{H}\dot{\text{O}}_2 \rightarrow \text{C}_4\text{H}_6\text{1-3OOH4}$
ROCCSD(T)/CBS	15.12	9.05
G4	12.96	8.66
G3	\	8.12
CBS-QB3	13.35	5.94
CBS-APNO	12.93	6.83
(Miyoshi, 2010)	13.14	5.73
TSs	$\text{C}_4\text{H}_7\text{1-OO4} \rightarrow \text{C}_4\text{H}_6\text{1-3OOH4}$	
ROCCSD(T)/CBS	17.19	
G4	15.27	
G3	16.66	
CBS-QB3	12.77	
CBS-APNO	\	
(Miyoshi, 2010)	11.95	
Species	$\text{C}_4\text{H}_7\text{1-OO4}$	$\text{C}_4\text{H}_6\text{1-3OOH4}$
ROCCSD(T)/CBS	-12.93	-13.76

cyclizing to cyclic ether C=C(CYCO) and OH radical and C₄H₇-OO₄ cyclizing to cyclic peroxidealkyl radicals (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 + HO₂ will be performed, and kinetically favoured reaction pathways for 1,3-butadiene + HO₂ will be determined.

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