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Original Research Article

Unraveling the Ozonolysis Mechanism of Terpinolene: Insights from DFT Studies

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ABSTRACT

A computational investigation of the ozonolysis of *terpinolene* has been fulfilled by using density functional (*DFT*) method. To specify primary intermediates' formation from the ozonolysis of terpinolene, quantum chemical calculations were done. Using B3LYP method with 6-311++G(d,p) basis set, the structures were optimized for all suggested reaction mechanisms. The primary reaction steps of terpinolene ozonolysis were studied focusing on the primary ozonide formation and its fragmentation into Criegee intermediates and carbonyl compounds. Two distinct mechanistic pathways were delved into for the ozonolysis of terpinolene that results in ketone compounds. The activation energy formation of the primary ozonide intermediate in pathways 1 and 2 are 37.88 & 46.29 kcal mol^{-1}, respectively. The results would increase the conception of the reaction mechanism of alkene ozonolysis and supply a vision into the realization the mechanism of transformation of this pollutant into non-toxic structures.

Keywords: Ozonolysis mechanism, Terpinolene, Quantum chemical calculations, DFT

Introduction

Ozonolysis is a chemical reaction that involves the breaking of carbon-carbon double bonds in the presence of ozone (O_3). This process plays a significant role in atmospheric chemistry, contributing to the formation of secondary organic aerosols and the degradation of volatile organic compounds emitted by various sources. Chemical oxidation procedures in the atmosphere have a major effect on the composition of the atmosphere and cause the elimination of primary released species and the production of secondary products. In numerous instances, the emitted species and their oxidation products adversely affect air and climate quality [1]. Across the many components of atmospheric aerosol fragments, organic aerosol particles are the less well known [2]. Secondary organic aerosol (SOA) is the main component of organic aerosols. Recognizing the chemical pathways of compressible products is crucial for anticipating SOA formation [3-6].

Stable Criegee intermediates (SCIs), or carbonyl oxides, are known to be another major oxidant in the troposphere [7]. From the reaction of ozone with unsaturated hydrocarbons, SCIs are thought to create mostly in the atmosphere.

Monoterpenes which are produced by a widespread range of vegetation, specially from boreal jungles, are volatile organic compounds (VOCs) with the general formula $C_{10}H_{16}$. Furthermore, they are present in significant amounts in indoor environments, where air fresheners and cleaning products are common in use [8, 9], and where their ozonolysis products can impact indoor health and chemistry [10, 11]. Because of the presence of multiple double bonds, monoterpenes are extremely reactive. A wide range of multi-functional gas-phase and aerosol products were produced from the oxidation of monoterpenes. This process can be begun by O_3. As mentioned before, ozonolysis is efficient in producing low-volatility products which can form SOA [5].

Ozonolysis is a powerful chemical reaction widely used in organic synthesis and analytical chemistry to cleave double bonds. It involves the reaction of ozone (O_3) with unsaturated compounds, such as alkenes or alkynes, leading to the formation of ozonides, which subsequently decompose to yield a variety of functional groups. Understanding the mechanism behind ozonolysis is crucial for researchers and chemists to employ this reaction effectively in

various applications. In this article, we will explore the mechanism of ozonolysis of double bonds, shedding light on the intricate steps involved in this important chemical transformation.

Terpinolene is a naturally occurring terpene found in various essential oils, such as those derived from conifers and citrus fruits. It possesses an intricate molecular structure with multiple double bonds, making it an interesting candidate for studying ozonolysis reactions. Terpinolene arises naturally in lots of plant species and can be distribute into the atmosphere through their decomposition or distribution of volatile oils. It may also evaporate from some terpene-based cleaners, air fresheners and perfumes [12, 13].

Over the years, several computational studies have shed light on the ozonolysis of monoterpenes, employing a range of theoretical methods and models to investigate the reaction pathways and products. These researches identified the most favorable reaction pathways for the ozonolysis of monoterpenes and characterized the formation of key intermediate species [14-16]. As mentioned before, ozonolysis of terpinolene plays a significant role in atmospheric chemistry, as well as in the synthesis of valuable compounds. In this article, we delve into the mechanism of the ozonolysis of terpinolene, shedding light on its intricacies through the lens of Density Functional Theory (DFT) calculations.

The ozonolysis reaction begins with the initial step of the formation of the primary ozone complex (POZ). Ozone, a highly reactive molecule, first approaches the double bond, aligning one of its oxygen atoms near one carbon atom of the double bond. This results in the formation of an intermediate complex, called the primary ozonide or the Criegee intermediate (CI). The Criegee intermediate is an important reactive species that plays a pivotal role in the subsequent steps of the ozonolysis reaction. The ozonolysis of terpinolene commences with the approach of an ozone molecule (O_3) to one of the double bonds in terpinolene. Through DFT calculations, it has been determined that the most favorable site for ozone addition in terpinolene is the double bond adjacent to the isopropyl group. Upon the addition of ozone, a primary ozonide is formed. DFT calculations indicate that the formation of the primary ozonide (POZ) proceeds via a concerted pathway, where the ozone molecule interacts with the double bond, leading to the formation of a cyclic intermediate.

The primary ozonide is a strained three-membered cyclic structure, highly unstable in nature. It undergoes homolytic cleavage, splitting into two fragments. One fragment is a carbonyl oxide (also known as a Criegee biradical) containing a carbonyl group, and the other fragment is an aldehyde or a ketone. The homolytic cleavage is facilitated by the high strain energy stored in the primary ozonide due to its small ring size. The primary ozonide is highly strained due to the small ring size, and it undergoes homolytic cleavage to generate a carbonyl oxide (Criegee intermediate) and an aldehyde or ketone fragment. DFT studies provide insights into the energetics and transition states involved in this decomposition process.

The stability of the large POZs formed in monoterpene ozonolysis is anticipated to be unimportant. Although, a main discrepancy in ozonolysis of endocyclic bonds is that during POZ decomposition, the carbonyl fractions and carbonyl oxide are linked together as section of the identical molecule, affording the potential for additional interactions between the two. These can react together to produce secondary ozonides (SOZ), that can be persist for many hours [17].

The carbonyl oxide intermediate resulting from the decomposition of the primary ozonide is a highly reactive species. It can undergo several reaction pathways, leading to various products depending on the nature of the starting compound. In some cases, the carbonyl oxide undergoes a Criegee rearrangement, in which the oxygen atom migrates to a neighboring carbon atom, forming a new carbonyl group. This rearrangement can occur in alkenes or alkynes with suitable substitution patterns, resulting in the formation of a new aldehyde or ketone.

Alternatively, the carbonyl oxide can undergo a second homolytic cleavage to yield two oxygen-centered radicals. These radicals can further react with other molecules, such as water, to form alcohols, or with other functional groups present in the molecule, leading to the formation of a diverse array of products. In the presence of reducing agents, such as dimethyl sulfide (DMS), the carbonyl oxide can be reduced to yield alcohols. This reduction pathway is commonly used in laboratory synthesis to selectively obtain alcohol products from ozonolysis reactions.

In this study we explored the ozonolysis of terpinolene, which has both exo- and endo-cyclic double bonds but the more substituted outer bond is anticipated to have much higher reactivity. It is worth mentioning that ozone can also stick to internal double bond. As will be shown, our findings suggest that this is a minor procedure. DFT study was carried out to clarify the potential

energy surface of the primary ozonide formation and its fragmentation into Criegee intermediates and diverse carbonyl structures.

Thermodynamic parameters of the two main oxidation levels, which include the development and decomposition of initial ozonide, in addition to the intrinsic reaction pathways and the variational transition state were investigated. A computational study of the ozonolysis of terpinolene can supply useful information that will increase our awareness of the oxidation procedure and the parameters that effect the reaction mechanism of monoterpenes with ozone. In this study, quantum chemical computation was used to support CI formation and disclose the mechanism of terpinolene ozonolysis. Feasible reaction paths were anticipated by quantum chemical calculations. By supplying more detailed data on this reaction, we hope this theoretical study will profit experimentalists, and probably benefit the design of new experiments for further understand and evolve of synthetic processes for the reaction products. DFT calculations have provided valuable insights into the ozonolysis mechanism of terpinolene. Through computational studies, researchers have been able to unravel the intricate steps involved in the reaction, including the initial ozone addition, formation and decomposition of the primary ozonide, and subsequent pathways of the carbonyl oxide intermediate. Understanding the ozonolysis mechanism of terpinolene not only enhances our knowledge of atmospheric chemistry but also aids in the rational design of synthetic methodologies for the production of valuable compounds. The combination of experimental investigations and computational approaches, such as DFT, continues to play a crucial role in advancing our understanding of complex chemical transformations. Fig. 1, demonstrates the expected mechanism for the ozonolysis of terpinolene.

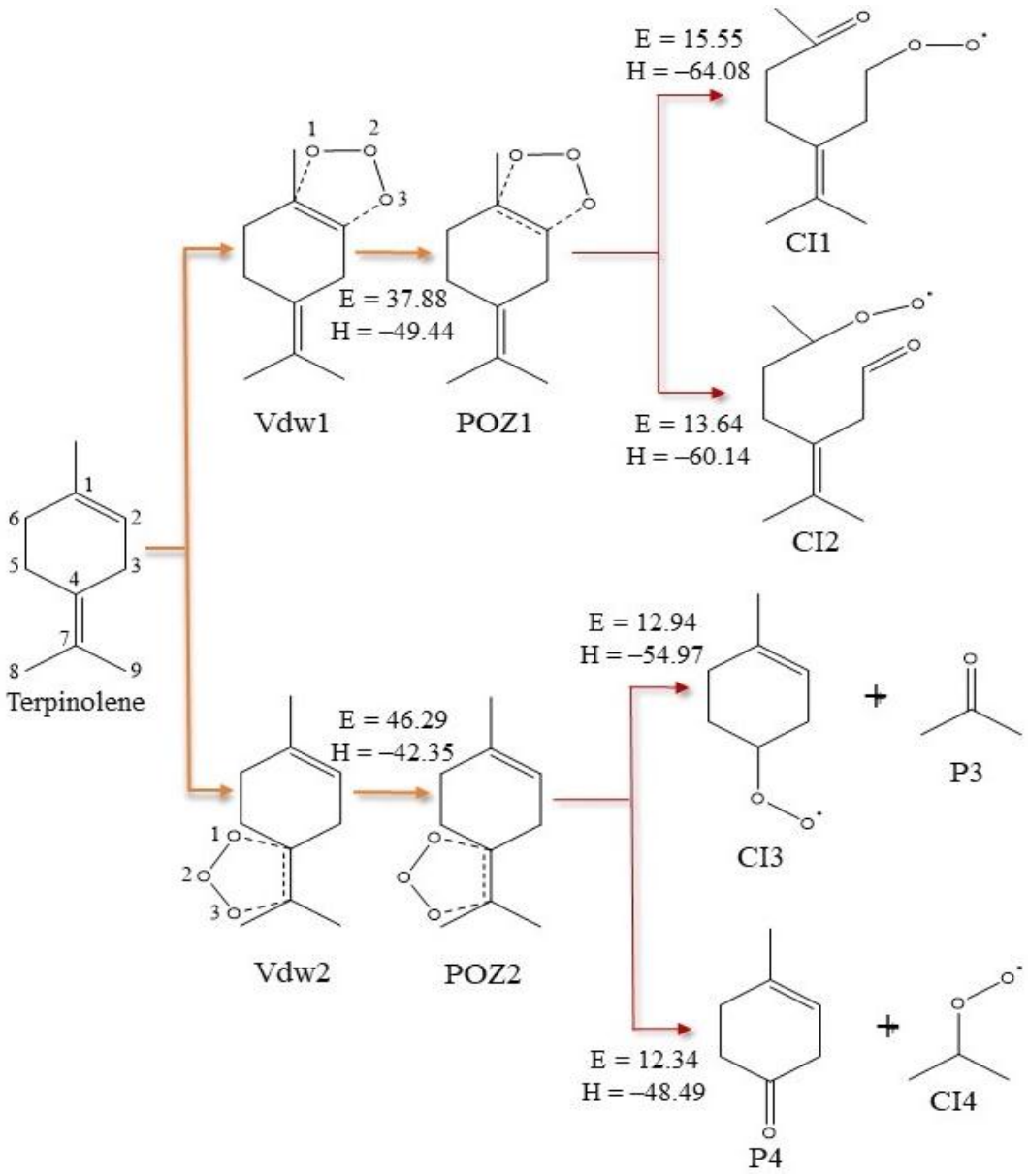

Figure 1. Mechanism of ozonolysis of terpinolene along with values of potential energy (ΔE) and reaction enthalpy (ΔH) (all values in kcal mol^{-1}, 298.15 K).

In this research, the ozonolysis mechanism of terpinolene as a monoterpene was investigated using DFT calculations. It should be mentioned that the proposed mechanism for the mentioned reaction was investigated. We hope that the obtained findings can be generalized to the process of ozonolysis of other alkenes and will be helpful in providing a proposed mechanism for converting pollutants into non-polluting substances.

Computational Methods

The ozonolysis of terpinolene has been investigated by DFT calculations. All computations were performed using the quantum chemistry package Gaussian 16 [18]. All geometries were completely optimized with no geometric restrictions and confirmed as minimum or saddle points on the PES along with harmonic vibrational frequency analysis. Geometry optimizations and vibrational calculations were performed using DFT/B3LYP/6-311++(d, p) level of theory [19]. It is important to mention that this study consist of non-covalently bonded complexes, so the B3LYP method is appropriate for non-covalent interactions [20, 21]. The optimized geometries of the reactants, transition states, intermediates, and products were investigated in the gas phase [22]. Intrinsic reaction coordinate (IRC) calculations [23-25] were used to determine the transition states (TS) on the potential energy surface (PES). Frequency analyses were performed to certify the existence of only one imaginary frequency in the transition states. In addition, the minima were verified by ensuring the absence of any imaginary frequencies. Also, the thermodynamic function ΔH and activation energies E_a were calculated for each reaction path studied. The energies of all optimized structures are corrected with zero-point vibrational energies.

Results and Discussion

Optimized Geometries

These findings consistent with the earlier studies by Zhang et al., [14, 26] Leonardo et al., [19] and Nguyen et al.,[27, 28] which show that DFT methods are trusty for computing geometrical parameters of terpenes and ozonolysis products. Geometric Parameters for the Ozonolysis of terpinolene are shown in Table 1 and 2. Ozonide formation happens when O_3 nears the double bond and the $rC_1–C_2$ and $rC_4–C_7$ bond distances enhance. The computed rC–O bond length for POZ were about 1.4 Å at the B3LYP level. These findings are consistent with prior literature results for ozonolysis, [14, 19, 26, 29, 30] suggesting that the ozonide has a specific structure irrespective of the terpene under discussion. POZ degradation is pursued by elongation of the $rC_1–C_2$ and $rC_4–C_7$ bond till the ring opens (POZ1 route) or creates two parts (POZ2 route). Also, one O–O bond is broken to form a Criegee intermediate and a primary carbonyl. If the C–O bond relates to a carbonyl group, the computed bond distance may correspond to the model value for a C=O double bond.

Table 1. Geometric Parameters for the Ozonolysis of Terpinolene

	TS0	POZ1	TS1	TS2	CI1	CI2
$rC_1–O_1$	1.877	1.449	1.292	1.360	1.212	1.270
$rC_2–C_3$	1.514	1.532	1.513	1.549	1.477	1.519
$rC_1–C_2$	1.483	1.574	1.870	1.889	4.651	3.881
$\theta C_1O_1O_2$	99.273	103.207	103.33	112.113	78.343	118.111
$\Psi C_1O_1O_2O_3$	58.075	-49.60	-20.34	-56.63	50.974	-56.341

The numbering of structures conforms to the symbols used in Scheme 1. The TS- prefix refers to the transition states structures of each channel. Bond distances are in angstroms and bond and dihedral angles are in degrees.

Table 2. Geometric Parameters for the Ozonolysis of Terpinolene

	TS0´	POZ2	TS1´	TS2´	CI3	CI4
$rC_4–O_1$	1.799	1.452	1.368	1.298	1.263	1.217
$rC_7–O_3$	1.846	1.443	1.297	1.369	1.217	1.265
$rC_4–C_7$	1.521	1.568	1.906	1.884	3.603	3.637
$\theta C_4O_1O_2$	101.31	106.59	111.548	102.179	117.921	67.713
$\Psi C_4O_1O_2O_3$	56.331	17.051	50.100	-8.595	70.993	131.668

The numbering of structures conforms to the symbols used in Scheme 1. The TS- prefix refers to the transition states structures of each channel. Bond distances are in angstroms and bond and dihedral angles are in degrees.

At the B3LYP level, the TS0 for the terpinolene endocyclic reaction has an imaginary frequency of –410.30 cm^{-1}, indicating that ozone is close to the double bond. At maintenance level of theory, the TS0´ for the exocyclic reaction of terpinolene has an imaginary frequency of –335.24 cm^{-1}, indicating that ozone approaches the double bond as in the endocyclic reaction. Fig. 2 and 3 show the investigated optimized structures.

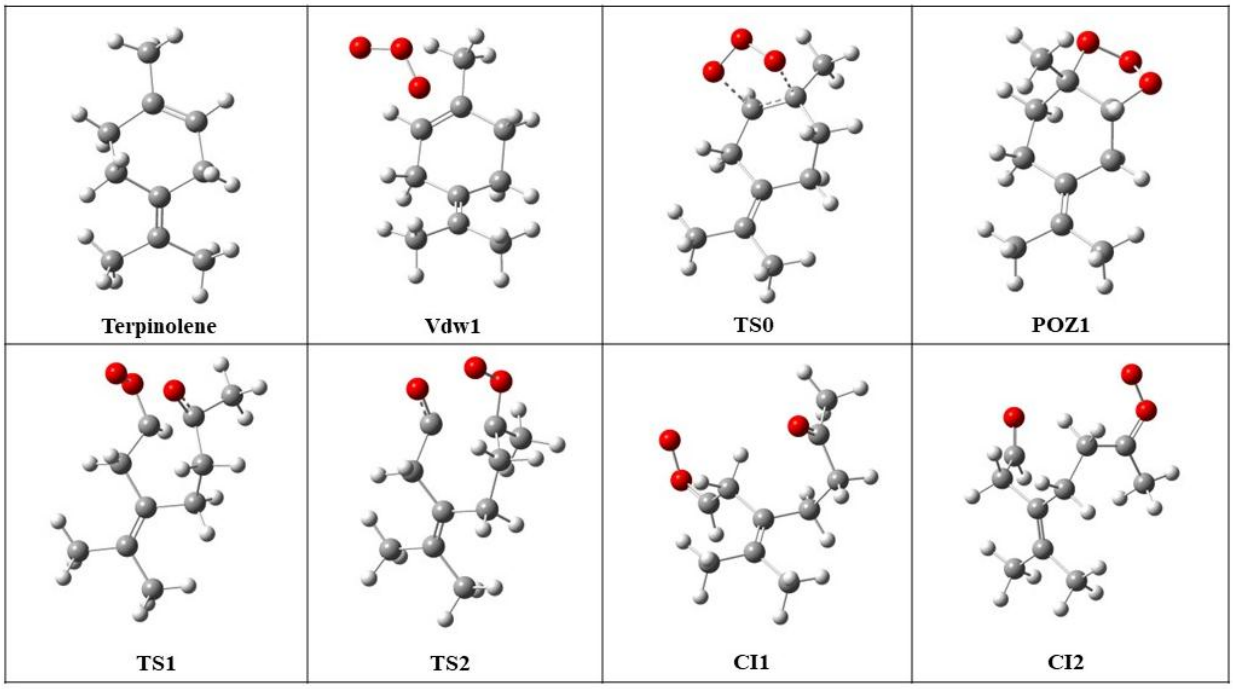

Figure 2. Optimized molecular structures of the desired structures in ozonolysis terpinolene (ozone interacts with the C=C double bond in the carbon ring of the terpinolene).

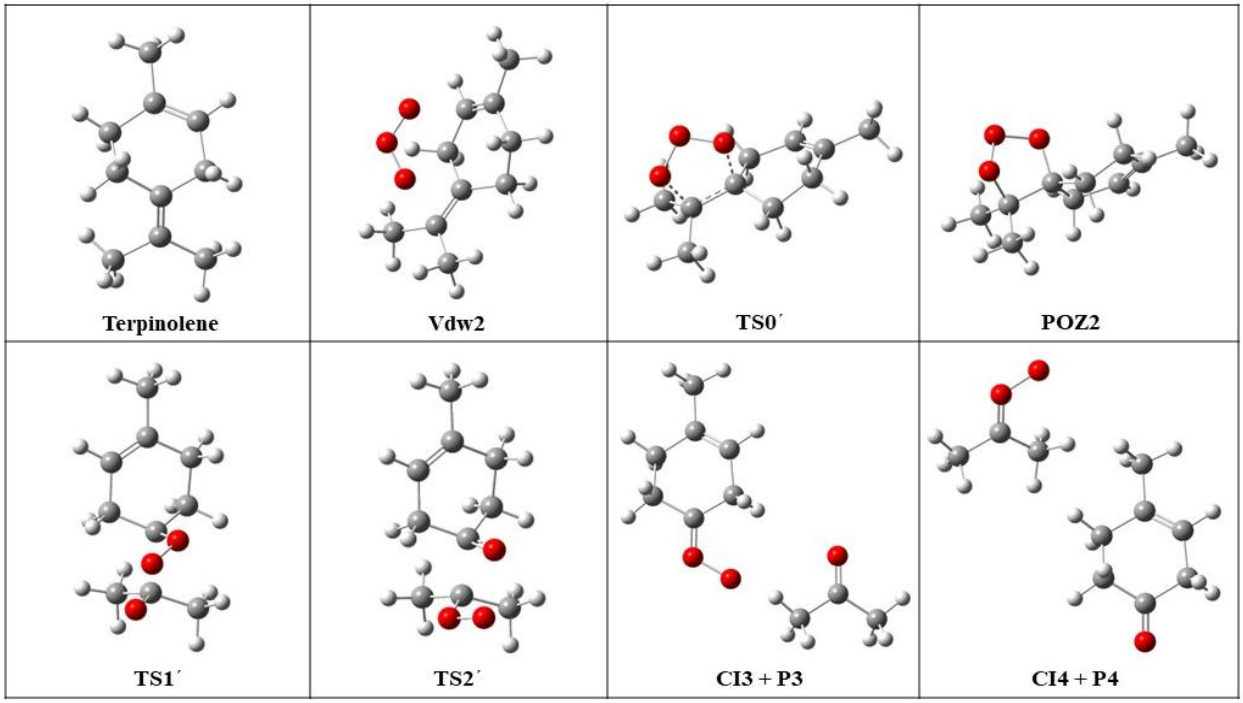

Figure 3. Optimized molecular structures of the desired structures in the ozonolysis of terpinolene (ozone interacts with the C=C double bond in the side chain of the terpinolene).

Ozonolysis of Terpinolene (Theoretical Anticipated Mechanism)

The ozonolysis mechanism of terpinolene and the corresponding PES are depicted in Fig. 1 and 4, respectively. Ozone can interact with the endocyclic C=C double bond using the carbon ring of the terpinolene molecule to produce Vdw1, or interact with the exocyclic C=C double bond in the side chain and lead to Vdw2. The development of Vdw1 is more desirable than Vdw2. The production of both POZs from the respective van der Waals complexes is highly exothermic (about –50 kcal.mol^{-1}) and has a low potential barrier.

It is worth noting that the reactions related to POZ1 are more significant compared to the reactions correspond to POZ2. The –OOO– ring in POZ1 can be opened by two paths to develop CI1 and CI2 because POZ1 is asymmetric. The production potential barrier of CI1 is 15.55 kcal mol^{-1}, which is approximately 2 kcal mol^{-1} higher than that of CI2.

Therefore, the formation of CI2 dominates over CI1, and subsequent reactions of CI1 are not discussed. Likewise, POZ2 can form CI3 and CI4 through the cleavage of –OOO– ring. According to reaction energy barrier studies, the production of CI3 is predicted to be much more desirable than CI4. Since the ozonides are formed with the release of a large amount of energy, all of feasible decay products may be produced from these species.

As mentioned before, the optimized molecular structures of the compounds discussed in Fig. 4 are depicted in Fig. 2 and 3.

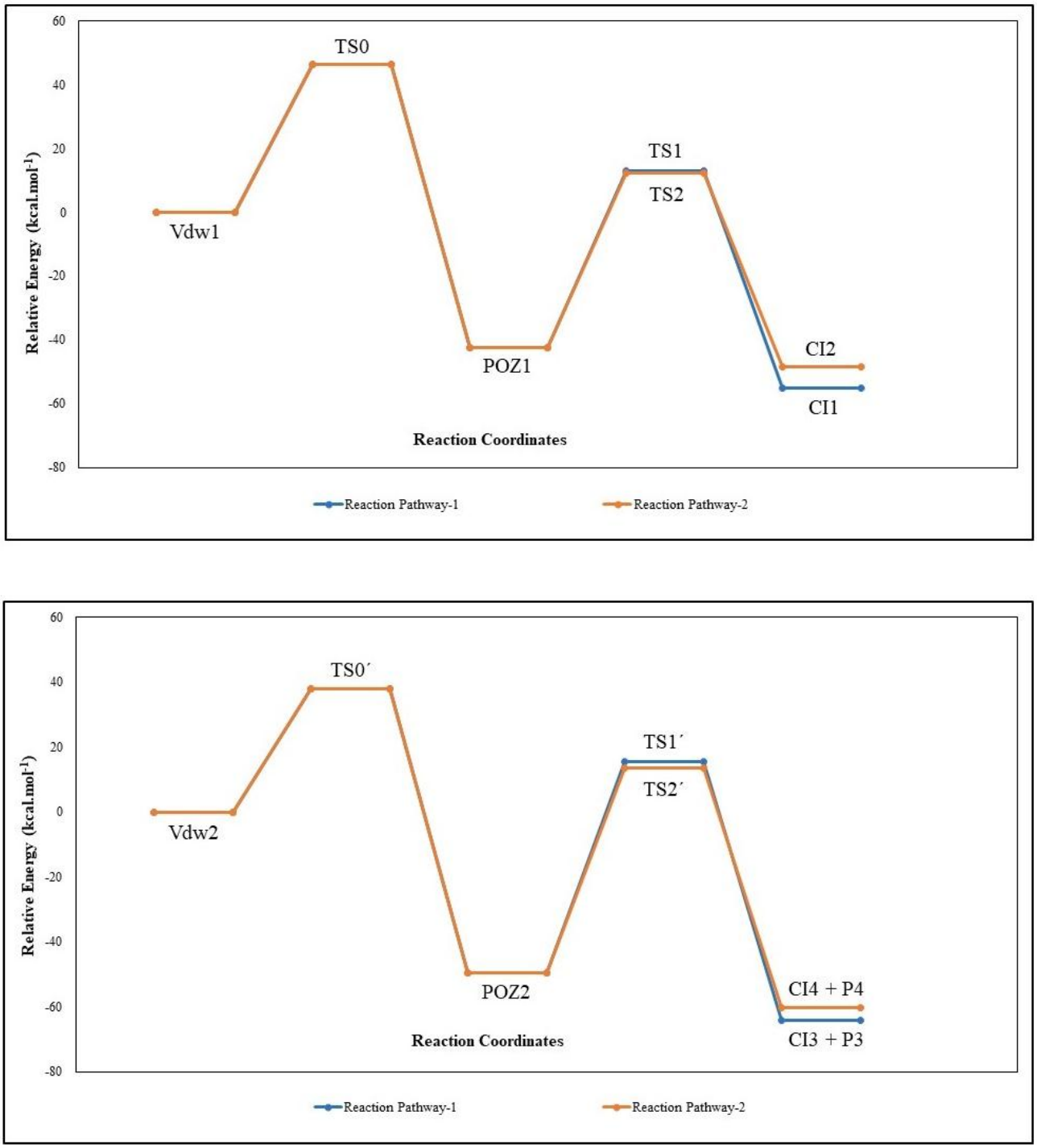

Figure 4. Potential energy surface (PES) of the ozonolysis of terpinolene. Up: ozone interacts with the endocyclic double bond of the terpinolene molecule. Down: ozone interacts the exocyclic double bond of the terpinolene molecule.

Conclusions

A computational study of the reaction of ozone gas with terpinolene in the gas phase, a monoterpene containing cyclic internal and external double bonds, was carried out. In this work, the primary intermediate products developed during the ozonolysis of terpinolene were proposed by quantum chemical computations. Primary and secondary ozonides and also Criegee intermediates were determined by computational results. The ozonolysis of terpinolene corresponds to the Criegee mechanism, and the prevailing routes in these reactions were identified. The findings in this work provide theoretical support for the ozonolysis mechanism of alkenes. Furthermore, the primary reaction steps for the ozonolysis of terpinolene has been investigated, and the thermochemical parameters controlling the method have been considered. As mentioned, the generation of POZs is extremely exothermic, and the PES around the TS seems to be weak, allowing the formation of a precomplex. The complexity of the PES needs a very precise method to characterize the energy barriers for the development of POZs. The B3LYP functionals accurately depict the geometry of each structure participating in the mechanism.

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