Quantum chemical study of the (Z)-2-penten-1-ol (HOCH\(\text{CH} = \text{CHCH}_2\text{CH}_3\)) + OH + O\(_2\) reactions

Weichao Zhang and Benni Du

College of Chemistry and Chemical Engineering, Jiangsu Key Laboratory of Green Synthetic Chemistry for Functional Materials, Jiangsu Normal University, Xuzhou, Jiangsu, People’s Republic of China

1. Introduction

Unsaturated alcohols are emitted into the atmosphere as primary pollutants by vegetation. (Z)-3-hexen-1-ol ((Z)-CH\(_3\)CH\(_2\)CH = CHCH\(_2\)CH\(_3\)OH) is emitted globally from a wide range of plants including grass, clover, alfalfa, grape, lettuce, onion, orange, peach, and oak [1,2]. Some unsaturated C5 alcohols derived from \(\alpha\)-linolenic acid are also emitted by vegetation for the purpose of microbiological protection. For example, emissions of 1-penten-3-ol (CH\(_3\)CH\(_2\)CH(\(\text{OH}\))CH = CH\(_2\)) and 2-penten-1-ol (CH\(_3\)CH\(_2\)CH = CHCH\(_2\)OH) have been observed from a variety of plants [2–5]. Degradation processes and products of unsaturated alcohols in the atmosphere are of interest, considering the potentially high emission rates of these unsaturated alcohols into the atmosphere and the potentially profound influence on tropospheric chemistry.

Unsaturated alcohols are primarily removed from the atmosphere by reaction with the free radicals and oxidants (such as OH radical [6–9], NO\(_3\) radical [10,11], ozone [12,13], halogen atoms [14–17] and their oxides). Among the above reactive species, the OH radical is clearly the most important one. The initial step for the OH-initiated oxidation of unsaturated alcohols in the troposphere is often dominated by addition of the OH radical to the double bond, leading to the formation of two distinct hydroxyalkyl radicals. In the atmosphere, these hydroxyalkyl radicals add O\(_2\) to form the corresponding hydroxyalkyl peroxy radicals (RO\(_2\)).
R₁CH = CHCH₂OH \overset{OH}{\rightarrow} R₁CHCH(OH)CH₂OH \overset{\Delta}{\rightarrow} R₁CH(OO)CH(\cdot)CH₂OH,

R₁CH = CHCH₂OH \overset{OH}{\rightarrow} R₁CH(OH)CH₂OH \overset{\Delta}{\rightarrow} R₁CH(OH)(\cdot)CH(O)CH₂OH.

Under atmospheric conditions, the dominant fate of RO₂ radicals is reaction with either HO₂ or NO [18]. The reaction of RO₂ with NO can form either the organic nitrate or NO₂ plus the corresponding hydroxynitrate radical. The resulting hydroxynitrate radicals R₁CH(OH)CH(\cdot)CH₂OH and R₁CH(OH)(\cdot)CH(O)CH₂OH can decompose by C–C bond scission to form carbonyl products.

In 2001, Orlando et al. [19] studied the atmospheric chemistry of (Z)-2-penten-1-ol at 298 K using an environmental chamber/FTIR apparatus. Rate coefficients for the reaction of (Z)-2-penten-1-ol with OH (determined by the relative rate technique) were found to be (10.6 ± 1.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}. Products observed (with molar yields in brackets) from the OH-initiated oxidation of (Z)-2-penten-1-ol in 1 atm air at 298 K were propanal (91 ± 13%), glycolaldehyde (87 ± 11%) and formaldehyde (11 ± 2%).

Recently, Davis et al. [20] measured the rate coefficients for the gas-phase reaction of the OH radical with (E)-2-penten-1-ol ((E)-CH₂CH₂CH = CHCH₂OH) over the temperature range 243–404 K at pressures between 20 and 100 Torr (He) using pulsed laser photolysis (PLP) and laser-induced fluorescence (LIF). The reported rate coefficient is (6.76 ± 0.70) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} at 297 K. Furthermore, the obtained rate coefficients were independent of pressure with negative temperature dependences that is well described by the Arrhenius expression: 

\[ k = (6.8 ± 0.8) \times 10^{-12} \times \exp[(680 ± 20)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}. \]

Lately, a number of experimental and computational studies regarding the reactivity of peroxy radicals (RO₂) have been reported [21–27]. Functionalised peroxy radicals are known to undergo unimolecular hydrogen migrations from neighbouring substituents [28,29]. Recent theoretical studies have revealed that a unimolecular pathway involving a 1,5 H-shift from the terminal hydroxyl group to the terminal O atom of RO₂ could be of significance in the production of carbonyl products and epoxides [27,30]. In this work, the kinetics and mechanism of the reaction of (Z)-PO₂1 with OH radical in the presence of O₂ have been studied using quantum chemical calculations. The primary focus of this study is to investigate the internal rearrangement reaction of (Z)-PO₂1-derived RO₂ radicals and to provide temperature dependent rate constants.

2. Computational methods

DFT and \textit{ab initio} calculations were performed using the Gaussian 09 [31] suite of programmes. Geometry optimisation of the reactants, products, intermediates, reactant complexes, and transition states was made at the BH&HLYP [32,33] level of theory using 6-311++G(d,p) basis set [34]. It is noted that the BH&HLYP geometry optimisation has been adopted to predict accurate TS structures for the reactions of alkane, alkene, and aldehyde with the OH radical [35,36]. Vibrational frequencies, the thermal contributions to the Gibbs energy (TCG) and zero-point energies (ZPE) were determined at the same level of theory as geometries. The ZPE scaling factor (0.9335) [37] was used at the BH&HLYP/6-311+G(d,p) level of theory. To confirm the connection of the transition states with the designated local minima, intrinsic reaction coordinate (IRC) calculations [38] were performed at the same level.

For all stationary points, single-point energy calculations were carried out at high levels of theory by taking the previously optimised geometries. Electronic energies were obtained by employing the \textit{ab initio} coupled-cluster singles and doubles method including a perturbative estimate of triples (CCSD(T)) [39,40] with the 6-311+G(d,p) basis set. The Gibbs free energies in this study were calculated by adding the gas-phase TCG corrections to the single-point CCSD(T) energies. The energies of relevant stationary point include the scaled ZPE corrections unless otherwise specified. These \( \Delta(E+ZPE) \) values at CCSD(T)/6-311+G(d,p)//BH&HLYP/6-311++G(d,p)+ 0.9335 \times ZPE level were used throughout for the following discussion. In all cases, the multireference character was not significant for the calculated radicals because \( T1 \) diagnostic value was found to be less than 0.044 [41] at CCSD(T)/6-311+G(d,p) level of theory.

According to conventional transition state theory \( k(T) \) (TST) [42], the rate constants \( k \) have been evaluated for the bimolecular reaction

\[ (Z) - PO₂1 + OH \overset{k_b}{\rightarrow} RC \overset{k_c}{\rightarrow} Products. \]

The bimolecular reaction represented in this work is assumed to follow a two-step mechanism involving a fast pre-equilibrium between the reactants and the reactant complex [43–45] (first step) followed by either an addition or an abstraction leading to the products (second step).

Applying steady-state conditions [46], the rate constant \( k \) (in cm³ molecule⁻¹ s⁻¹) can be written as

\[ \frac{k_a}{k_b} k_c = K_{eq} k_c. \]
Figure 1. Energy level diagram for the OH + (Z)-PO21 reaction through all the transition states obtained at the CCSD(T)/6-311+G(d,p)//BH&HLYP/6-311++G(d,p) + 0.9335 × ZPE level of theory.

\[ k = \kappa(T) \sigma \frac{k_B T}{h} \frac{10^6 RT}{N_A} \exp \left( -\frac{\Delta_r G^o}{RT} \right), \]

where \( k_B \), \( h \), \( R \) and \( T \) are the Boltzmann’s constant, the Plank’s constant, the ideal gas constant and the absolute temperature, respectively; \( \Delta_r G^o \) is the activation Gibbs free energy barrier; \( N_A \) is the Avogadro number; \( 10^6 \) is a conversion factor; \( \sigma \) is the reaction path degeneracy; \( \kappa(T) \) is the tunnelling correction factor of Wigner [47].

3. Results and discussion

3.1. Entrance channels

The structure of the reactants, minima, and transition states calculated in the present paper are shown in Figure S1 in Supplementary Material. The total energies and relative energies together with the ZPE corrections and T1 diagnostic values are given in Tables S1 in Supplementary Material. The profile of the potential energy surface for the (Z)-PO21 + OH reaction at the CCSD(T)/6-311+G(d,p)//BH&HLYP/6-311++G(d,p) + 0.9335 × ZPE level is shown in Figure 1.

The oxidation reaction of (Z)-PO21 by OH radical implies two elementary reactions: OH-addition on the C=C double bond and H-abstraction. As observed in Figure 1, the reactants can form an adduct RC1 or RC2 via a barrierless process. RC2 is energetically 9.63 kJ/mol lower than the reactants. RC1 is more stable than RC2 by 9.25 kJ/mol. RC1 and RC2 are the complexes of the OH radical interacting the C=C double bond of the (Z)-PO21, respectively. Beginning with the RC1 and RC2, the hydroxyl oxygen atom can add to the two unsaturated carbon atom of (Z)-PO21 leading to the formation of four intermediates HOCH\(_2\)C=HCH(OH)CH\(_2\)CH\(_3\) (denoted as IM1 and IM3) and HOCH\(_2\)CH(OH)C=HCH\(_2\)CH\(_3\) (denoted as IM2 and IM4), respectively. The corresponding transition states for these addition steps are
TSRC1-1, TSRC2-3, TSRC1-2, and TSRC2-4, respectively. These associations proceed with entrance barriers of 1.62, 15.58, 2.92 and 1.81 kJ/mol, and they are exothermic by 118.77, 112.94, 125.48, and 117.70 kJ/mol, respectively. One can notice in Figure 1 and Table S1 that TSRC1-1, TSRC1-2 and TSRC2-4 lie below the reactants by 17.26, 15.96 and 7.82 kJ/mol, respectively. Conversely, TSRC2-3 lies above the reactants by 5.95 kJ/mol. Thus, the formation of IM3 and IM4 cannot compete with the formation of IM1 and IM2 at low to fairly high temperatures.

Let us now take into account the H-abstraction pathways between (Z)-PO21 with OH radical. There are four different types of H atom (vinyllic, allylic, alkyl, and hydroxyl hydrogens) in the reactant (Z)-PO21 and the OH radicals can abstract different H atoms to form H2O and different (Z)-PO21 radicals.

The OH radical can abstract two vinyllic hydrogens of (Z)-PO21 directly to form products of HOCH2C=CHCH2CH3 (P1) + H2O or HOCH2CH = C=CH2CH3 (P2) + H2O via TS1 or TS2, respectively. The relative energies of TS1 and TS2 are 13.15 and 13.18 kJ/mol, respectively.

The OH radical can attack four allylic hydrogens of (Z)-PO21 to form H2O and corresponding products. In these processes, the reactions begin with the barrierless formation of four reactant complexes (denoted as RC3, RC3A, RC4 and RC4A) in the entrance channels. This means that these abstraction reactions may proceed via an indirect mechanism. RC3, RC3A, RC4 and RC4A lie 21.42, 3.18, 21.42 and 22.88 kJ/mol below the reactants, respectively, and they are characterised as true local minimum on the PES. Starting from these reactant complexes, the hydrogen atoms in the two -CH2- groups of (Z)-PO21 may also be abstracted by OH radical via TS3, TS3A, TS4 and TS4A to form products of HOCH2CH = C=CH2CH3 (P3) + H2O, HOCH2CH = C=CH2CH3 (P3A) + H2O, HOCH2CH = C=CH2CH3 (P4) + H2O and HOCH2CH = C=CH2CH3 (P4A) + H2O, respectively. The barrier heights of TS3, TS3A, TS4 and TS4A are 22.56, 1.75, 19.41 and 24.01 kJ/mol, respectively. From the PES one can see that TS3A and TS4 are predicted to lie below the reactants by 1.43 and 2.01 kJ/mol, whereas TS3 and TS4A are predicted to lie above the reactants by only 1.14 and 1.13 kJ/mol, respectively. This indicates that the allylic H-abstraction reactions will be feasible for the title reaction.

The OH radical can directly abstract the hydroxyl hydrogen of (Z)-PO21 via TS5 to produce •OCH2CH = CHCH2CH3 (P5) + H2O with a barrier height of 13.68 kJ/mol. Apparently, this channel is not competitive for the P5 + H2O formation.

Finally, the OH radical can also abstract one hydrogen atom from -CH3 groups of (Z)-PO21 via TS6, TS6A and TS6B to form the identical products (HOCH2CH = CHCH2C•H2 (P6)+H2O. The barrier heights of these three steps are 13.80, 14.72 and 10.99 kJ/mol. Kinetically, these pathways are not competitive, either.

In summary, the calculational results in this part show that there are several reaction pathways for OH + (Z)-PO21 reaction, of which only eight pathways are expected to be predominant. These pathways can be denoted schematically as follows:

(1) OH+(Z)-PO21→RC1→TSRC1-1→IM1,
(2) OH+(Z)-PO21→RC1→TSRC1-2→IM2,
(3) OH+(Z)-PO21→RC2→TSRC2-3→IM3,
(4) OH+(Z)-PO21→RC2→TSRC2-4→IM4,
(5) OH+(Z)-PO21→RC3→TS3→P3+H2O,
(6) OH+(Z)-PO21→RC3A→TS3A→P3A+H2O,
(7) OH+(Z)-PO21→RC4→TS4→P4+H2O,
(8) OH+(Z)-PO21→RC4A→TS4A→P4A+H2O.

Therefore, we will only focus on the rate constants for the eight reaction pathways in the next section.

3.2. Rate constants

As mentioned before, the theoretical rate constants are computed using the traditional transition state theory with the activation Gibbs free energy barrier \( \Delta G^\# \) (the difference between Gibbs free energy of the transition state and the sum of the \( G \) of the reactants (isolated (Z)-PO21 and the OH radical)). The variations in Gibbs free energy (\( \Delta G \)) of various species calculated at the CCSD(T)/6-311+G(d,p)//BH&HLYP/6-311++G(d,p)+T CG levels of theory are listed in Table S2 in Supplementary Material. The rate constants for the reaction channels (1)–(8) calculated over the temperature range of 220–500 K are shown in Table 1.

The \( \Delta G \) calculated at the CCSD(T)/6-311+G(d,p)//BH&HLYP/6-311++G(d,p)+T CG level are 21.77 and 20.80 kJ/mol at 298 K for channel (1) and channel (2), respectively. The \( \Delta G \) for the other channels range from 28.22 to 39.13 kJ/mol. The calculated rate constants of the reactions (at 298 K) are 4.85 \( \times \) 10\(^{-11}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) (channel 1) and 6.62 \( \times \) 10\(^{-11}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) (channel 2). The calculated rate constants for the other channels are 7.17 \( \times \) 10\(^{-12}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\). Therefore, the reaction channels (1) and (2) is about 17 times faster than the others. Recently, Orlando et al. [19] determined experimentally the rate constant of the reaction between (Z)-PO21 and OH radical to be equal to \((1.06 \pm 0.15) \times 10^{-10}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) at 298 K.
### Table 1. The computed rate constants (cm$^3$ molecule$^{-1}$ s$^{-1}$) for the reaction of OH + (Z)-PO21 at temperatures of 220–500 K.

| T/K  | $k_{TSRC1}$-1 | $k_{TSRC1}$-2 | $k_{TSRC2}$-1 | $k_{TSRC2}$-2 | $k_{TSRC2}$-3 | $k_{TSRC2}$-4 | $k_{TS3}$  | $k_{TS3A}$ | $k_{TS4}$  | $k_{TS4A}$ | $k_{Total}$ |
|------|---------------|---------------|---------------|---------------|---------------|---------------|-----------|-----------|-----------|-----------|-----------|
| 220  | 6.56E-10      | 6.48E-10      | 1.77E-14      | 9.62E-12      | 5.26E-14      | 2.25E-13      | 2.35E-12 | 9.82E-13 | 1.32E-09 | 1.15E-09 | 6.48E-10  |
| 260  | 1.40E-10      | 1.67E-10      | 3.13E-14      | 5.09E-12      | 4.85E-14      | 1.74E-13      | 3.08E-12 | 9.63E-13 | 3.16E-10 | 1.67E-10 | 1.40E-10  |
| 298  | 4.85E-11      | 6.62E-11      | 4.82E-14      | 3.37E-12      | 4.71E-14      | 1.52E-13      | 2.58E-12 | 9.87E-13 | 1.22E-10 | 8.71E-11 | 4.85E-11  |
| 340  | 2.03E-11      | 3.11E-11      | 7.20E-14      | 2.46E-12      | 4.75E-14      | 1.36E-13      | 2.29E-12 | 1.02E-12 | 5.47E-11 | 2.03E-11 | 3.11E-11  |
| 380  | 1.08E-11      | 1.81E-11      | 9.97E-14      | 1.99E-12      | 4.92E-14      | 1.30E-13      | 2.16E-12 | 1.09E-12 | 3.44E-11 | 1.08E-11 | 1.81E-11  |
| 420  | 6.58E-12      | 1.19E-11      | 1.33E-13      | 1.72E-12      | 5.18E-14      | 1.29E-13      | 2.11E-12 | 1.18E-12 | 2.38E-11 | 6.58E-12 | 1.19E-11  |
| 460  | 4.45E-12      | 8.58E-12      | 1.72E-13      | 1.54E-12      | 5.33E-14      | 1.30E-13      | 2.12E-12 | 1.28E-12 | 1.83E-11 | 4.45E-12 | 8.58E-12  |
| 500  | 3.25E-12      | 6.60E-12      | 2.16E-13      | 1.44E-12      | 5.96E-14      | 1.33E-13      | 2.17E-12 | 1.41E-12 | 1.53E-11 | 3.25E-12 | 6.60E-12  |

At this temperature, the total rate constant calculated by TST is $1.22 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, which is in very good agreement with the experimental values.

As shown in Table 1, at the 220–500 K temperature range, the total rate constants slowly decreases with an increase in temperature. Clearly, the total rate constants exhibit a negative temperature dependence, and the calculated total rate constants can be well fitted using a rate expression over a temperature range of 220–500 K: $k = 3.69 \times 10^{-12} \times \exp(1763.7/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$. Our computations show that the activation energy for the reaction of (Z)-PO21 with OH is -14.66 kJ/mol. There are no literature data available to support this assertion. However, a negative temperature dependence has been reported for many OH-unsaturated alcohols addition reactions, in particular the OH+(E)-PO21 [20], OH + CH$_2$ = C(CH$_3$)$_2$CH$_2$OH [48], OH + CH$_3$CH = CHCH$_2$OH [48], OH + CH$_2$ = C(CH$_3$)$_2$OH [48] and OH + CH$_2$ = CHCH$_2$CH$_2$OH [48] reactions. It is well-known that OH radical addition to unsaturated alcohols proceeds with submerged activation barriers, and this phenomenon is explained with the existence of pre-reactive complexes.

### 3.3. Subsequent reactions of IM1 and IM2 with triplet O$_2$

As can be seen from the discussion above and from Figure 1, the adducts IM1 and IM2 are found to be major and predominant on the doublet energy surface, whereas H-abstraction channels can be neglected. Under atmospheric conditions the newly formed hydroxyalkyl radicals IM1 and IM2 can further react with triplet O$_2$ (abbreviated as O$_2$, the same below) as their degradation processes. The structures of all stationary points involved in the reactions of IM1+O$_2$ and IM2+O$_2$ are presented in Figures S2 and S3 in Supplementary Material, respectively. The relative energies including the zero point energy (ZPE) obtained for all stationary points using different theoretical levels are summarised in Tables S3 and S4 in Supplementary Material, respectively. The schematic potential energy surfaces (PESs) of IM1+O$_2$ and IM2+O$_2$ reactions with ZPE corrections obtained at the CCSD(T)/6-311+G(d,p)//BH&HLYP/6-311++G(d,p) level of theory are plotted in Figure 2 and Figure 3, respectively.

The calculations reveal that the O$_2$ molecule can react with IM1 and IM2 via barrierless addition to the C2 atom of IM1, and the C3 atom of IM2 leading to the peroxy radicals HOCH$_2$C(OO•)HCH(OH)CH$_2$CH$_3$ (denoted as IM5) and HOCH$_2$CH(OH)(C(OO•))HCH$_2$CH$_3$ (denoted as IM6), respectively. These doublet collision complexes are stabilised by 246.57, and 255.72 kJ/mol with respect to the reactants. We are now focusing on the possible unimolecular reaction channels of the peroxy radicals IM5. Direct and detailed mechanistic information on the unimolecular molecule reaction of IM5 can be obtained from Figure 2.

The terminal O atom in IM5 can abstract an alkyl hydrogen in CH$_2$(OH) group through transition state TS5-P7 with a barrier height of 131.22 kJ/mol leads to the HO$_2$ + CH(OH) = CHCH(OH)CH$_2$CH$_3$ (P7) products. On the other hand, the terminal O atom of IM5 can also abstract an alkyl hydrogen in CH(OH) group through transition state TS5-P8 with a high barrier height of 144.16 kJ/mol results in the formation of HO$_2$ + CH$_2$(OH) CH = C(OH)CH$_2$CH$_3$ (P8).

The third channel is that IM5 can easily convert via hydroxyl H atom of CH$_2$(OH) group migration to the terminal O atom to form •OCH$_2$C(OO•)HCH(OH)CH$_2$CH$_3$ (IM7) by overcoming cyclic six-membered transition state TS5-7 with a barrier height of 103.89 kJ/mol. Afterward, direct bond fission of C–C in intermediate IM7 through transition state TS7-P9 with a barrier height of 41.53 kJ/mol leads to the formation of HCHO+CH$_3$CH$_2$CH(OH)C(O)H (P9)+OH.

The fourth pathway is that IM5 can readily transform to HOCH$_2$C(OOH)HCH(O•)CH$_2$CH$_3$ (IM7A) by hydroxyl H atom of CH(OH) group migration to the terminal O atom via a six-membered ring transition state TS5-7A over a barrier of 98.33 kJ/mol.
Products CH$_3$CH$_2$C(O)H (P10) + HOCH$_2$C(O)H + OH result from direct C–C bond cleavage of IM7A through transition state TS7A-P10, facing a barrier height of 36.01 kJ/mol.

The fifth channel from IM5 is that it isomerises to HOCC(OOH)HCH(OH)CH$_3$ (IM7B) by a 1,4-H migration (an alkyl hydrogen in CH(OH) group migration to the terminal O atom) via TS5-7B after clearing an energy barrier of 114.72 kJ/mol. Starting from IM7B, there are two possible reaction pathways: IM7B can dissociate into product CH(OH) = CHCH(OH)CH$_2$CH$_3$ (P7) by releasing a HO$_2$ moiety via TS7B-P7, overcoming a barrier of 60.70 kJ/mol. IM7B can also undergo a simultaneous OH loss and ring closure via TS13-P14 to produce the epoxide P11 via TS7B-P11. The corresponding barrier height is estimated to be 18.70 kJ/mol.

The sixth pathway is that IM5 can rearrange to HOCH$_2$C(OOH)HC(OH)CH$_2$CH$_3$ (IM7C) by a 1,4-H migration (an alkyl hydrogen in CH(OH) group migration to the terminal O atom) via a five-membered ring transition state TS5-7C with a barrier height of 120.23 kJ/mol. Two competing cleavage pathways exist for energised IM7C. Direct HO$_2$–CH bond cleavage leads to the formation of HO$_2$+CH$_2$(OH)–CH = C(OH)CH$_2$CH$_3$ (P8) by TS7C-P8 with a barrier height of 55.14 kJ/mol, direct HO–OCH bond cleavage results in the second epoxide P12 plus OH products via TS7C-P12 with a barrier height of 31.14 kJ/mol.

Figure 2. Potential energy diagram for the reaction of IM1 + O$_2$ through all the transition states obtained at the CCSD(T)/6-311+G(d,p)//BH&LYP/6-311++G(d,p)+0.9335 × ZPE levels of theory.
The seventh pathway is that IM5 undergoes the isomerisation process involving the H atom shift from CH₂ group to the terminal O atom for the formation of HOCH₂C(OOH)HCH(OH)C-HCH₃ (IM7D) by overcoming the six-centre transition state TS5-7D. The corresponding barrier height is predicted to be 122.10 kJ/mol. Afterward, IM7C can eventually decompose into the third epoxide P13 by a concerted OH loss and cyclisation via TS7D-P13 over a barrier of 71.53 kJ/mol.

On the last pathway, IM5 can undergo further isomerisation step leading to the formation of HOCH₂C(OOH)HCH(OH)CH₂C (IM7E). The formation of IM7E involves the migration of the H atom from the CH₃ group to the terminal O atom by passing the seven-centre transition state TS5-7E, facing a barrier of 123.95 kJ/mol. Then, IM7E dissociates to the fourth epoxide P14 and OH via TS7E-P14, 20.38 kJ/mol above IM7E.

Let us now consider the predicted reaction pathways for another peroxy radical IM6. As can be seen in Figure 3, eight different pathways are calculated to be present. These possible reaction pathways depicted in Figure 3 are analogous to those found in Figure 2.

The terminal O atom in IM6 can either abstract an alkyl hydrogen in CH(OH) group to produce HO₂ + HOCH₂C(OH) = CHCH₂CH₃ (P15) by passing the five-membered-ring transition state TS6-P15 or abstract an H atom of the methylene CH₂ group to yield HO₂ + HOCH₂CH(OH)CH = CHCH₃ (P16) by passing the five-membered-ring transition state TS6-P16. The corresponding barrier heights for these two steps are estimated to be 152.88 and 138.48 kJ/mol, respectively.
Third, a hydroxyl hydrogen migration from the CH(OH) group of IM6 to the terminal O atom to form HOCH₂CH(O)C(OH)HCH₂CH₃ (IM8) is associated with the lowest energy barrier, which is located 100.77 kJ/mol above IM6. Eventually, IM8 dissociates via C–C bond breaking to form CH₃CH₂C(O)H (P10)+HOCH₂C(O)H + OH. The corresponding transition state is TS8-P10, which sits 24.22 kJ/mol above IM8.

Fourth, isomerisation of IM6 to •OCH₂CH(OH)C(O)HCH₂CH₃ (IM8A) occurs by a 1,6-H shift (a hydroxyl hydrogen migration from the CH₂(OH) group to the terminal O atom) via a seven-centre transition state TS6-8A with a barrier height of 117.07 kJ/mol. Subsequently, direct bond decomposition of C–C in intermediate IM8A through transition state TS8A-HCHO over a barrier height of 37.68 kJ/mol leads to the formation of HCHO+CH₃CH₂CHOH(C•H)(OH).

Fifth, transformation of IM6 to HOCH₂C•(OH)C(OOH)HCH₂CH₃ (IM8B) takes place by a 1,4-H migration via a five-membered ring transition state TS6-8B after climbing a barrier height of 132.14 kJ/mol. Subsequently, IM8B can either eliminate a HO₂ group to form the enol HOCH₂C(OH) = CHCH₂CH₃ (P15) via TS88-P15 with a barrier height of 66.70 kJ/mol or release a OH group to produce the fifth epoxide P17 via TS88-P17 with a barrier height of 46.58 kJ/mol.

Sixth, IM6 can undergo the internal conversion to form HOC•HCH•(OH)C(OOH)HCH₂CH₃ (IM8C) via a six-member ring transition state TS6-8C, facing an energy barrier of 103.89 kJ/mol. Afterward, IM8C undergoes cyclisation to the sixth epoxide P18 through a OH group loss via TS8C-P18 after passing an energy barrier of 63.80 kJ/mol. From Figure 3, one can notice that TS6-8C lies only 3.12 kJ/mol above TS6-8 and TS8C-P18 lies only 0.38 kJ/mol below TS8-P10. Apparently, the sixth reaction channel of IM6 is feasible kinetically.

Seventh, IM6 converts to form HOCH₂CH(OH)C(OOH)HC•H₃ (IM8D) via TS6-8D, followed by decomposition of IM8D either to produce HO₂ + HOCH₂CH(OH)CH = CHCH₂ (P16) via TS8D-P16 or to produce the seventh epoxide P19 and OH via TS8D-P19. The barrier for isomerisation and decomposition paths is 145.13, 68.70 and 36.67 kJ/mol, respectively.

Finally, IM6 transforms into HOCH₂CH(OH)C(OOH)HCH₂CH₂ (IM8E) via a 1,5-H migration, followed by dissociation to produce to the eighth epoxide P20 plus OH via a direct C–C bond cleavage. The corresponding transition states are TS6-8E and TS8E-P20, whose barrier heights are estimated to be 111.91 and 64.99 kJ/mol, respectively.

Overall, the theoretical results obtained for the unimolecular molecule reaction channels of the peroxy radicals IM5 and IM6 indicate that the most facile channels for the titled reaction are predicted to be the IM5→IM7A→CH₃CH₂C(O)H (P10)+HOCH₂C(O)H+OH and the IM6→IM8→CH₃CH₂C(O)H (P10)+HOCH₂C(O)H+OH pathways. While, the IM5→IM7→HC(O)H+CH₃CH₂CH(OH)C(O)H (P9)+OH and the IM6→IM8C→P18+OH pathways are expected to be minor product channels. As for the other isomerisation pathways, leading to seven epoxide conformers and four enol conformers, highly unlikely because of the high isomerisation barriers involved. Therefore, the products propanal [CH₃CH₂C(O)H] and glycolaldehyde [HOCH₂C(O)H] are anticipated to be major and predominant for the titled reaction. Whereas formaldehyde [HC(O)H], 2-hydroxybutanal [CH₃CH₂CH(OH)C(O)H] and the epoxide P18 are found to be minor products. Experimentally, Orlando et al. [19] provide an explanation for the observed products. In the atmosphere, i.e. in the presence of O₂/NO₂, two adducts IM1 and IM2 formed via addition of OH radical to the two unsaturated carbon atoms of (Z)-PO21, will react with O₂ firstly to form two peroxy radicals HOCH₂C(OO•)CH(OH)CH₂CH₃ (IM5 in this paper) and HOCH₂CH(OH)C(OO•)HCH₂CH₃ (IM6 in this paper), which are followed by the formations of two corresponding peroxy nitrites via combination with NO, respectively. Subsequently, with the departure of NO₂, two alkoxy radicals HOCH₂C(O•)CH(OH)CH₂CH₃ and HOCH₂CH(OH)C(O•)HCH₂CH₃ will be formed. Then the two alkoxy radicals proceed through dissociation and association reactions with O₂ to form the final major products of propanal+glycolaldehyde and minor products of formaldehyde+2-hydroxybutanal. The calculated results are in qualitative accordance with the available experimental observations [19]. Our present calculations also show that the major products and minor products are same as the experimental observations even if in the absence of NO.

4. Conclusions

We carried out an *ab initio* and TST study of the reaction of the OH-initiated atmospheric oxidation of (Z)-PO21 using density functional theory and the CCSD(T) method. The optimised geometries of the reactants, reactant complexes, intermediates, transition states and products along the various reaction pathways have been obtained. The rate constants for four addition pathways and four abstraction pathways have been calculated at the range of temperatures between 220 and 500 K. The calculated results clearly indicate that the total rate constants of the title reaction should show a slightly negative
temperature dependence. The calculated rate constants also show that the abstraction reactions cannot compete with the addition reactions at the temperature range of 220–500 K. The major pathways are found to be the formation of two adducts HOCH₂C•HCHOH(CH₂)₂CH₃ (IM1) and HOCH₂CHOH(C•HCHOH(CH₂)₂CH₃ (IM2). In the presence of O₂, the newly formed adducts IM1 and IM2 will add O₂ to generate alkyl peroxy radicals ROO• (IM5 and IM6), followed by isomerisation to yield four major hydroperoxyalkyl radicals R’OOH (IM7A, IM7, IM8 and IM8C). The ultimate fate of these hydroperoxyalkyl radicals is that they can dissociate to C–C or O–O bond cleavage to form carbonyl products such as propanal, glycolaldehyde, formaldehyde, 2-hydroxybutanal and the epoxide P18. The enols pathways are, however, highly unlikely due to the high isomerisation barriers involved.

**Disclosure statement**

No potential conflict of interest was reported by the authors.

**Funding**

This work is jointly supported by the Natural Science Foundation for Colleges and Universities in Jiangsu Province, People’s Republic of China [grant number 10KJB150017]; a Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

**References**

[1] J. Arey, A.M. Winer, R. Atkinson, S.M. Aschmann, W.D. Long, and C.L. Morrison, Atmos. Environ. 25, 1063 (1991).
[2] W. Kirstine, I. Galbally, Y.R. Ye, and M. Hooper, J. Geo-phys. Res. Atmos. 103, 10605 (1998).
[3] A.J. Fisher, H.D. Grimes, and R. Fall, Phytochemistry 62, 159 (2003).
[4] A.C. Heiden, K. Kobel, C. Langebartels, G. Schuh-Thomas, and J. Wildt, J. Atmos. Chem. 45, 143 (2003).
[5] T. Karl, R. Fall, A. Jordan, and W. Lindinger, Environ. Sci. Technol. 35, 2926 (2001).
[6] M. Baasandorj, and P.S. Stevens, J. Phys. Chem. A 111, 640 (2007).
[7] E. Jiménez, B. Lanza, M. Antíoñio, and J. Albaladejo, Environ. Sci. Technol. 43, 1831 (2009).
[8] C. Papagni, J. Arey, and R. Atkinson, Int. J. Chem. Kinet. 33, 142 (2001).
[9] H.P. Upadhyaya, A. Kumar, P.D. Naik, A.V. Sapre, and J.P. Mittal, Chem. Phys. Lett. 349, 279 (2001).
[10] J. Noda, G. Nyman, and S. Langer, J. Phys. Chem. A 106, 945 (2002).
[11] C. Pétrang, M.T.B. Romero, B. Cabanas, C.E. Canosa-Mas, F. Villanueva, and R.P. Wayne, Atmos. Environ. 41, 1652 (2007).
[12] A. Alvarado, E.C. Tuazon, S.M. Aschmann, J. Arey, and R. Atkinson, Atmos. Environ. 33, 2893 (1999).
[13] E. Grosjean and D. Grosjean, J. Atmos. Chem. 27, 271 (1997).
[14] K. Takahashi, J.H. Xing, M.D. Hurley, and T.J. Wallington, J. Phys. Chem. A 114, 4224 (2010).
[15] D. Rodriguez, A. Rodriguez, A. Soto, A. Aranda, Y. Diaz-de-Mera, and A. Notario, J. Atmos. Chem. 59, 187 (2008).
[16] A. Aranda, E. Martínez, Y.D. de Mera, A. Rodríguez, D. Rodriguez, and J. Cuartero, Atmos. Environ. 37, 4361 (2003).
[17] G. Fantechi, N. Jensen, O. Saastad, J. Hjorth, and J. Peeters, J. Atmos. Chem. 31, 247 (1998).
[18] T.J. Wallington, P. Dagaht, and M.J. Kurylo, Chem. Rev. 92, 667 (1992).
[19] J.J. Orlando, G.S. Tyndall, and N. Ceazan, J. Phys. Chem. A 105, 3564 (2001).
[20] M.E. Davis, and J.B. Burkholder, Atmos. Chem. Phys. 11, 3347 (2011).
[21] S. Jørgensen, H.C. Knap, R.V. Otkjær, A.M. Jensen, M.L.H. Kjeldsen, P.O. Wennberg, and H.G. Kjærgaard, J. Phys. Chem. A 120, 266 (2016).
[22] G. Muller, A. Scheer, D.L. Osborn, C.A. Taatjes and G. Meloni, J. Phys. Chem. A 120, 1677 (2016).
[23] S. So, U. Wille, and G. da Silva, J. Phys. Chem. A 119, 9812 (2015).
[24] X.T. Le, T.V.T. Mai, A. Ratkiewicz, and L.K. Huynh, J. Phys. Chem. A 119, 3689 (2015).
[25] A. Rodriguez, O. Frottier, O. Herbinet, R. Fournet, R. Bounaceur, C. Fitschsen, and F. Battin-Leclerc, J. Phys. Chem. A 119, 7905 (2015).
[26] M.Y. Ng, B.M. Bryan, J. Nelson, and G. Meloni, J. Phys. Chem. A 119, 8667 (2015).
[27] R. Asatryan, G. da Silva, and J.W. Bozzelli, J. Phys. Chem. A 114, 8302 (2010).
[28] J.J. Orlando, and G.S. Tyndall, Chem. Soc. Rev. 41, 6294 (2012).
[29] J.D. Crounse, L.B. Nielsen, S. Jørgensen, H.G. Kjærgaard and P.O. Wennberg, J. Phys. Chem. Lett. 4, 3513 (2013).
[30] J. Peeters, T.L. Nguyen, and L. Vereecken, Phys. Chem. Chem. Phys. 11, 5935 (2009).
[31] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery Jr, J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, and D.J. Fox, Gaussian 09, Revision C.01, (Gaussian Inc., Wallingford, CT, 2010).
[32] C. Lee, W. Yang, and R.G. Parr, Phys. Rev. B 37, 785 (1988).
[33] A.D. Becke, J. Chem. Phys. 98, 1372 (1993).
[34] M.J. Frisch, J.A. Pople, and J.S. Binkley, J. Chem. Phys. 80, 3265 (1984).
[35] L.K. Huynh, A. Ratkiewicz, and T.N. Truong, J. Phys. Chem. A 110, 473 (2005).
[36] A. Vega-Rodriguez and J.R. Alvarez-Idaboy, Phys. Chem. Chem. Phys. 11, 7649 (2009).
[37] J.P. Merrick, D. Moran, and L. Radom, J. Phys. Chem. A 111, 11683 (2007).
[38] H.P. Hratchian and H.B. Schlegel, J. Chem. Phys. 120, 9918 (2004); J. Chem. Theory Comput. 1, 61 (2005).
[39] J.A. Pople, M. Head-Gordon, and K. Raghavachari, J. Chem. Phys. 87, 5968 (1987).
[40] K. Raghavachari, G.W. Trucks, J.A. Pople, and M. Head-Gordon, Chem. Phys. Lett. 157, 479 (1989).
[41] J.C. Rienstra-Kiracofe, W.D. Allen, and H.F. Schaefer III, J. Phys. Chem. A 104, 9823 (2000).
[42] M.J. Pilling and P.W. Seakins, Reaction Kinetics, Oxford University Press Inc.: New York, NY, 1999.
[43] A. Galano, J.R. Alvarez-Idaboy, M.E. Ruiz-Santoyo, and A. Vivier-Bunge, J. Phys. Chem. A 109, 169 (2005).
[44] J.R. Alvarez-Idaboy, N. Mora-Diez, and A. Vivier-Bunge, J. Am. Chem. Soc. 122, 3715 (2000).
[45] H. Sun and C.K. Law, J. Phys. Chem. A 114, 12088 (2010).
[46] D.L. Singleton and R.J. Cvetanovic, J. Am. Chem. Soc. 98, 6812 (1976).
[47] E. Wigner, J. Chem. Phys. 5, 720 (1937).
[48] P.M. Cometto, P.R. Dalmaso, R.A. Taccone, S.I. Lane, F. Oussar, V. Daële, A. Mellouki, and G. Le Bras, J. Phys. Chem. A 112, 4444 (2008).