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# Computational study on the mechanism and kinetics for the reaction between HO<sub>2</sub> and *n*-propyl peroxy radical†

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The *n*-propyl peroxy radical (*n*-C<sub>3</sub>H<sub>7</sub>O<sub>2</sub>) is the key intermediate during atmospheric oxidation of propane (C<sub>3</sub>H<sub>8</sub>) which plays an important role in the carbon and nitrogen cycles in the troposphere. In this paper, a comprehensive theoretical study on the reaction mechanism and kinetics of the reaction between HO<sub>2</sub> and *n*-C<sub>3</sub>H<sub>7</sub>O<sub>2</sub> was performed at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-311G(d,p) level of theory. Computational results show that the HO<sub>2</sub> + *n*-C<sub>3</sub>H<sub>7</sub>O<sub>2</sub> reaction proceeds on both singlet and triplet potential energy surfaces (PESs). From an energetic point of view, the formation of C<sub>3</sub>H<sub>7</sub>O<sub>2</sub>H and <sup>3</sup>O<sub>2</sub> via triplet hydrogen abstraction is the most favorable channel while other product channels are negligible. In addition, the calculated rate constants for the title reaction over the temperature range of 238–398 K were calculated by the multiconformer transition state theory (MC-TST), and the calculated rate constants show a negative temperature dependence. The contributions of the other four reaction channels to the total rate constant are negligible.

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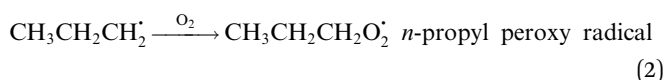
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## 1. Introduction

Propane (C<sub>3</sub>H<sub>8</sub>) is one of the most important nonmethane hydrocarbons (NMHCs) with a lifetime of about 14 days and its global emissions are estimated to be 15–20 Tg per year.<sup>1,2</sup> For decades, propane oxidation has been of great interest, and the *n*-propyl peroxy radical (*n*-C<sub>3</sub>H<sub>7</sub>O<sub>2</sub>) is one of the key intermediates during propane oxidation.<sup>3–6</sup>



In clean environments where NO<sub>x</sub> concentrations are low, the reactions of HO<sub>2</sub> with organic peroxy radicals (RO<sub>2</sub>) are generally considered as an important sink.<sup>7–11</sup> The reaction mechanisms and kinetic data of HO<sub>2</sub> + RO<sub>2</sub> reactions have not

yet been well-established mainly because of inherent problems in exploring radical–radical reactions.<sup>12</sup> Besides, to the best of our knowledge, only a few studies for both kinetics and mechanism of the HO<sub>2</sub> + *n*-C<sub>3</sub>H<sub>7</sub>O<sub>2</sub> reaction have been reported. One of the difficulties is that the *n*-C<sub>3</sub>H<sub>7</sub>O<sub>2</sub> radical is more complex than CH<sub>3</sub>O<sub>2</sub> and C<sub>2</sub>H<sub>5</sub>O<sub>2</sub> due to its rich conformational variety. It has been reported that the *n*-C<sub>3</sub>H<sub>7</sub>O<sub>2</sub> radical has five different conformers: G<sub>1</sub>G<sub>2</sub>, G<sub>1</sub>T<sub>2</sub>, G<sub>1</sub>G<sub>2</sub>, T<sub>1</sub>G<sub>2</sub> and T<sub>1</sub>T<sub>2</sub> (see Fig. S1 in the ESI†).<sup>13–15</sup>

Hou and co-workers have developed a structure–activity relationships (SAR) model to study structure–activity relationships and the characteristics of the HO<sub>2</sub> + RO<sub>2</sub> reactions.<sup>10</sup> They reported the calculated rate constant for HO<sub>2</sub> + C<sub>3</sub>H<sub>7</sub>O<sub>2</sub> reaction as 9.12 × 10<sup>–12</sup> cm<sup>3</sup> per molecule per s. However, the detailed reaction mechanism and kinetic data of HO<sub>2</sub> + *n*-C<sub>3</sub>H<sub>7</sub>O<sub>2</sub> reaction are still unclear. To better understanding of this issue, a systematic theoretical investigation on the HO<sub>2</sub> + *n*-C<sub>3</sub>H<sub>7</sub>O<sub>2</sub> reaction is required. In this work, quantum chemistry calculations have been performed to explore the detailed reaction mechanism of HO<sub>2</sub> + *n*-C<sub>3</sub>H<sub>7</sub>O<sub>2</sub> reaction both on the singlet and triplet potential energy surfaces. Then the rate constant of the title reaction was calculated using the multiconformer transition state theory (MC-TST) which considered that the *n*-C<sub>3</sub>H<sub>7</sub>O<sub>2</sub> radical has multiple conformers.

## 2. Computational methods

The geometries of the reactants, intermediates, transition states and products in the HO<sub>2</sub> + *n*-C<sub>3</sub>H<sub>7</sub>O<sub>2</sub> reaction were fully

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optimized by Density Functional Theory (DFT) method at the B3LYP/6-311G(d,p) level of theory.<sup>16,17</sup> Harmonic vibrational frequencies were calculated at the same level to confirm that all minima are real frequencies, and transition states have only a single imaginary frequency. Vibrational frequencies and coordinates of all stationary points in the title reaction have been summarized Tables S1 and S2,<sup>†</sup> respectively (see ESI<sup>†</sup>). In addition, the intrinsic reaction coordinate (IRC) calculations were also carried out to verify that the transition states structures can be connected to the corresponding reactants and products.<sup>18–21</sup> The zero-point energies (ZPEs) and the thermodynamic corrections at the temperature of 298.15 K and pressure of 1 atm were evaluated at the B3LYP/6-311G(d,p) level of theory and were incorporated in to the final energy barrier, enthalpy and Gibbs free energy. To get more reliable energy information, single point energy calculations were carried out at CCSD(T)/aug-cc-pVDZ level of theory.<sup>22</sup> In CCSD (T) calculation, T<sub>1</sub> diagnostic is thought to assess the reliability of the methods with respect to a possible multireference feature of the wave functions. For open-shell systems, if the T<sub>1</sub> diagnostic value do not exceed 0.044, the wave functions of CCSD are considered to be reliable.<sup>23–26</sup> The T<sub>1</sub> diagnostic values of the stationary points are presented in Table S3 (ESI<sup>†</sup>). T<sub>1</sub> diagnostic values of the stationary points except for G<sub>1</sub>G<sub>2</sub>-<sup>3</sup>TS1, G<sub>1</sub>T<sub>2</sub>-<sup>3</sup>TS1, G<sub>1</sub>G<sub>2</sub>-<sup>3</sup>TS1 are less than 0.044 from Table S3,<sup>†</sup> revealing that the CCSD wave function could be reliable. All the computations were performed with Gaussian 09 program package.<sup>27</sup> The CCSD(T) single point energy computations were carried out by Molpro package.<sup>28,29</sup>

Since that the *n*-C<sub>3</sub>H<sub>7</sub>O<sub>2</sub> has multiple conformers, such complexity should be taken account into the rate constant formula, multiconformer transition state theory (MC-TST) method were carried out for rate constant calculations.<sup>30–33</sup> Within the framework of the conventional transition state theory (TST),<sup>34–36</sup> the MC-TST expression for a rate constant *k* at temperature *T* can be written as

$$k_{\text{MC-TST}} = \kappa \frac{k_{\text{B}}T}{h} \frac{\sum_i^{\text{all TS conf.}} \exp\left(\frac{-\Delta E_i}{k_{\text{B}}T}\right) Q_{\text{TS},i}}{\sum_j^{\text{all R conf.}} \exp\left(\frac{-\Delta E_j}{k_{\text{B}}T}\right) Q_{\text{R},j}} \times \exp\left(-\frac{E_{\text{TS},0} - E_{\text{R},0}}{k_{\text{B}}T}\right) \quad (3)$$

Here  $\kappa$  is the Eckart tunneling correction<sup>37</sup> factor associated with the lowest energy transition state.  $k_{\text{B}}$  and  $h$  are Boltzmann's constant and Planck's constant, respectively.  $\Delta E_i$  represents the difference in zero-point corrected energy between the transition state conformer *i* and the lowest energy transition state conformer, and  $Q_{\text{TS},i}$  represents the total partition function of the transition state conformer *i*.  $\Delta E_j$  denotes zero-point corrected energy of reactant conformer *j* relative to the lowest energy reactant conformer, and  $Q_{\text{R},j}$  represents the partition function of reactant conformer *j*.  $E_{\text{TS},0}$  and  $E_{\text{R},0}$  represent the zero-point corrected energy of the lowest energy conformer of the transition state and reactant, respectively. The energies in

the MC-TST expression were computed at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-311G(d,p) level of theory and the partition functions were obtained at the B3LYP/6-311G(d,p) level of theory.

### 3. Results and discussion

The scheme of the possible reaction routes for the HO<sub>2</sub> + *n*-C<sub>3</sub>H<sub>7</sub>O<sub>2</sub> reaction has been showed in Fig. 1. In this section, the reaction mechanism and kinetics of the HO<sub>2</sub> + *n*-C<sub>3</sub>H<sub>7</sub>O<sub>2</sub> reaction have been discussed. For simplicity, we first focus on the reaction mechanism of HO<sub>2</sub> and the most stable G<sub>1</sub>G<sub>2</sub> conformer reaction in the following parts. The HO<sub>2</sub> + G<sub>1</sub>T<sub>2</sub>, G<sub>1</sub>G<sub>2</sub>, T<sub>1</sub>G<sub>2</sub> and T<sub>1</sub>T<sub>2</sub> reactions are compared with the HO<sub>2</sub> + G<sub>1</sub>G<sub>2</sub> reaction. The schematic energy diagram of the HO<sub>2</sub> + G<sub>1</sub>G<sub>2</sub> reaction is depicted in Fig. 2, whereas the corresponding profiles of the schematic energy diagram are shown schematically in Fig. S2–S5<sup>†</sup> for the HO<sub>2</sub> + G<sub>1</sub>T<sub>2</sub>, G<sub>1</sub>G<sub>2</sub>, T<sub>1</sub>G<sub>2</sub> and T<sub>1</sub>T<sub>2</sub> reactions (ESI<sup>†</sup>), respectively. The selected geometric structures of the five reactions are displayed in Fig. 3 and S6–S9,<sup>†</sup> respectively. In what follows, energies of the HO<sub>2</sub> + G<sub>1</sub>G<sub>2</sub>, G<sub>1</sub>T<sub>2</sub>, G<sub>1</sub>G<sub>2</sub>, T<sub>1</sub>G<sub>2</sub> and T<sub>1</sub>T<sub>2</sub> reactions are shown in Tables 1 and S4–S7,<sup>†</sup> respectively. Besides, to study the relative importance of various products in the HO<sub>2</sub> + *n*-C<sub>3</sub>H<sub>7</sub>O<sub>2</sub>, the rate constants of the most favorable channel for the five different reactions have been discussed. Finally, Arrhenius plot for the triplet channel of HO<sub>2</sub> + *n*-C<sub>3</sub>H<sub>7</sub>O<sub>2</sub> reaction is displayed in Fig. 4 and the calculated rate constants are fitted into Arrhenius three parameter equation.

Throughout the discussions, the transition states and intermediates in each reaction are denoted by “TS” and “IM”, respectively, followed by a number. The optimized geometries involved in the five reactions are designated by the prefix G<sub>1</sub>G<sub>2</sub>, G<sub>1</sub>T<sub>2</sub>, G<sub>1</sub>G<sub>2</sub>, T<sub>1</sub>G<sub>2</sub> and T<sub>1</sub>T<sub>2</sub>, respectively, followed by the “TS” or “IM”.

#### 3.1 Mechanism of the HO<sub>2</sub> + *n*-C<sub>3</sub>H<sub>7</sub>O<sub>2</sub> reaction

**3.1.1 Reaction mechanism on triplet PES.** A schematic presentation of triplet potential energy surfaces for the reaction between HO<sub>2</sub> and individual *n*-C<sub>3</sub>H<sub>7</sub>O<sub>2</sub> conformer have been computed at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-311G(d,p) level of theory. For example, in the case of the HO<sub>2</sub> and G<sub>1</sub>G<sub>2</sub> conformer reaction, schematic energy diagram of the reaction is shown in Fig. 2 and the geometric structures of reactants, intermediates, transition states and products are depicted in Fig. 3. For the triplet potential energy surface, our calculations show one possible reaction pathway proceeding through a pre-

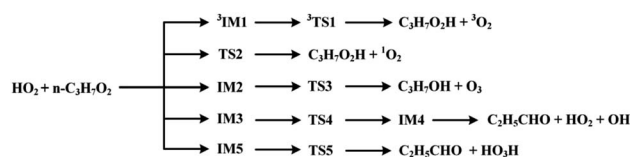


Fig. 1 The scheme of possible reaction routes of HO<sub>2</sub> + *n*-C<sub>3</sub>H<sub>7</sub>O<sub>2</sub> reaction on both the singlet and triplet potential energy surfaces.



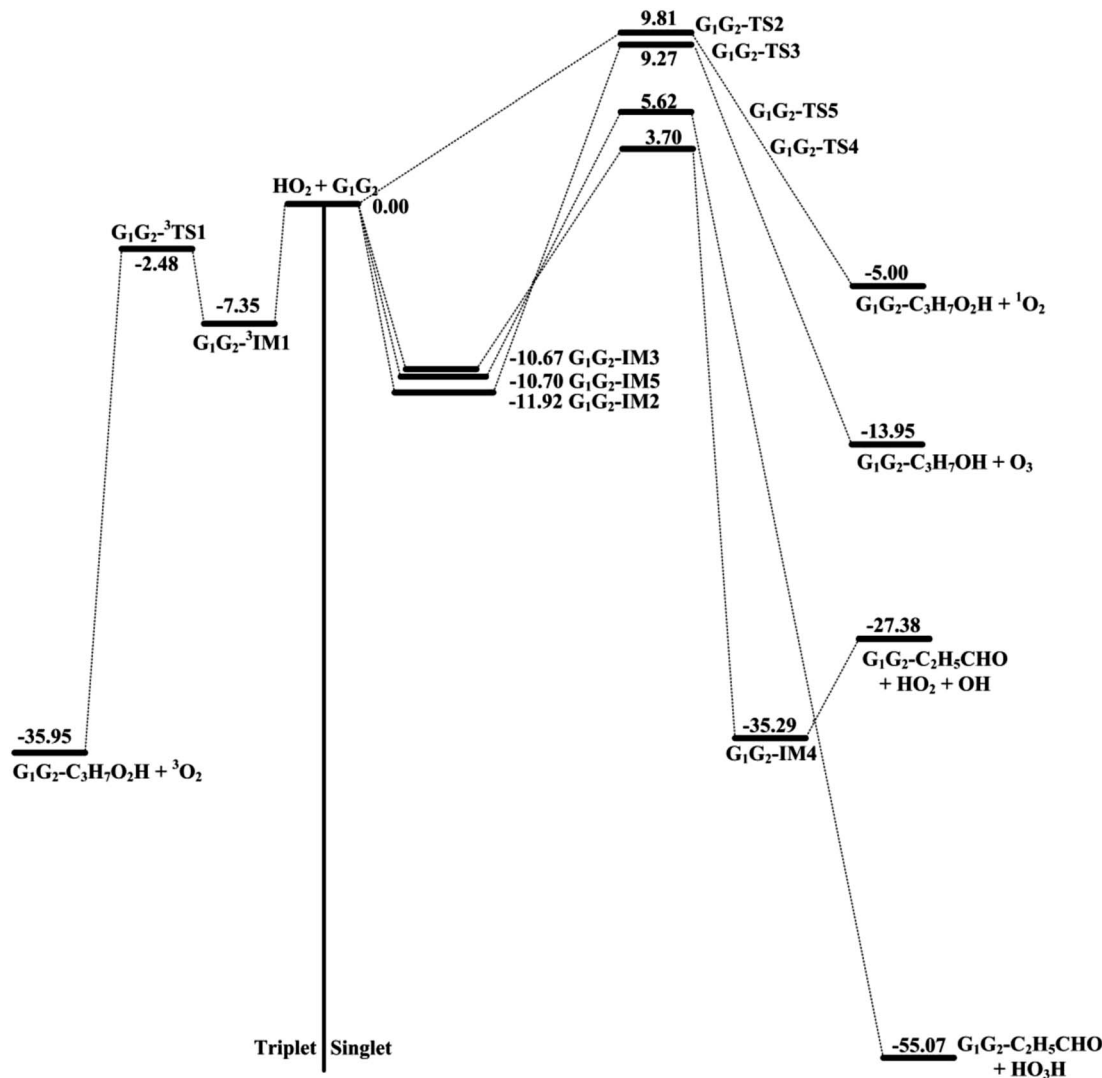


Fig. 2 Schematic energy diagram of  $\text{HO}_2 + \text{G}_1\text{G}_2$  reaction computed at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-311G(d,p) level of theory on both the singlet and triplet potential energy surfaces. Energies are in units of  $\text{kcal mol}^{-1}$ .

reaction complex  $\text{G}_1\text{G}_2\text{-}^3\text{IM1}$  and a transition state  $\text{G}_1\text{G}_2\text{-}^3\text{TS1}$  to produce  $\text{G}_1\text{G}_2\text{-C}_3\text{H}_7\text{O}_2\text{H}$  and triplet  $\text{O}_2$ . This pathway is a hydrogen abstraction process by the H atom on the  $\text{HO}_2$  radical migrates to the terminal oxygen of  $\text{G}_1\text{G}_2$ . In  $\text{G}_1\text{G}_2\text{-}^3\text{IM1}$ , the length of hydrogen bond between the terminal oxygen atom of  $\text{G}_1\text{G}_2$  and the hydrogen atom of  $\text{HO}_2$  is 1.801 Å, which is 0.408 Å longer than that in the  $\text{G}_1\text{G}_2\text{-}^3\text{TS1}$ . It is stabilized by the hydrogen bond interaction with a binding energy of  $-7.35 \text{ kcal mol}^{-1}$  relative to the  $\text{HO}_2 + \text{G}_1\text{G}_2$  reactants. From the equilibrium structure of  $\text{G}_1\text{G}_2\text{-}^3\text{TS1}$  shown in Fig. 3, the breaking H–O and the forming O–H bonds are 1.064 and 1.393 Å, respectively. The breaking H–O bond is only slightly longer by 0.089 Å compared to the equilibrium of H–O bond in  $\text{HO}_2$  radical. The  $\text{O}\cdots\text{H}\cdots\text{O}$  bond angle is nearly linear with a value of approximately  $171.93^\circ$ . The barrier of  $\text{G}_1\text{G}_2\text{-}^3\text{TS1}$  is  $-2.48 \text{ kcal mol}^{-1}$ .  $\text{G}_1\text{G}_2\text{-}^3\text{TS1}$  is an early barrier compared to other different channels in the reaction of  $\text{HO}_2 + \text{G}_1\text{G}_2$ .

For the triplet hydrogen abstraction process, the  $\text{HO}_2 + \text{G}_1\text{T}_2$ ,  $\text{G}'_1\text{G}_2$ ,  $\text{T}_1\text{G}_2$  and  $\text{T}_1\text{T}_2$  four reactions are also identified to be kinetically favorable pathways *via* the same reaction mechanism as that of  $\text{HO}_2 + \text{G}_1\text{G}_2$  reaction (see Fig. S2–S5†). The selected geometric structures for the reactants, intermediates, transition states and products of the four reactions were shown in Fig. S6–S9,† respectively. As shown in Fig. S2–S5,† all the four reactions take place on the triplet surfaces from the reactants *via* intermediates ( $\text{G}_1\text{T}_2\text{-}^3\text{IM1}$ ,  $\text{G}'_1\text{G}_2\text{-}^3\text{IM1}$ ,  $\text{T}_1\text{G}_2\text{-}^3\text{IM1}$  and  $\text{T}_1\text{T}_2\text{-}^3\text{IM1}$ ) and transition states ( $\text{G}_1\text{T}_2\text{-}^3\text{TS1}$ ,  $\text{G}'_1\text{G}_2\text{-}^3\text{TS1}$ ,  $\text{T}_1\text{G}_2\text{-}^3\text{TS1}$  and  $\text{T}_1\text{T}_2\text{-}^3\text{TS1}$ ) to produce the  $\text{C}_3\text{H}_7\text{O}_2\text{H}$  and triplet  $\text{O}_2$ . The four intermediates are hydrogen bond complexes. The binding energies of four intermediates are  $-6.83 \text{ kcal mol}^{-1}$  ( $\text{G}_1\text{T}_2\text{-}^3\text{IM1}$ ),  $-6.73 \text{ kcal mol}^{-1}$  ( $\text{G}'_1\text{G}_2\text{-}^3\text{IM1}$ ),  $-6.81 \text{ kcal mol}^{-1}$  ( $\text{T}_1\text{G}_2\text{-}^3\text{IM1}$ ) and  $-6.79 \text{ kcal mol}^{-1}$  ( $\text{T}_1\text{T}_2\text{-}^3\text{IM1}$ )  $\text{kcal mol}^{-1}$ , respectively. In the structure of  $\text{G}_1\text{G}_2\text{-}^3\text{IM1}$ , the binding energy is  $-7.35 \text{ kcal mol}^{-1}$ , which is close to that in the four intermediates above. The four corresponding transition states involve



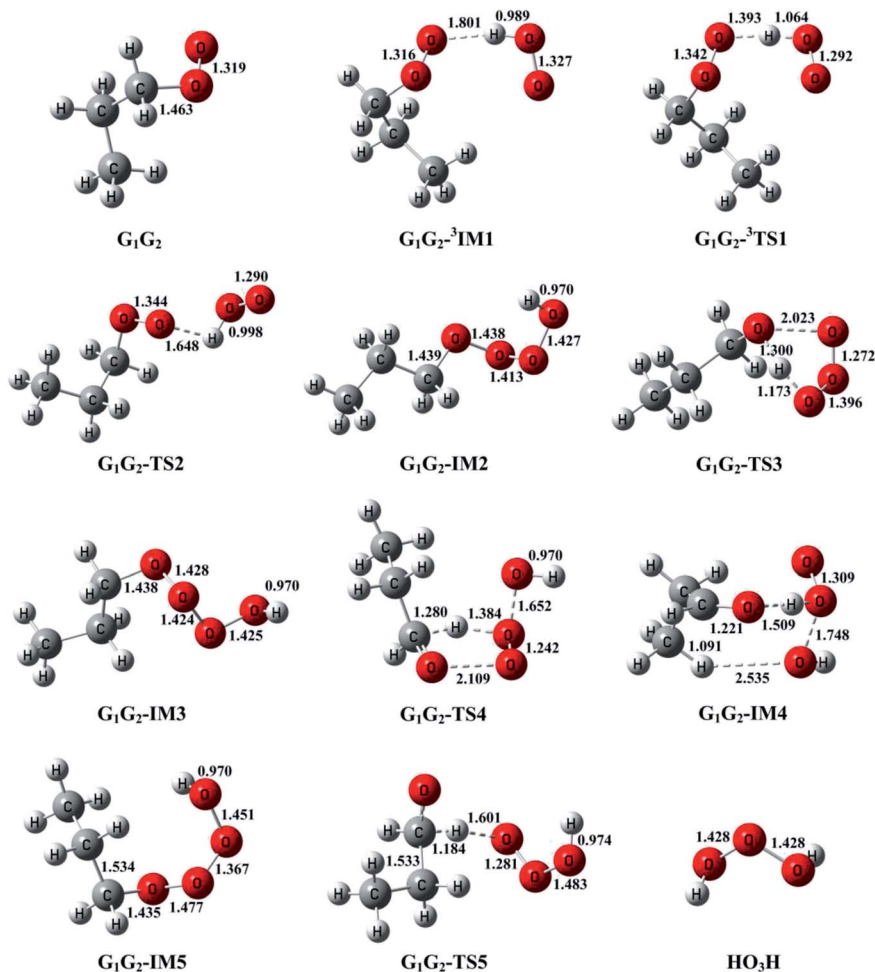


Fig. 3 Selected geometric structures of the reactants, intermediates and transition states of  $\text{HO}_2 + \text{G}_1\text{G}_2$  reaction computed at the B3LYP/6-311G(d,p) level of theory on both the singlet and triplet potential energy surfaces. Bond distances are given in angstroms.

Table 1 Zero point energies (ZPE), relative energies ( $\Delta E_{298\text{ K}}$ ), reaction enthalpies ( $\Delta H_{298\text{ K}}$ ) and Gibbs free energies ( $\Delta G_{298\text{ K}}$ ) of the stationary points involved in  $\text{HO}_2 + \text{G}_1\text{G}_2$  reaction. Energies are computed at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-311G(d,p) level of theory. Energy values are given in  $\text{kcal mol}^{-1}$

| Compound  | ZPE   | $\Delta E_{298\text{ K}}$ | $\Delta H_{298\text{ K}}$ | $\Delta G_{298\text{ K}}$ |
|---|-------|---------------------------|---------------------------|---------------------------|
| $\text{G}_1\text{G}_2 + \text{HO}_2$  | 71.62 | 0.00                      | 0.00                      | 0.00                      |
| $\text{G}_1\text{G}_2\text{-}^3\text{IM1}$                                      | 73.23 | -6.78                     | -7.37                     | 1.82                      |
| $\text{G}_1\text{G}_2\text{-}^3\text{TS1}$                                      | 70.85 | -2.47                     | -3.06                     | 7.59                      |
| $\text{G}_1\text{G}_2\text{-C}_3\text{H}_7\text{O}_2\text{H} + ^3\text{O}_2$    | 72.27 | -35.88                    | -35.88                    | -34.48                    |
| $\text{G}_1\text{G}_2\text{-TS2}$   | 72.41 | 9.96                      | 9.36                      | 20.45                     |
| $\text{G}_1\text{G}_2\text{-C}_3\text{H}_7\text{O}_2\text{H} + ^1\text{O}_2$    | 72.25 | -4.93                     | -4.93                     | -2.88                     |
| $\text{G}_1\text{G}_2\text{-IM2}$   | 74.18 | -12.02                    | -12.61                    | -0.41                     |
| $\text{G}_1\text{G}_2\text{-TS3}$   | 71.22 | 8.76                      | 8.17                      | 21.28                     |
| $\text{G}_1\text{G}_2\text{-C}_3\text{H}_7\text{OH} + \text{O}_3$               | 72.58 | -14.26                    | -14.26                    | -13.41                    |
| $\text{G}_1\text{G}_2\text{-IM3}$   | 73.98 | -10.77                    | -11.36                    | 0.85                      |
| $\text{G}_1\text{G}_2\text{-TS4}$   | 69.91 | 3.58                      | 2.99                      | 15.51                     |
| $\text{G}_1\text{G}_2\text{-IM4}$   | 72.52 | -34.70                    | -35.29                    | -24.64                    |
| $\text{G}_1\text{G}_2\text{-C}_2\text{H}_5\text{CHO} + \text{HO}_2 + \text{OH}$ | 66.88 | -26.53                    | -25.94                    | -36.40                    |
| $\text{G}_1\text{G}_2\text{-IM5}$   | 74.07 | -10.94                    | -11.53                    | 1.28                      |
| $\text{G}_1\text{G}_2\text{-TS5}$   | 68.74 | 6.10                      | 5.51                      | 15.13                     |
| $\text{G}_1\text{G}_2\text{-C}_2\text{H}_5\text{CHO} + \text{HO}_3\text{H}$     | 71.73 | -55.18                    | -55.18                    | -54.90                    |

nearly linear  $\text{O}\cdots\text{H}\cdots\text{O}$  bond angles and are early barriers. The average distances of the breaking H-O bonds and forming O-H bonds are 1.041 and 1.466 Å, respectively. The barrier heights of

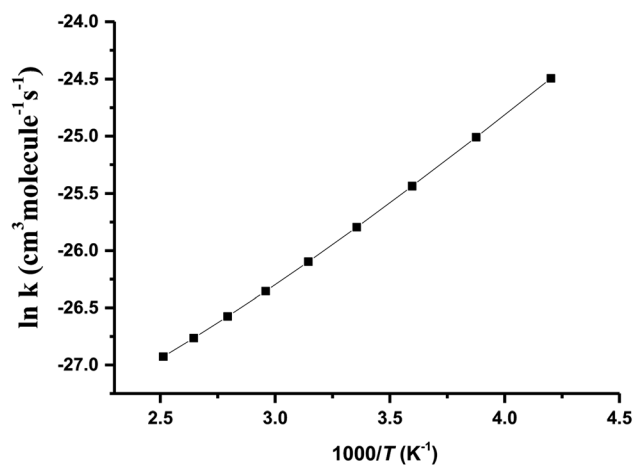


Fig. 4 Arrhenius plot of calculated rate coefficients for  $\text{G}_1\text{G}_2\text{-C}_3\text{H}_7\text{O}_2\text{H} + ^3\text{O}_2$  formation in  $\text{HO}_2 + n\text{-C}_3\text{H}_7\text{O}_2$  reaction within the temperature range of 238–398 K at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-311G(d,p) level of theory.





the  $G_1T_2$ - $^3TS1$ ,  $G'_1G_2$ - $^3TS1$ ,  $T_1G_2$ - $^3TS1$  and  $T_1T_2$ - $^3TS1$  are close to each other ( $-3.26$ ,  $-2.15$ ,  $-3.85$  vs.  $-3.90$  kcal mol $^{-1}$ ). The average barrier height of the four transition states is  $-3.29$  kcal mol $^{-1}$ , which is only  $0.81$  kcal mol $^{-1}$  lower than  $G_1G_2$ - $^3TS1$ . Evidently,  $G_1G_2$ - $^3TS1$ ,  $G_1T_2$ - $^3TS1$ ,  $G'_1G_2$ - $^3TS1$ ,  $T_1G_2$ - $^3TS1$  and  $T_1T_2$ - $^3TS1$  are all early barriers. The reactions of  $HO_2$  with the five different conformers ( $G_1G_2$ ,  $G_1T_2$ ,  $G'_1G_2$ ,  $T_1G_2$  and  $T_1T_2$ ) have same reaction mechanism and have simpler triplet potential energy surfaces *via* hydrogen abstraction routes to form  $C_3H_7O_2H$  +  $^3O_2$  molecule.

**3.1.2 Reaction mechanism on singlet PES.** It can be seen in Fig. 2, the  $HO_2$  +  $G_1G_2$  reaction has a more complicated singlet potential energy surface. In singlet reaction, there are four different reaction pathways in where products are  $G_1G_2$ - $C_3H_7O_2H$  +  $^1O_2$ ,  $G_1G_2$ - $C_3H_7OH$  +  $O_3$ ,  $G_1G_2$ - $C_2H_5CHO$  +  $HO_2$  +  $OH$  and  $G_1G_2$ - $C_2H_5CHO$  +  $HO_3H$ . The detailed reaction mechanisms of the  $HO_2$  +  $G_1G_2$  reaction are discussed in the following parts.

The formation of  $G_1G_2$ - $C_3H_7O_2H$  +  $^1O_2$  proceeds directly through one transition state  $G_1G_2$ - $TS2$  by abstracting the hydrogen atom of  $HO_2$  to the terminal O atom of  $G_1G_2$ , which has been shown in Fig. 2. The barrier height of  $G_1G_2$ - $TS2$  is calculated to be  $9.81$  kcal mol $^{-1}$  higher than that of the initial  $HO_2$  +  $G_1G_2$  reactants. This product channel is a hydrogen abstraction process, which is different from the hydrogen abstraction on the triplet surface. In summary, the singlet hydrogen abstraction process is distinct from the triplet one in three respects. Firstly, hydrogen abstraction process on the singlet potential energy surface may undergo directly through the transition state  $G_1G_2$ - $TS2$  producing  $G_1G_2$ - $C_3H_7O_2H$  and singlet  $O_2$  molecule, while the triplet one proceeds the intermediate  $G_1G_2$ - $^3IM1$  prior to the transition state  $G_1G_2$ - $^3TS1$  producing  $G_1G_2$ - $C_3H_7O_2H$  and triplet  $O_2$  molecule. Secondly, the  $O\cdots H\cdots O$  bond angle in  $G_1G_2$ - $TS2$  is much more bent (*i.e.*,  $107.77^\circ$  in  $G_1G_2$ - $TS2$  vs.  $171.93^\circ$  in  $G_1G_2$ - $^3TS1$ ). Thirdly, our calculation shows the barrier for  $G_1G_2$ - $TS2$  is much higher than that for  $G_1G_2$ - $^3TS1$  by about  $12.29$  kcal mol $^{-1}$ . The  $G_1G_2$ - $C_3H_7O_2H$  +  $^1O_2$  formation channel is of minor importance due to the high barrier height.

On the singlet potential energy surface, except for direct hydrogen abstraction mechanism described above, addition–elimination mechanism is located as well. The remaining three reaction pathways precede *via* an addition–elimination mechanism. As shown in Fig. 2,  $HO_2$  +  $G_1G_2$   $\rightarrow$   $G_1G_2$ - $IM2$   $\rightarrow$   $G_1G_2$ - $TS3$   $\rightarrow$   $G_1G_2$ - $C_3H_7OH$  +  $O_3$ , this channel involves a rather high barrier and is exothermic. The structures of  $G_1G_2$ - $IM2$  and  $G_1G_2$ - $TS3$  are shown in Fig. 3. The lengths of three O–O bonds of  $G_1G_2$ - $IM2$  are about  $1.4$  Å.  $G_1G_2$ - $IM2$  is  $-11.92$  kcal mol $^{-1}$  with respect to the initial  $HO_2$  +  $G_1G_2$  reactants.  $G_1G_2$ - $TS3$  is a five-membered ring structure. With respect to the  $HO_2$  +  $G_1G_2$  reactants, the barrier of  $G_1G_2$ - $TS3$  is as high as  $9.27$  kcal mol $^{-1}$ . Compared with other pathways, the formations of  $G_1G_2$ - $C_3H_7OH$  +  $O_3$  might be negligible because of the high barrier height.

The formation of  $G_1G_2$ - $TS4$  from the reactants  $HO_2$  +  $G_1G_2$  radicals could also occur *via*  $G_1G_2$ - $IM3$ . Similar to  $G_1G_2$ - $IM2$ ,  $G_1G_2$ - $IM3$  also has three OO bonds and the bond lengths are

about  $1.4$  Å. The computed binding energy for  $G_1G_2$ - $IM3$  are  $-10.67$  kcal mol $^{-1}$ . In  $G_1G_2$ - $TS4$ , the hydrogen atom migrates from the C to O to form  $HO_2$ , while the two O–O bonds cleavage to form post-reaction complex  $G_1G_2$ - $IM4$ . The barrier for  $G_1G_2$ - $TS4$  is relatively higher than that for  $G_1G_2$ - $^3TS1$  by about  $6.18$  kcal mol $^{-1}$ . After  $G_1G_2$ - $TS4$ , this product channel proceeds through  $G_1G_2$ - $IM4$  complex to form  $G_1G_2$ - $C_2H_5CHO$  +  $HO_2$  +  $OH$  products. It is found that the calculated relative energy of the  $G_1G_2$ - $IM4$  to the reactants  $HO_2$  +  $G_1G_2$  is  $-35.29$  kcal mol $^{-1}$ , which is lower than the products. It's worth noting that the reaction pathway of  $G_1G_2$ - $C_2H_5CHO$  +  $HO_2$  +  $OH$  formation could be viewed as a  $HO_2$ -mediated dissociation process of  $G_1G_2$  because the  $HO_2$  radical is also reproduced in the final products.

The last channel examined on the singlet potential energy surface is the formation of  $G_1G_2$ - $C_2H_5CHO$  and  $HO_3H$ . As shown in Fig. 2,  $HO_2$  +  $G_1G_2$   $\rightarrow$   $G_1G_2$ - $IM5$   $\rightarrow$   $G_1G_2$ - $TS5$   $\rightarrow$   $G_1G_2$ - $C_2H_5CHO$  +  $HO_3H$ , this pathway involves a high barrier and is extremely exothermic. Analogous to the energies of  $G_1G_2$ - $IM2$  and  $G_1G_2$ - $IM3$ , the binding energy for  $G_1G_2$ - $IM5$  is  $-10.70$  kcal mol $^{-1}$ .  $G_1G_2$ - $IM5$  also has three OO bonds, all of which are about  $1.4$  Å in length. The barrier height for  $G_1G_2$ - $TS5$  is about  $5.62$  kcal mol $^{-1}$  with respect to the reactants  $HO_2$  +  $G_1G_2$ . Clearly, the formation of  $G_1G_2$ - $C_2H_5CHO$  and  $HO_3H$  *via*  $G_1G_2$ - $TS5$  involves significant barrier and is the most exothermic pathway on the both triplet and singlet potential energy surfaces.

From the Fig. S2–S5 in the ESI,<sup>†</sup> we can see that the singlet potential energy surfaces for the  $HO_2$  +  $G_1T_2$ ,  $G'_1G_2$ ,  $T_1G_2$  and  $T_1T_2$  four reactions, as well as the  $HO_2$  +  $G_1G_2$  reaction proceed on the similar reaction mechanism which has been discussed above in detail in the present work. The formations of  $C_3H_7O_2H$  +  $^1O_2$ ,  $C_3H_7OH$  +  $O_3$  and  $C_2H_5CHO$  +  $HO_2$  +  $OH$  in  $HO_2$  +  $G_1T_2$ ,  $G'_1G_2$ ,  $T_1G_2$  and  $T_1T_2$  four reactions have similar energetic data as that of the  $HO_2$  +  $G_1G_2$  reaction. For example, in the  $C_3H_7O_2H$  +  $^1O_2$  formation pathway, the barrier heights of the four transition states  $G_1T_2$ - $TS2$ ,  $G'_1G_2$ - $^3TS2$ ,  $T_1G_2$ - $TS2$  and  $T_1T_2$ - $TS2$  are generally consistent with each other ( $9.82$ ,  $9.51$ ,  $9.53$  vs.  $9.52$  kcal mol $^{-1}$ ). The calculated barrier height for  $G_1G_2$ - $TS2$  is about  $9.81$  kcal mol $^{-1}$ . By comparison, we can conclude that the energy barriers of the above three channels in the five reactions of  $HO_2$  +  $G_1G_2$ ,  $G_1T_2$ ,  $G'_1G_2$ ,  $T_1G_2$  and  $T_1T_2$  have little difference. However, in the  $C_2H_5CHO$  and  $HO_3H$  formation pathways, the average barrier height for the four transition states ( $G_1T_2$ - $TS5$ ,  $G'_1G_2$ - $TS5$ ,  $T_1G_2$ - $TS5$  and  $T_1T_2$ - $TS5$ ) is  $14.80$  kcal mol $^{-1}$ , which is  $9.18$  kcal mol $^{-1}$  higher than  $G_1G_2$ - $TS5$ . As a result, for  $HO_2$  +  $G_1G_2$  reaction, the  $C_3H_7O_2H$  +  $^1O_2$  formation pathway is the highest barrier height, while  $C_2H_5CHO$  and  $HO_3H$  formation pathways are the highest barrier heights in the other four reactions. Compared with the energetically favorable triplet reactions, all the singlet reactions involve relatively high barriers.

In summary, the reactions of  $HO_2$  with the five different conformers ( $G_1G_2$ ,  $G_1T_2$ ,  $G'_1G_2$ ,  $T_1G_2$  and  $T_1T_2$ ) have simpler triplet potential energy surfaces *via* hydrogen abstraction routes to form  $C_3H_7O_2H$  +  $^3O_2$  molecule and more complicated singlet surfaces *via* direct hydrogen abstraction and addition–



elimination mechanisms form various products. From the mechanism discussed above, we can conclude that the pathway of formation of  $\text{C}_3\text{H}_7\text{O}_2\text{H} + {}^3\text{O}_2$  is the most important reaction channel and other channels can be negligible in the  $n\text{-C}_3\text{H}_7\text{O}_2 + \text{HO}_2$  reaction.

### 3.2 Kinetics of the $\text{HO}_2 + n\text{-C}_3\text{H}_7\text{O}_2$ reaction

Based on the singlet and triplet potential energy surfaces, the rate constants of different reaction pathways for the individual conformer have been evaluated using the conventional transition-state theory (TST) over the temperature range of 238–398 K. For example, in the case of the lowest energy conformer  $\text{HO}_2 + \text{G}_1\text{G}_2$  reaction, the calculated rate constants for individual channel are listed in Table 2. As can be seen from Table 2, results show that the rate constants for the triplet hydrogen abstraction reaction contributes significantly to the overall rate constants. The rate constant of triplet channel is at least four orders of magnitude higher than that of singlet ones over the temperature range. This indicates that the triplet hydrogen abstraction channel for formation of  $\text{G}_1\text{G}_2\text{-C}_3\text{H}_7\text{O}_2\text{H} + {}^3\text{O}_2$  products is the major channel, while the singlet channels can be negligible. The reactions of  $\text{HO}_2$  with the other conformers ( $\text{G}_1\text{T}_2$ ,  $\text{G}'_1\text{G}_2$ ,  $\text{T}_1\text{G}_2$  and  $\text{T}_1\text{T}_2$ ) have similar reaction mechanism and kinetic behavior as the  $\text{HO}_2 + \text{G}_1\text{G}_2$  reaction. Thus, only the rate constants of each individual triplet hydrogen abstraction

channel are considered in the total rate constants calculations of the  $\text{HO}_2 + n\text{-C}_3\text{H}_7\text{O}_2$  reaction. The triplet channels for each  $n\text{-C}_3\text{H}_7\text{O}_2$  conformer are displayed in Table 3. It is clear that rate constants for each triplet hydrogen abstraction channel give the total rate constants for the  $\text{HO}_2 + n\text{-C}_3\text{H}_7\text{O}_2$  reaction. Considering that  $n\text{-C}_3\text{H}_7\text{O}_2$  has multiple conformers, the total rate constants for  $\text{HO}_2$  with  $n\text{-C}_3\text{H}_7\text{O}_2$  reaction are obtained by MC-TST method. Overview of triplet channels for the reactions of  $\text{HO}_2$  with the five conformers ( $\text{G}_1\text{G}_2$ ,  $\text{G}_1\text{T}_2$ ,  $\text{G}'_1\text{G}_2$ ,  $\text{T}_1\text{G}_2$  and  $\text{T}_1\text{T}_2$ ) showing the individual conformer of the reactants, intermediates, transition states, and products are shown in the Fig. 5. The MC-TST rate constant can be regarded as a sum of the individual TST reaction rate constants which weighted by the Boltzmann population of the corresponding  $n\text{-C}_3\text{H}_7\text{O}_2$  conformers. The overall calculated rate constant of the  $\text{HO}_2 + n\text{-C}_3\text{H}_7\text{O}_2$  reaction over the temperature range of 238–398 K are listed in Table 4. Moreover, the calculated rate constants are fitted into Arrhenius three parameter equation as follows:

$$k = 3.97 \times 10^{-15} \left( \frac{T}{300} \right)^{2.49} \exp \left( \frac{2200}{T} \right) \quad (4)$$

The Arrhenius plot for the reaction of  $\text{HO}_2$  and  $n\text{-C}_3\text{H}_7\text{O}_2$  is shown in Fig. 4. From the Arrhenius plot, it can be seen clearly that the negative temperature dependence for the title reaction in lower temperature regime (e.g.  $T < 400$  K). This can be

**Table 2** Theoretical rate coefficients ( $\text{cm}^3$  per molecule per s) for  $\text{HO}_2 + \text{G}_1\text{G}_2$  reaction within the temperature range of 238–398 K at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-311G(d,p) level of theory.  ${}^3\text{O}_2$ ,  ${}^1\text{O}_2$ ,  $\text{O}_3$ , OH and  $\text{HO}_3\text{H}$  denote the rate constant of product channel  $\text{G}_1\text{G}_2\text{-C}_3\text{H}_7\text{O}_2\text{H} + {}^3\text{O}_2$ ,  $\text{G}_1\text{G}_2\text{-C}_3\text{H}_7\text{O}_2\text{H} + {}^1\text{O}_2$ ,  $\text{G}_1\text{G}_2\text{-C}_3\text{H}_7\text{OH} + \text{O}_3$ ,  $\text{G}_1\text{G}_2\text{-C}_2\text{H}_5\text{CHO} + \text{HO}_2 + \text{OH}$  and  $\text{G}_1\text{G}_2\text{-C}_2\text{H}_5\text{CHO} + \text{HO}_3\text{H}$  for the reaction, respectively

| T (K) | ${}^3\text{O}_2$       | ${}^1\text{O}_2$       | $\text{O}_3$           | OH                     | $\text{HO}_3\text{H}$  |
|-------|------------------------|------------------------|------------------------|------------------------|------------------------|
| 238   | $3.44 \times 10^{-12}$ | $4.70 \times 10^{-24}$ | $9.71 \times 10^{-22}$ | $6.18 \times 10^{-19}$ | $2.57 \times 10^{-19}$ |
| 258   | $2.22 \times 10^{-12}$ | $2.43 \times 10^{-23}$ | $8.96 \times 10^{-22}$ | $9.85 \times 10^{-19}$ | $6.70 \times 10^{-19}$ |
| 278   | $1.56 \times 10^{-12}$ | $1.01 \times 10^{-22}$ | $1.08 \times 10^{-21}$ | $1.52 \times 10^{-18}$ | $1.56 \times 10^{-18}$ |
| 298   | $1.16 \times 10^{-12}$ | $3.49 \times 10^{-22}$ | $1.52 \times 10^{-21}$ | $2.27 \times 10^{-18}$ | $3.30 \times 10^{-18}$ |
| 318   | $9.13 \times 10^{-13}$ | $1.05 \times 10^{-21}$ | $2.35 \times 10^{-21}$ | $3.28 \times 10^{-18}$ | $6.47 \times 10^{-18}$ |
| 338   | $7.45 \times 10^{-13}$ | $2.79 \times 10^{-21}$ | $3.78 \times 10^{-21}$ | $4.62 \times 10^{-18}$ | $1.19 \times 10^{-17}$ |
| 358   | $6.27 \times 10^{-13}$ | $6.73 \times 10^{-21}$ | $6.14 \times 10^{-21}$ | $6.35 \times 10^{-18}$ | $2.07 \times 10^{-17}$ |
| 378   | $5.42 \times 10^{-13}$ | $1.49 \times 10^{-20}$ | $9.91 \times 10^{-21}$ | $8.53 \times 10^{-18}$ | $3.43 \times 10^{-17}$ |
| 398   | $4.80 \times 10^{-13}$ | $3.06 \times 10^{-20}$ | $1.57 \times 10^{-20}$ | $1.12 \times 10^{-17}$ | $5.47 \times 10^{-17}$ |

**Table 3** Theoretical rate coefficients ( $\text{cm}^3$  per molecule per s) of the triplet channel for the five reactions within the temperature range of 238–398 K at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-311G(d,p) level of theory

| T (K) | $\text{HO}_2 + \text{G}_1\text{G}_2$ | $\text{HO}_2 + \text{G}_1\text{T}_2$ | $\text{HO}_2 + \text{G}'_1\text{G}_2$ | $\text{HO}_2 + \text{T}_1\text{G}_2$ | $\text{HO}_2 + \text{T}_1\text{T}_2$ |
|-------|--------------------------------------|--------------------------------------|---------------------------------------|--------------------------------------|--------------------------------------|
| 238   | $3.44 \times 10^{-12}$               | $1.05 \times 10^{-11}$               | $1.12 \times 10^{-12}$                | $2.83 \times 10^{-11}$               | $4.61 \times 10^{-11}$               |
| 258   | $2.22 \times 10^{-12}$               | $6.30 \times 10^{-12}$               | $8.27 \times 10^{-13}$                | $1.57 \times 10^{-11}$               | $2.53 \times 10^{-11}$               |
| 278   | $1.56 \times 10^{-12}$               | $4.11 \times 10^{-12}$               | $6.45 \times 10^{-13}$                | $9.57 \times 10^{-12}$               | $1.53 \times 10^{-11}$               |
| 298   | $1.16 \times 10^{-12}$               | $2.87 \times 10^{-12}$               | $5.27 \times 10^{-13}$                | $6.31 \times 10^{-12}$               | $1.00 \times 10^{-11}$               |
| 318   | $9.13 \times 10^{-13}$               | $2.12 \times 10^{-12}$               | $4.45 \times 10^{-13}$                | $4.42 \times 10^{-12}$               | $7.00 \times 10^{-12}$               |
| 338   | $7.44 \times 10^{-13}$               | $1.64 \times 10^{-12}$               | $3.87 \times 10^{-13}$                | $3.26 \times 10^{-12}$               | $5.14 \times 10^{-12}$               |
| 358   | $6.27 \times 10^{-13}$               | $1.31 \times 10^{-12}$               | $3.44 \times 10^{-13}$                | $2.50 \times 10^{-12}$               | $3.93 \times 10^{-12}$               |
| 378   | $5.42 \times 10^{-13}$               | $1.08 \times 10^{-12}$               | $3.12 \times 10^{-13}$                | $1.99 \times 10^{-12}$               | $3.11 \times 10^{-12}$               |
| 398   | $4.80 \times 10^{-13}$               | $9.19 \times 10^{-13}$               | $2.88 \times 10^{-13}$                | $1.63 \times 10^{-12}$               | $2.54 \times 10^{-12}$               |



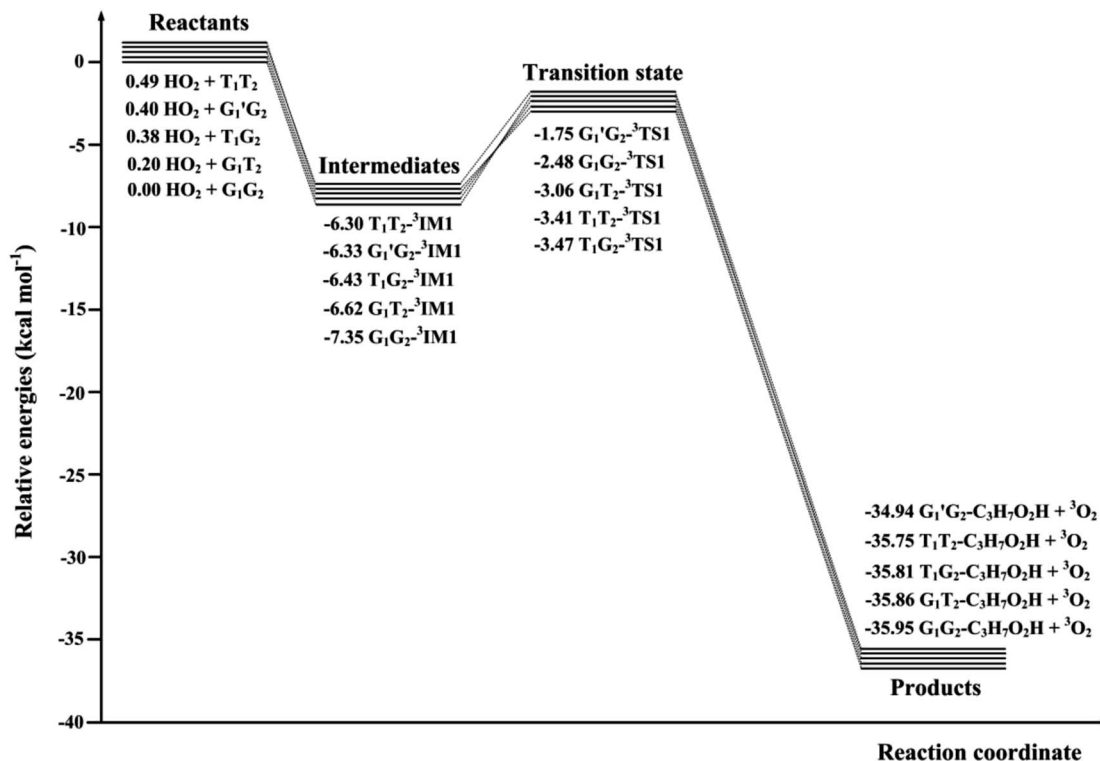


Fig. 5 In the multiconformer system, diagram showing triplet channels for the reactions of HO<sub>2</sub> radical with the five conformers (G<sub>1</sub>G<sub>2</sub>, G<sub>1</sub>T<sub>2</sub>, G<sub>1</sub>'G<sub>2</sub>, T<sub>1</sub>G<sub>2</sub> and T<sub>1</sub>T<sub>2</sub>). All the energies ( $\Delta(E + ZPE)$ ) are relative to the energies of HO<sub>2</sub> + G<sub>1</sub>G<sub>2</sub>.

attributed to the formation of the pre-reaction complexes with negative barriers in the triplet channels of the title reaction. For example, in the triplet channel of HO<sub>2</sub> + G<sub>1</sub>G<sub>2</sub> reaction, the values of the rate coefficients of reverse process (G<sub>1</sub>G<sub>2</sub>-<sup>3</sup>IM1 to HO<sub>2</sub> and G<sub>1</sub>G<sub>2</sub>) increases with the rising temperature, which reduces the value of the equilibrium constant. It can be said that when the reaction reaches equilibrium, the macroscopic rate coefficient decreases. This downward trend can be seen in the other four reactions of HO<sub>2</sub> with the different conformers (G<sub>1</sub>T<sub>2</sub>, G<sub>1</sub>'G<sub>2</sub>, T<sub>1</sub>G<sub>2</sub> and T<sub>1</sub>T<sub>2</sub>). Thus, the overall rate coefficient of the title reaction shows negative temperature dependence. The calculated rate constants for HO<sub>2</sub> + *n*-C<sub>3</sub>H<sub>7</sub>O<sub>2</sub> reaction is predicted to be  $6.27 \times 10^{-12}$  cm<sup>3</sup> per molecule per s at 298 K. The kinetic results shown good agreement with the value  $9.12 \times$

$10^{-12}$  cm<sup>3</sup> per molecule per s reported by Hou and his co-workers using structure–activity relationships (SAR) analysis.<sup>10</sup> It shows that our CCSD(T)/aug-cc-pVDZ//B3LYP/6-311G(d,p) calculated rate constants are in good agreement with the available recent theoretical result in the related reference.

## 4. Summary and conclusions

In present study, the detailed mechanism and kinetics of the reaction of HO<sub>2</sub> and *n*-C<sub>3</sub>H<sub>7</sub>O<sub>2</sub> (including five conformers G<sub>1</sub>G<sub>2</sub>, G<sub>1</sub>T<sub>2</sub>, G<sub>1</sub>'G<sub>2</sub>, T<sub>1</sub>G<sub>2</sub> and T<sub>1</sub>T<sub>2</sub>) have been investigated by quantum chemistry and MC-TST method. The mechanism for the reaction between HO<sub>2</sub> and *n*-C<sub>3</sub>H<sub>7</sub>O<sub>2</sub> radical on both singlet and triplet potential energy surfaces mainly includes hydrogen abstraction and addition–elimination mechanisms. The energy barriers show the main products are C<sub>3</sub>H<sub>7</sub>O<sub>2</sub>H and <sup>3</sup>O<sub>2</sub> on the triplet potential energy surface *via* the hydrogen abstraction mechanism. In addition, the rate constants of HO<sub>2</sub> + *n*-C<sub>3</sub>H<sub>7</sub>O<sub>2</sub> reaction were further studied over the temperature range of 238–398 K which show a negative temperature dependent. The kinetic calculations indicate that the formation of C<sub>3</sub>H<sub>7</sub>O<sub>2</sub>H + <sup>3</sup>O<sub>2</sub> channel is most kinetically favorable since that the rate constant of which is at least four orders of magnitude larger than that of the other channels at the studied temperature range. The calculated rate constant for HO<sub>2</sub> + *n*-C<sub>3</sub>H<sub>7</sub>O<sub>2</sub> reaction is predicted to be  $6.27 \times 10^{-12}$  cm<sup>3</sup> per molecule per s at 298 K, which match good with the results from SAR analysis.<sup>10</sup> The

**Table 4** The overall rate constants (cm<sup>3</sup> per molecule per s) within the temperature range 238–398 K for the HO<sub>2</sub> + *n*-C<sub>3</sub>H<sub>7</sub>O<sub>2</sub> reaction at CCSD(T)/aug-cc-pVDZ//B3LYP/6-311G(d,p) level of theory

| <i>T</i> (K) | <i>k</i> <sub>total</sub> |
|--------------|---------------------------|
| 238          | $2.30 \times 10^{-11}$    |
| 258          | $1.38 \times 10^{-11}$    |
| 278          | $8.98 \times 10^{-12}$    |
| 298          | $6.27 \times 10^{-12}$    |
| 318          | $4.64 \times 10^{-12}$    |
| 338          | $3.58 \times 10^{-12}$    |
| 358          | $2.88 \times 10^{-12}$    |
| 378          | $2.38 \times 10^{-12}$    |
| 398          | $2.02 \times 10^{-12}$    |



theoretical results can be helpful to deeply understand the chemical behaviors of  $\text{HO}_2 + n\text{-C}_3\text{H}_7\text{O}_2$  reaction.

## Conflicts of interest

There are no conflicts to declare.

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