Original Article

Theoretical Kinetics Study of The HO_2 and C_2H_5OH: Hydrogen Abstraction Reaction

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Abstract: C_2H_5OH has been using as an alternative fuel for decades; HO_2 also plays a pivotal role in the combustion. The kinetics and mechanism for the reaction between C_2H_5OH and HO_2 radical have been investigated using the molecular parameters for the reactants, transition states and products predicted at the CCSD(T)//B3LYP/6-311++G(3df,2p) level of theory. There are ten pair products have been found including $C_2H_5O + H_2O_2$ (PR1), $CH_3CHOH + H_2O_2$ (PR2), $CH_2CH_2OH + H_2O_2$ (PR3), $CH_3CH_2OOOH + H$ (PR4), $C_2H_5 + HOOOH$ (PR5), $CH_3CH_2OOH + OH$ (PR6), $CH_3CH(OH)OOH + H$ (PR7), $HOCH_2CH_2OH + H$ (PR8), $HOOCH_3 + CH_2OH$ (PR9), and $CH_3 + HOOCH_2OH$ (PR10) in which the second and third ones are the major channels. The rate constants and branching ratios for all H-abstraction reactions have been calculated using the conventional transition state theory with asymmetric Eckart tunneling corrections for the temperature ranging from 298 to 2000 K.

Keywords: DFT, C_2H_5OH, HO_2, potential energy surface, kinetics.

1. Introduction

HO_2 radical plays a pivotal role at intermediate temperatures in the combustion.[1] It has been detected in the experimental studies where the reaction between the O_2 molecule and H atom was suggested as a source of HO_2 radical: $O_2 + H \rightarrow HO_2$.[1-3] The reactions of HO_2 radical with alcohols such as CH_3OH, $n/i/s/t-C_4H_9OH$ have been investigated by both experimental and theoretical techniques.[2-7] The theoretical studies only focused on hydrogen abstractions. Moreover, the reaction

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of the HO_2 radical with ethanol (C_2H_5OH), an important species in the combustion system has not been studied yet.

In this study, the potential energy surface (PES) of the $HO_2 + C_2H_5OH$ reaction has been revealed at the CCSD(T)//B3LYP/6-311++G(3df,2p) level of theory. Based on the predicted PES, we have estimated the individual and total rate constants using the transition-state theory (TST) considering Eckart tunneling correction for low-lying channels.

2. Computational methods

All the quantum calculations have been performed using the Gaussian 09 suite programs.[8] The geometries of the related species have been optimized at the DFT-B3LYP/6-311++G(3df,2p) level of theory. The B3LYP method uses a combination of the Becke's three-parameter exchange functional (B3) and the correlation functional of Lee, Yang, and Parr (LYP). Use of the vibrational frequencies calculated at the same level of theory, B3LYP/6-311++G(3df,2p) is to confirm that the optimized structures are true minima (number of imaginary frequencies = 0) or transition states (number of imaginary frequencies = 1), as well as to estimate the rate constants. The transition states have been further confirmed by IRC (Intrinsic reaction coordinate) calculations at the same level of theory. Single-point energies of the species have been refined using the coupled-cluster CCSD(T), with the 6-311++G(3df,2p) basis set.

The kinetics calculations have been performed by the Multiwell code [9] based on the PES and the molecular parameters such as vibrational frequencies and rotational constants predicted at the CCSD(T)//B3LYP/6-311++G(3df,2p)level of theory. The rate constants of all the reaction pathways have been predicted with the transition state theory (TST)[10] with Eckart tunneling effects [11] in the temperature range of 298 - 2000 K as follows:

$$k = \sigma \frac{k_B T}{h} \frac{Q_{TS}}{N_A Q_A Q_B} \exp\left[-\frac{E_0}{k_B T} \right]$$

Where, σ is symmetry number, k_B is Boltzmann's constant, T is the temperature, h is the Planck's constant, N_A is Avogadro's number, Q_{TS}, and Q_A, Q_B are partition functions of the transition state and reactants, E_0 is the classical barrier height. The branching ratios have been estimated from the values for each and total reaction pathways.

3. Results and discussion

First, the optimized structures of C_2H_5OH and HO_2 at the B3LYP/6-311++G(3df,2p) level of theory have been compared with the available experimental data.[12, 13] The results Tables I show that the optimized parameters agree well with the experimental values. The predicted bond lengths of C-O (1.427 Å), O-H (0.960 Å), C-C (1.515 Å) of the C_2H_5OH molecule, and O-H (0.975 Å), O-O (1.324 Å) of the HO_2 radical are agree well with the available experiment values of 1.431, 0.971, 1.512, and 0.971, 1.331 Å respectively.[12,13] Similarly, the bond angles of $\angle CCO$ (108.1°) and $\angle OOH$ (105.5°) are in good agreement with the experimental values of 107.8° and 104.29° for C_2H_5OH and HO_2, respectively, (see Table 1).

Table 1. Molecular structure parameters

Bond length (Å) Bond angle (°)	B3LYP	Exp.[12,13]
C_2H_5OH		
rC-O	1,427	1.431[12]
rO-H	0.960	0.971[12]
rC-C	1.515	1.512[12]
∠CCO	108.1	107.8[12]
HO_2		
rO-H	0.975	0.971[13]
rO-O	1.324	1.331[13]
∠OOH	105.5	104.29[13]

3.1. Mechanism of the reaction
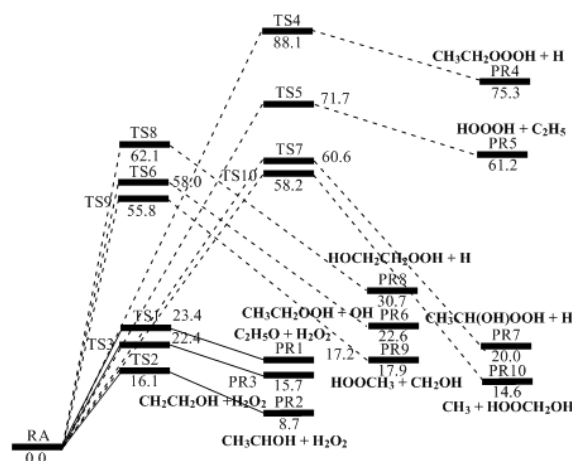
Figure 1. PES of the $HO_2 + C_2H_5OH$ reaction. Relative energies are given in kcalmol^{-1} at 0 K.

The mechanism of the $HO_2 + C_2H_5OH$ reaction predicted at the CCSD(T)//B3LYP/6-311++G(3df,2p) level of theory is shown in Fig. 1 in which the symbols TSi (i = 1 - 10) are the transition states forming products PRi (i = 1 - 10). The geometries HO_2, C_2H_5OH, PRi and TSi are in Figs. 2 and 3, respectively.

The PES in Fig. 1 shows that the $HO_2 + C_2H_5OH$ reaction can occur via abstraction channels giving PR1 ($CH_3CH_2O + H_2O_2$), PR2 ($CH_3CHOH + H_2O_2$), PR3 ($CH_2CH_2OH + H_2O_2$), and substitution channels giving the others. The abstraction channels have significant lower barrier energies of > 30 kcal/mol.

Formation of PR1 ($CH_3CH_2O + H_2O_2$), PR2 ($CH_3CHOH + H_2O_2$) and PR3 ($CH_2CH_2OH + H_2O_2$): The pair products can be formed when the HO_2 radical abstracts the H atoms in the OH, CH_2 and CH_3 groups via TS1, TS2 and TS3, respectively as clearly shown in Fig. 1. The relative energies for TS1 and TS2 predicted at the CCSD(T)//B3LYP/6-311++G(3df,2p) level of theory in this work are 23.4 and 16.1 kcal/mol which are in good agreement with 21.24 and 15.27 kcal/mol, respectively, for the $HO_2 + CH_3OH$ abstraction reactions computed at the UCCSD(T)/CBS//CASPT2/CC-PVTZ level reported by Klippenstein et al.[3] In addition, Fig. 1 shows that the energy barrier at TS3 corresponding to the β-H abstraction is only 1 kcal/mol lower than that for the O-H abstraction but 6.3

kcal/mol higher than α-H abstraction. This picture also agrees with the HO_2 + n-C_4H_9OH reaction when the barrier heights are β-H < α-H < O-H with the differences of 0.5 − 2.9 and 3.2 − 5.6, respectively, calculated at the CCSD(T)/CC-PVTZ level. Similarly, the geometries of TS1 − TS3 agree well with the previous studies. For example, the length of the formed O…H bond distance calculated in this work, 1.224 Å, is close to 1.275 Å for the HO_2 + n-C_4H_9OH by Zhou et al.[2]
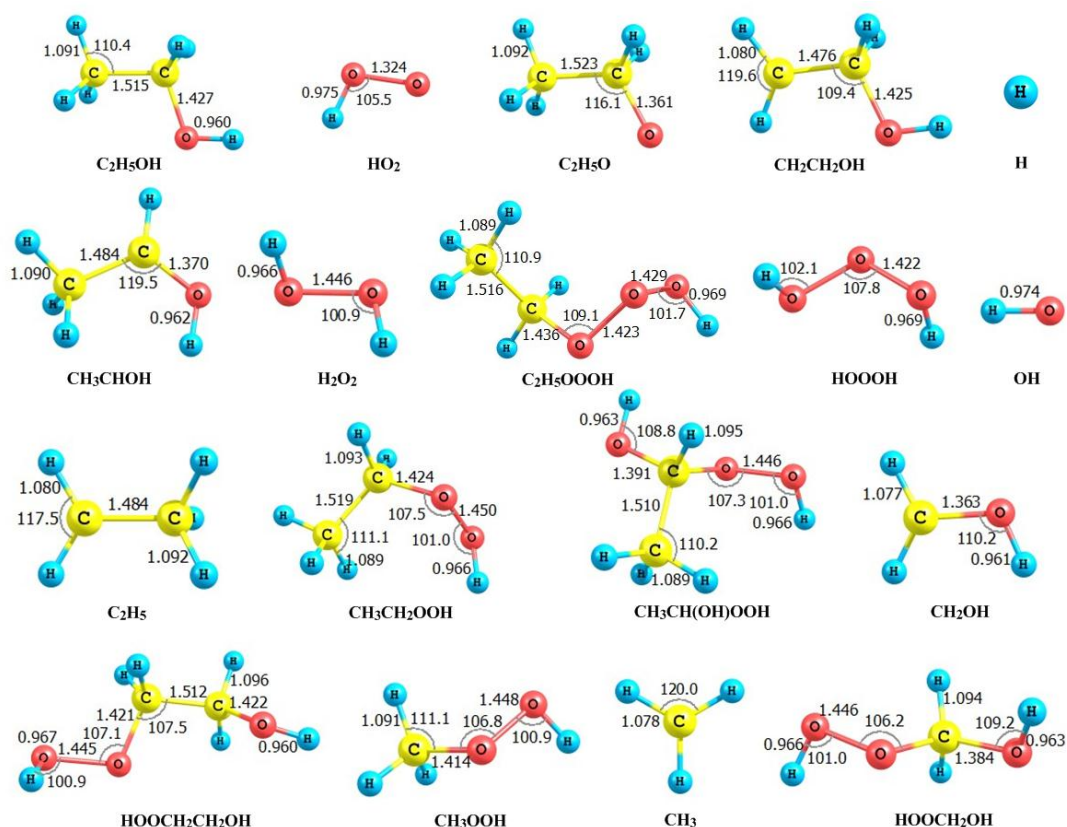

Figure 2. Optimized geometries of the reactants and products. Selected bond lengths are given in angstrom and angles in degree.

Formation of PR4 (CH_3CH_2OOOH + H), PR5 (HOOOH +C_2H_5), PR6 (CH_3CH_2OOH + OH), PR7 ($CH_3CH(OH)OOH$ + H), PR8 ($HOCH_2CH_2OOH$ + H), PR9 ($HOOCH_3$ + CH_2OH), PR10 (CH_3 + $HOOCH_2OH$): These pair products can be formed when the HO_2 radical substitutes the H atoms, OH, CH_3 and C_2H_5 groups in the C_2H_5OH molecule via TS4 − TS10 (see Fig. 2). Fig.3 shows that the TS4 − TS9 proceed through stretching the broken and formed bonds by 36% - 72% relative to the reactants and the corresponding products; the values are significantly higher than those for the TS1 − TS3 (see Fig. 3). For example, the broken O-H bond in TS4, 1.654 Å, is much higher than that in TS1, 1.307 Å. Similarly, the bond lengths of the broken C-H bond in TS2, TS3 and TS8 are 1.322, 1.399 and 1.555 Å, respectively. The relative energies of TS4 − TS9, therefore, are much higher than those for TS1 − TS3 as shown in Fig. 1. It is obvious that these substitution channels should be ignored because of the very high barrier energies.
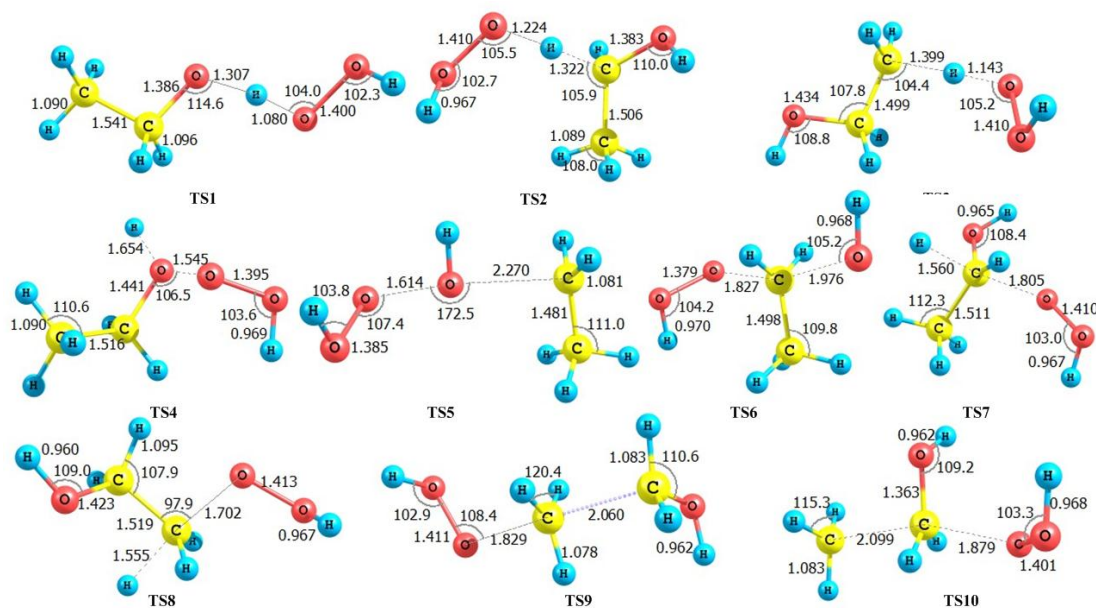
Figure 3. Optimized geometries of the transition states. Selected bond lengths are given in angstrom and angles in degree.
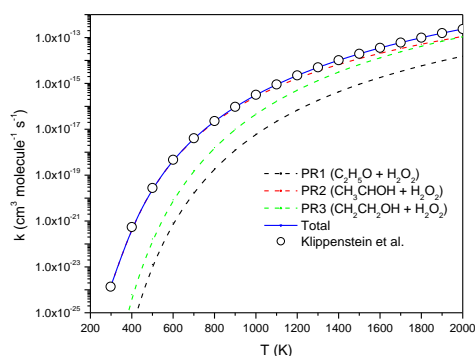
3.2. Rate constant calculations

Figure 4. Plot of the rate constants for the $HO_2 + C_2H_5OH$ reaction.

The abstraction channels via TS1 – TS3 and total rate constants have been calculated with TST considering the Eckart tunneling effect in the temperature range of 298 – 2000 K based on the PES computed at the CCSD(T)//B3LYP/6-311++G(3df,2p) level of theory. The rate constants and branching ratios for each channel are presented in Figs. 2 and 3, respectively.

It can be seen in Fig. 4 that the rate constants for all channels increase when temperature increases; the values for the channels via TS1, TS2, and TS3 are 1.29×10^{-23}, 2.74×10^{-20}, 1.67×10^{-22} (cm^3 molecule^{-1} s^{-1}) at 500 K and 9.26×10^{-16}, 1.21×10^{-14}, 6.68×10^{-15} (cm^3 molecule^{-1} s^{-1}) at 1500 K, respectively. There are no experimental results for the $HO_2 + C_2H_5OH$ reaction so far. However, the kinetics results for the reaction of the HO_2 radical and CH_3OH has been reported (see Fig. 4). One can

see that the total rate constants in this work are in good agreement with the values by Klippenstein et al.[3] For example, the total rate constants for the $HO_2 + C_2H_5OH/CH_3OH$ reactions are 3.71×10^{-16} and 3.20×10^{-16} (cm^3 molecule^{-1} s^{-1}) at 1000 K, and 1.83×10^{-13} and 2.36×10^{-13} (cm^3 molecule^{-1} s^{-1}) at 2000 K.
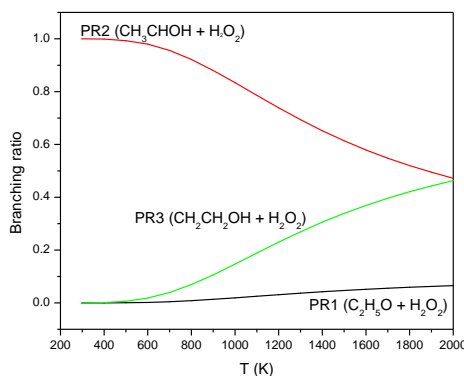

Figure 5. Site-specific computed branching ratios for the $HO_2 + C_2H_5OH$ reaction.

Fig. 5 shows that the channel via TS2 giving $CH_3CHOH + H_2O_2$ is dominant while channel via TS1 has a small contribution through whole temperature range of 298 – 2000 K. However, branching ratio for the $CH_3CHOH + H_2O_2$ channel via TS2 decreases from ~ 100% at 298 K to 47.2% at 2000 K. The channels via TS1 and TS3 increase from ~ 0% at 298 K to 6.53% and 46.3% at 2000 K, respectively.

4. Conclusions

Hydrogen abstraction reactions of C_2H_5OH by HO_2 radical has been investigated at the CCSD(T)/6-311++G(3df,2p) level theory. The individual and total coefficients, as well as branching ratios for the reactions, have been calculated in the temperature ranging from 298 to 2000 K with TST including tunneling correction. The results show that the pathways giving PR2 ($CH_3CHOH + H_2O_2$) and PR3 ($CH_2CH_2OH + H_2O_2$) are dominant through the whole temperature range with the branching ratios of 47.2% and 46.3% at 2000 K, respectively. While the pathway giving PR1 ($CH_3CH_2O + H_2O_2$) has a small contribution of 6.53% at 2000 K.

Acknowledgments

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