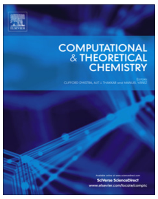
Computational and Theoretical Chemistry 1130 (2018) 63–67

Contents lists available at ScienceDirect

Computational and Theoretical Chemistry

journal homepage: www.elsevier.com/locate/comptc



H proton intramolecular transformation in OH-OO$^{\cdot}$-isoprene radicals

Min Ruan [a], Hua Hou [b], Wen Li [a], Xiaohua Zuo [a], Yue Chen [a], Baoshan Wang [b,*], Xiangyi Deng [a,*]

[a] *Institute of Materials Science and Engineering, Hubei Key Laboratory of Mine Environmental Pollution Control & Remediation, Hubei Polytechnic University, Huangshi, China*
[b] *College of Chemistry and Molecular Sciences, Wuhan Universtiy, Wuhan, China*

ARTICLE INFO

Article history:
Received 3 January 2018
Received in revised form 24 February 2018
Accepted 8 March 2018
Available online 9 March 2018

Keywords:
OH-OO$^{\cdot}$-isoprene radical
Intramolecular transformation
Ab initio
Calculation

ABSTRACT

In this study, ab initio calculations have been performed to investigate the H proton intramolecular transformation in OH-OO$^{\cdot}$-isoprene radicals. Geometry optimizations and transition states were performed using density functional theory at the UB3LYP/6–31+G** and M06-2X/6-311++G** level. It was found that the migration H atoms was all from the hydroxy-H in the predominant energetic route of 1-OH-2-OO$^{\cdot}$-isoprene and 4-OH-3-OO$^{\cdot}$-isoprene radicals with the energy barrier of 17.7 and 17.0 kcal/mol at the UB3LYP/6-31+G** level, respectively. The migration H atoms were all from the CH_2 groups next to hydroxy of Z-1-OH-4-OO$^{\cdot}$-isoprene and Z-4-OH-1-OO$^{\cdot}$-isoprene radicals in the energetic predominant routes with the energy barrier of 14.9 and 25.9 kcal/mol at the UB3LYP/6-31+G** level, respectively, then the intermediates overcome 7.7 and 7.2 kcal/mol to react with O_2 molecule to regenerate HO_2.

1. Introduction

Approximately 80% of our air pollution stems from hydrocarbons released by vegetation [1]. Isoprene (2-methyl-1,3-butadiene, $CH_2{=}C(CH_3){-}CH{=}CH_2$) is the most abundant hydrocarbons emitted by the terrestrial biosphere during the daylight hours with a global average production rate of ~550 Tg C yr^{-1} [2,3] whose annual emission is about half of the total Biogenic Volatile Organic Compounds (BVOC) emissions [4,5], and is comparable to the total emission of methane from all sources [6].

The atmospheric degradation of isoprene occurs via a multi-step chemical process and is initiated by an attack from OH radical, O_3, or NO_3 radical [7,8]. The dominant pathway is the addition reaction of OH to the carbon–carbon double bonds, yielding a thermodynamically favored hydroxyalkyl radicals [9,10], which followed by the reaction with oxygen molecules to from hydroxyalkyl peroxy radicals under atmospheric conditions [11]. Peroxy species are key intermediates in chemical reactions in both combustion and troposphere [12].

The trans- structure of isoprene is the more stable dominant conformer, however, the OH-addition reaction of isoprene releases 38 kcal/mol, which makes the interconvert of trans- and cis-hydroxyisoprene radical more easily with barriers of only 14–15 kcal/mol [13]. North et al. calculated the high-pressure rate constants for hydroxyisoprene radical formation with RRKM/ME method and found that the 1-OH, 2-OH, 3-OH and 4-OH branching ratio of hydroxyisoprene radical is 56%, 2.3%, 4.6% and 37%, respectively [14]. The relative energy of OH-addition reaction of isoprene is 34.8, 24.2, 22.3, 32.3 kcal/mol, respectively, at the level of CCSD (T)/6-311G$**$//B3LYP/6-31G** [9] and 37.9, 25.6, 24.2, 35.4 kcal/mol at level of PMP4W/6-311G**//MP2/6-311G** [15].

In this work, only the 1-OH and 4-OH two major adducts are considered as the initial structure to form OH-perroxy-isoprene radicals, and their resulting peroxys denoted as, E-1-OH-4-OO$^{\cdot}$-isoprene, Z-1-OH-4-OO$^{\cdot}$-isoprene, 1-OH-2-OO$^{\cdot}$-isoprene, E-4-OH-1-OO$^{\cdot}$-isoprene, Z-4-OH-1-OO$^{\cdot}$-isoprene and 4-OH-3-OO$^{\cdot}$-isoprene. For instance, Z-1-OH-4-OO$^{\cdot}$-isopreneis for the 4-peroxyradical from Z-1-OH-isoprene. The H proton transformation mechanism in the oxidation of OH-peroxy-isoprene was investigated using density functional theory.

2. Methodologies

All minima and transition states discussed here were calculated using UB3LYP density functional theory for geometries, vibrational frequencies and energies, combined with 6-31+G** basis sets. The conclusions were verified at the calculated level of M06-2X/6-311++G** [16]. All quantum chemical calculations were performed using the Guassian program suite [17]. Vibrational frequency calculations were also performed at the same level in order to obtain zero point correction energies.

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* Corresponding authors.

E-mail addresses: amin0241@sina.com (M. Ruan), houhua@whu.edu.cn (H. Hou), arlxfl@126.com (W. Li), 695408985@qq.com (X. Zuo), chenyue1020@163.com (Y. Chen), baoshan@whu.edu.cn (B. Wang), 38049763@qq.com (X. Deng).

https://doi.org/10.1016/j.comptc.2018.03.006
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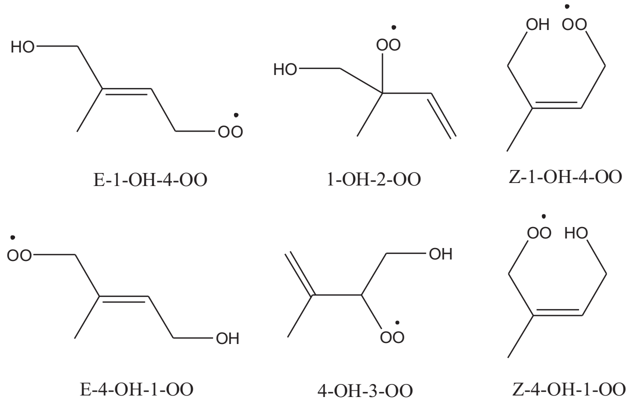

Fig. 1. Six kinds of OH-peroxy-isoprene radicals.

3. The initial OH-peroxy-isoprene radicals

The OH-peroxy-isoprene radicals derived from 1-OH and 4-OH two major adducts are considered as the initial structures in this work, and they are denoted as E-1-OH-4-OO$^{\cdot}$-isoprene, Z-1-OH-4-OO$^{\cdot}$-isoprene, 1-OH-2-OO$^{\cdot}$-isoprene, E-4-OH-1-OO$^{\cdot}$-isoprene, Z-4-OH-1-OO$^{\cdot}$-isoprene and 4-OH-3-OO$^{\cdot}$-isoprene, respectively as shown in Fig. 1. Between the six kinds of OH-peroxy-isoprene radicals, when OH and peroxy radicals are located on the adjacent carbons as in 1-OH-2-OO$^{\cdot}$-isoprene and 4-OH-3-OO$^{\cdot}$-isoprene, they are named β-OH-peroxy-isoprene radicals with stabilization energies of −50.4 and −51.0 kcal/mol respectively. As δ-OH-peroxy-isoprene radicals, E-1-OH-4-OO$^{\cdot}$-isoprene, Z-1-OH-4-OO$^{\cdot}$-isoprene, E-4-OH-1-OO$^{\cdot}$-isoprene and Z-4-OH-1-OO$^{\cdot}$-isoprene have the stabilization energies of −46.5, −50.5, −46.0 and −49.6 kcal/mol, respectively. From the stabilization energies of δ-OH-peroxy-isoprene radicals, it can be seen that the cis-conformation of Z-1-OH-4-OO$^{\cdot}$-isoprene and Z-4-OH-1-OO$^{\cdot}$-isoprene are about 4 kcal/mol lower than the -trans of E-1-OH-4-OO$^{\cdot}$-isoprene and E-4-OH-1-OO$^{\cdot}$-isoprene is more stable than the trans. Only the -cis conformations are considered in the H regeneration reactions.

4. Hydrogen regeneration of OH-OO-isoprene radicals

Fig. S1 shows the migration H sites of each route for the OH regeneration of OH-peroxy-isoprene radicals, and all of the H proton transformation routes of OH-OO$^{\cdot}$-isoprene radicals are shown in Figs. S2–S5. The relative energies and Gibbs free energies of the reactants, transition states, intermediates and products of the H proton transformation in the oxidation of OH-peroxy-isoprene radicals at B3LYP/6-31+G** level are listed in Table S1. It can be seen from Figs. S2–S5 and Table S1 that the predominant energetic routes of the H proton transformation for 1-OH-2-OO$^{\cdot}$-isoprene, 4-OH-3-OO$^{\cdot}$-isoprene, Z-1-OH-4-OO$^{\cdot}$-isoprene and Z-4-OH-1-OO$^{\cdot}$-isoprene radicals are from the reactants of R1512, R1543, R1614 and R1641, respectively. We performed the calculations of the OH transformation for 1-OH-2-OO$^{\cdot}$-isoprene and Z-1-OH-4-OO$^{\cdot}$-isoprene with M06-2X/6-311++G** calculated level, and the routes are shown as Figs. S6 and S7 respectively. The electronic energies and Gibbs free energies of the stationary points are listed in Table S2 and it can be seen that the predominant energetic routes is the same as at B3LYP/6-31+G** level. The geometries of stationary points for the OH regeneration of 1-OH-2-OO$^{\cdot}$-isoprene and Z-1-OH-4-OO$^{\cdot}$-isoprene radicals with both methods are listed in Fig. S8, and the geometries of the predominant energetic routes are listed in Fig. 6. The predominant energetic routes at B3LYP/6-31+G** level are shown in Figs. 2–5 for 1-OH-2-OO$^{\cdot}$-isoprene, 4-OH-3-OO$^{\cdot}$-isoprene, Z-1-OH-4-OO$^{\cdot}$- isoprene and Z-4-OH-1-OO$^{\cdot}$ - isoprene radicals, respectively.

Fig. 2 shows the predominant energetic route at B3LYP/6-31 +G$**$ level of the H proton transformation route of 1-OH-2-OO$^{\cdot}$-isoprene. The migration of the hydroxy-H to the peroxy radical site leads to the elimination formaldehyde [18] and an α-OOH alkyl radical which have been shown to be thermally unstable [19] and eliminate an methylvinylketone (MVK) and an OH radical without barrier. The energy of this transition state is 17.7 and 22.4 kcal/mol for B3LYP/6-31+G** and M06-2X/6-311++G** level respectively compared to the R12 reactant. The bond between the migration H atom and hydroxy oxygen is 1.35 and 1.31 Å and that is 1.09 and 1.10 Å between H with peroxy oxygen atom for B3LYP/6-31+G** and M06-2X/6-311++G** level respectively.

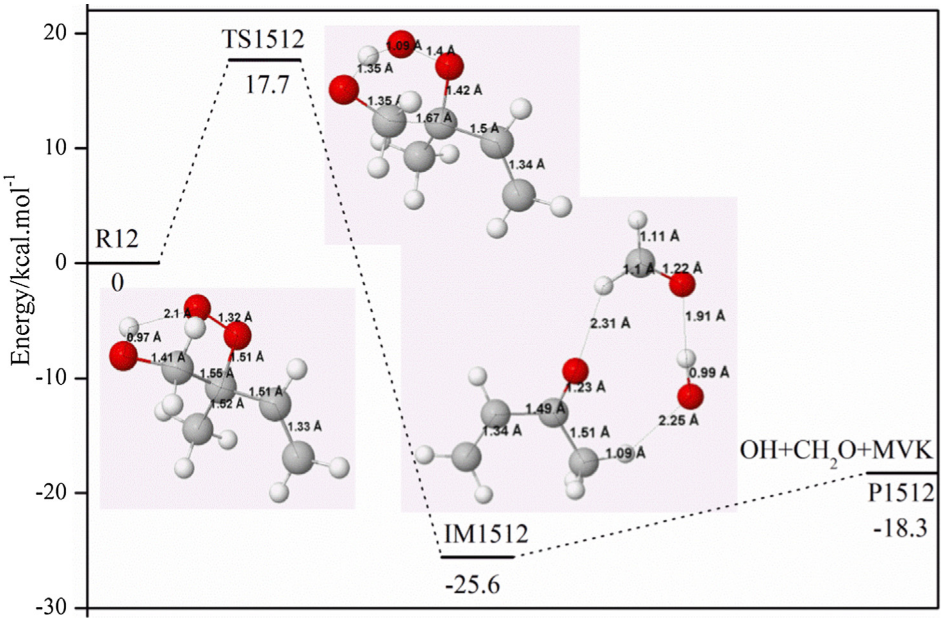

Fig. 2. Predominant energetic route at B3LYP/6-31+G** level for the OH generation of 1-OH-2-OO.-isoprene radical.