Bulgarian Chemical Communications, Volume 48, Number3 (pp. 359– 363) 2016

Mechanism of hydrogen transfer from 1-methylbutyl peroxide to hydroxyl radical

S. Q. Zhou*, H. W. Kuai, Y. X. Gu, W. Zhou, A. P. Li

Faculty of Chemical Engineering, Huaiyin Institute of Technology, Huai'an, 223003, P. R. China

Received November 4, 2015, Accepted December 28, 2015

The density functional theory method was used to study the mechanism for the hydrogen transfer from 1-methylbutyl peroxide [n-$C_3H_7CH(CH_3)OOH$] to hydroxyl radical. The B3LYP method was used in conjunction with the 6-311++G** basis set. The geometrical configurations of reactants, products and transition states were fully optimized on the potential energy surfaces. The activation energies for the hydrogen transfer are in the range from 0.37 to 7.9 kJ/mol. The results suggest that the alkyl β-H is the easiest to transfer in view of both thermodynamics and kinetics. On the contrary, the γ-H transfer requires larger activation energy compared to α- and β-H. All three types of hydrogen transfers become much easier in the presence of hydroxyl radical compared to the intramolecular hydrogen transfer, which is in good agreement with the experimental fact that the emulsification of diesel oil and water results in improved combustion properties.

Keywords: 1-Methylbutyl peroxide, Hydroxyl radical, Intermolecular hydrogen-atom transfer, Density functional theory.

INTRODUCTION

The diesel engine is still one of the most fuel-efficient combustion engines at present [1-4]. Diesel emulsion is considered one of the possible alternative fuels for curtailing the emission pollution of combustion equipment such as diesel engines and large power boilers [5-8]. Emulsion fuels are defined as emulsions of water in fuel with the typical composition of 5–20% of water, surfactant and based fuel such as kerosene or diesel. It is consistently proven that emulsion fuels significantly lower emissions of hydrocarbons, carbon monoxide/dioxide and especially hazardous nitrous oxides and particulate matters [9-12].

Diesel oil primarily consists of hydrocarbons with *n*-alkanes being the dominant components. It converts to self-ignited peroxides of hydrocarbons prior to complete combustion. The easiness of formation of hydrocarbon peroxides determines whether or not the engine is knocking. Of all types of peroxides, the di-peroxyl hydrocarbons have been believed to be the precursors of the final products carbon oxide and water. These di-peroxyl hydrocarbons are expected to play an important role in eliminating the diesel engine knocking. The key steps to produce di-peroxyl hydrocarbons are the intramolecular hydrogen-atom transfer reactions [13-16]. However, on the condition of water existing, the hydroxyl radical that is produced from water takes part in the process of the formation of di-peroxyl hydrocarbons (Fig. 1). Hydroxyl radical assimilates a hydrogen atom from the mono-peroxyl hydrocarbon. The process yields the formation of a carbon radical. Once the products of alkyl radicals come into being, they are easy to further react with oxygen to produce di-peroxyl hydrocarbons. Here, 1-methylbutyl peroxide was used as the computational model of hydrocarbon peroxide.

The main objective of this work is to explore energies and mechanisms for the hydroxyl assimilating a hydrogen from 1-methylbutyl peroxide [synonym, 2-pentyl peroxide, chemical formula n-$C_3H_7CH(CH_3)OOH$] as a computational model.

COMPUTATIONAL METHODS

The molecular structures and energies of the reaction stationary points were calculated with the density functional theory (DFT) B3LYP technique [17-19]. Unrestricted wave function was employed for the open-shell systems. The geometries of all species (reactants, transition states and products) were optimized at the B3LYP/6-311++G** level. The corresponding vibration frequencies were calculated at the same level. All located transition states exhibited one normal imaginary frequency with a transition vector corresponding to the motion of a H-atom during the intermolecular H-atom-transfer process. All calculations were performed with Gaussian 03 package of programs [20].

---

* To whom all correspondence should be sent:
E-mail: zhousuqin7803@sina.com

RESULTS AND DISCUSSION

Structures and geometries

Fig. 2 shows the optimized geometries of the transition states. The imaginary frequencies of TS1, TS2, TS3 and TS4 are –446.16, –257.60, –823.85 and –240.27 cm^{-1}, respectively. The vibrational normal modes of the four transition states correspond to the wagging of a hydrogen atom towards the hydroxyl radical. On going from the reactant to TS, one of the C–H bonds elongates toward the hydroxyl radical. The O···H lengths of partially formed water moiety in TS1, TS2, TS3 and TS4 are 1.412 Å, 1.460 Å, 1.333 Å and 1.444 Å, respectively. The lengths of the C–H bonds associated with the transfer of a H atom are 1.188 Å, 1.167 Å, 1.211 Å and 1.172 Å, for TS1, TS2, TS3 and TS4, respectively. The lengths of these C–H bonds are increased by about 10% compared to their corresponding C–H bond lengths in the reactants. The structure of TS2 differs more from that of its product than that of the other three TS. However, there is a six-membered ring with an intramolecular hydrogen bond in TS2, which attributes it with lower activation energy as discussed below.

Change of energy

The hydroxyl radical approaches the alkyl hydrogen atoms, resulting in the formation of TS1-TS4. Table 1 collects the total energies, zero point vibrational energies and relative energies at the B3LYP/6-311++G** level. The relative energy, after being corrected for the zero point vibrational energy, refers to the corresponding reactant, i.e., the complex of 1-methylbutyl peroxide and hydroxyl radical. The relative energy is the energy barrier needed to be overcome during the intermolecular hydrogen transfer reaction. As can be seen from Table 1 and Fig. 3, for α-H, the methylene hydrogen is energetically favorable to be transferred in comparison with methyl hydrogen. In other words, the α-H transfer from methylene to hydroxyl results in the largest energy release. All four reactions are firstly endothermic to overcome the energy barrier from the reactants to the transition states. But these reactions are exothermic from the reactants to the products. The activation energy of 0.37 kJ/mol for reaction (2) is the lowest one, that is, the alkyl β-H is the easiest to transfer. The β-H transfer is a favorable process in view of both thermodynamics and kinetics. On the contrary, the reaction (4) of alkyl γ-H transfer requires the largest activation energy. Table 1 also lists the relative energies of the transition states for the corresponding intrahydrogen transfers. β-H is the easiest to transfer in the process of intramolecular hydrogen transfer in comparison with α-H and γ-H. Notably, β-H is also the easiest to transfer assisted by hydroxyl in comparison of α-H and γ-H. However, all types of H transfer become much easier in the presence of hydroxyl radical. This finding can explain the fact that the combustion of diesel oil is accelerated by the addition of small amounts of water.

Atomic Mulliken charge and spin density

As can be seen from Table 2, the Mulliken charges on C_3, C_2, C_5 and C_1 atoms for TS1, TS2, TS3 and TS4, respectively, decrease (more negatively charged) in comparison with those of the reactant. However, their corresponding charges on C_3, C_2, C_5 and C_1 atoms increase on going from reactant to products. It is interesting to note that the C_3 and C_2 atoms, for P1 and P2, respectively, are positively charged with 0.3 a.u.; on the contrary, the C_5 and C_1 atoms, for P3 and P4, respectively, are negatively charged with –0.4 a.u. This large difference of charges is due to the C_5 and C_1 atoms being at the end of the carbon chain. There are less hyper-conjugation effects between the single electron on the end carbon and its neighbor C-H bond. More electron charges (negative charges) are built up on O_7 on going from reactants to products. And much more electron charges (negative charges) are built up on O_8 on going from reactants to products.

The electrons on the transferred hydrogen atoms are attracted by the hydroxyl oxygen atom in the reaction process. On going from the reactants to their corresponding TS1-TS4, the Mulliken charges on the transferred H_{11} atom increase dramatically, since its electrons are shared by both neighbor carbon and oxygen atoms. On going from the TS1-TS3 to their corresponding products P1-P3, the Mulliken charges on the transferred H_{11} atom decrease just slightly. Although the electronegativity of oxygen is larger than that of carbon, the transferred H_{11} atom is closer to carbon than to oxygen.

Table 3 lists the spin densities of hydroxyl atoms, transferred hydrogen atom and its neighbor carbon. The total spin density of hydroxyl for the reactant is 1.0 a.u. However, on going from reactant to TS1-TS4, the spin densities of hydroxyl oxygen atoms decrease by about 0.3 a.u., but those of the carbon atoms increase from near zero to 0.3-0.4 a.u. This indicates that a hydrogen atom is partially transferred from carbon to hydroxyl oxygen.

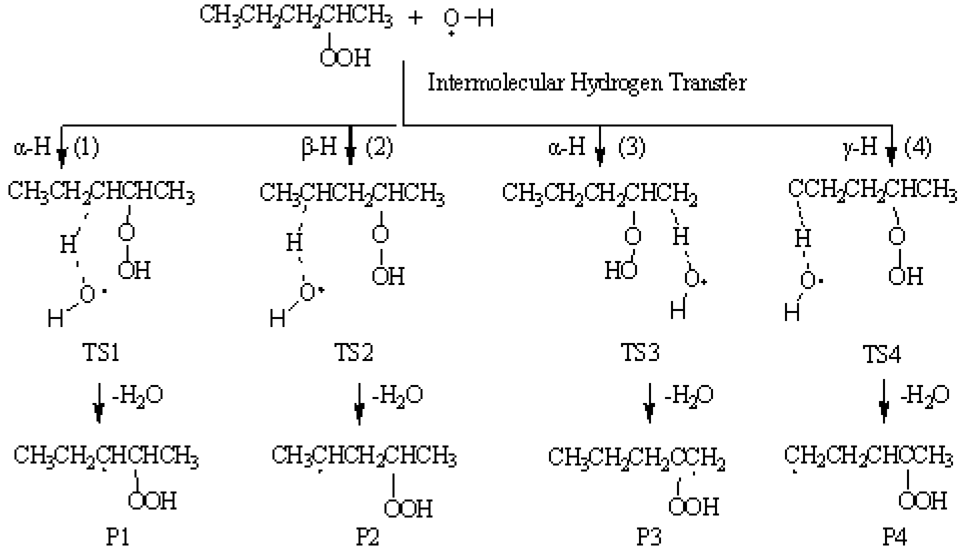

Fig. 1. Intermolecular hydrogen-atom transfer from 1-methylbutyl peroxide to hydroxyl radical for hydrogen at different positions.

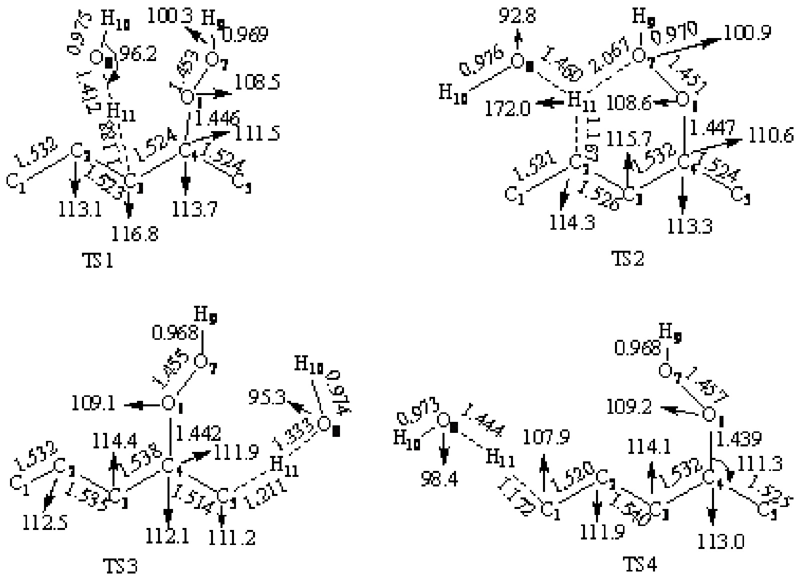

Fig. 2. Optimized structures of transition states (bond length in Angström, bond angle in degree).

Table 1. Total energies (E, in Hartree), zero point vibrational energies (E_{vib}, in kJ/mol) and relative energies (ΔE, in kJ/mol) at the B3LYP level [a]

Species	E	E_{vib}	ΔE	ΔE [c]	Species	E	E_{vib}	ΔE [d]
Reactant[b]	–423.997945	468.80	0.00	—	P1	–347.557871	400.87	–60.52
TS1	–423.993055	458.61	2.65	140.41	P2	–347.559594	399.39	–66.52
TS2	–423.994906	461.19	0.37	90.02	P3	–347.551672	399.32	–45.79
TS3	–423.990191	456.34	7.90	152.10	P4	–347.554205	399.76	–52.00
TS4	–423.989281	458.27	12.22	100.76	H_2O	–76.458531	55.87	—

[a] ΔE were corrected with zero-point vibrational energy. Relative energy refers to the corresponding reactant, i.e., the complex of 1-methylbutyl peroxide and hydroxyl radical. [b] Complex of 2-pentyl peroxide and hydroxyl radical. [c] Relative energies of transition states for the corresponding intrahydrogen transfers from Ref. [4]. [d] Energy of water is included.

Table 2. Atomic Mulliken charges along the reaction pathways at the B3LYP/6-311++G** level.

Atom	Reactant	TS1	TS2	TS3	TS4	P1	P2	P3	P4
C_1	-0.625	-0.604	-0.644	-0.635	-0.644	-0.453	-0.755	-0.620	-0.386
C_2	0.054	-0.100	-0.100	-0.040	-0.100	-0.442	0.318	-0.046	-0.136
C_3	-0.336	-0.397	-0.451	-0.297	-0.451	0.331	-0.424	-0.490	-0.313
C_4	-0.130	-0.183	0.029	-0.114	0.029	-0.326	-0.122	0.152	-0.023
C_5	-0.585	-0.576	-0.615	-0.634	-0.615	-0.652	-0.592	-0.473	-0.607
O_6	-0.088	-0.067	-0.090	-0.009	-0.090	-0.044	-0.056	-0.066	-0.059
O_7	-0.188	-0.192	-0.197	-0.258	-0.197	-0.214	-0.207	-0.198	-0.198
O_8	-0.248	-0.318	-0.358	-0.367	-0.358	-0.502	-0.502	-0.502	-0.502
H_{11} [a]	0.097−0.189	0.361	0.333	0.301	0.239	0.251	0.251	0.251	0.251

[a] Refers to the transferred hydrogen atom.

Table 3. Atomic spin densities for the transferred hydrogen atom and its neighbor atoms along the reaction pathways at the B3LYP/6-311++G** level.

Atom [a]	Reactant	TS1	TS2	TS3	TS4	P1	P2	P3	P4
O_8	1.021	0.685	0.721	0.629	0.712	0.000	0.000	0.000	0.000
H_{10}	-0.021	-0.003	0.001	0.002	-0.011	0.000	0.000	0.000	0.000
C	-0.005−0.002	0.344	0.293	0.410	0.300	1.018	1.095	1.117	1.156
H	0.00	-0.020	-0.023	-0.028	-0.016	0.000	0.000	0.000	0.000

[a] H and C atoms refer to the transferred hydrogen atom and its neighbor carbon, respectively.

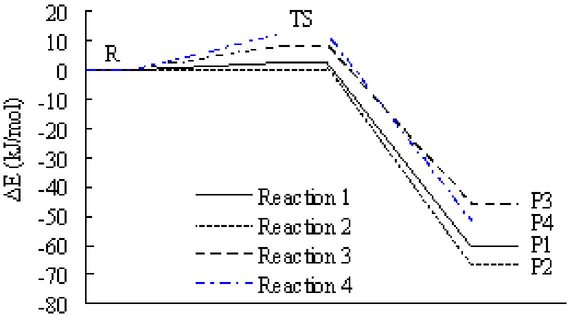

Fig. 3. Energy changes along the reaction pathway at B3LYP/6-311++G** level.

All the spin density primarily locates on the carbon atom in the products. This clearly indicates that it is the hydrogen radical that transfers from the carbon atom to the hydroxyl oxygen atoms with water as a leaving moiety.

CONCLUSIONS

The reactions of hydrogen atom migration from one of the C−H of 1-methylbutyl peroxide to hydroxyl radical were investigated by the DFT-B3LYP method. Transition states with six-membered rings were formed in the process of β-H transfer when the hydrogen atom migrates from the methylene group to hydroxyl radical. The six-membered ring facilitates the formation of transition state. The atomic charges and spin distribution on the radical seem to be adequate in helping to understand the trends of the intermolecular hydrogen transfer. The β-H is easier to transfer than the α- and γ-H. The hydroxyl radical greatly facilitates all three types of hydrogen transfer. This presents a rational explanation of the fact that the combustion of diesel oil is accelerated by the addition of small amounts of water.

Acknowledgements: *We gratefully thank for the support by the Nature Science Foundation of Jiangsu Higher Education Institutions of China (Grant No. 13KJB530002) and the National Natural Science Foundation of China (Grant No. 11404127). S.-Q. Zhou thanks the Research Support of Huaiyin Institute of Technology (Grant No. HGA1008).*

REFERENCES

1. F. -F. Pischinger, in: E. Sher (ed.). Handbook of Air Pollution from Internal Combustion Engines. London: Academic Press, 1998, p. 261.
2. M. Lapuerta, R. García-Contreras, J. Campos-Fernández, *Energ. Fuel*, **24**, 4497 (2010).

3. Y.-C. Lin, W.-J. Lee, H.-R. Chao, *Environ. Sci. Technol.*, **42**, 3849 (2008).
4. J.-B. Huang, D. Wu, H. Tong, W.-M. Li, *J. Energy Inst.*, **86**, 189 (2013).
5. G. Chen, D. Tao, *Fuel Process. Technol.*, **86**, 499 (2005).
6. Y. Liu,; G.-H. Huang, Y.-P. Cai, C. Dong, *Int. J. Green Energy*, **11**, 1013 (2014).
7. P. Manivasagan, P. Sivasankar, J. Venkatesan, K. Sivakumar, S.-K. Kim, *Bioprocess Biosyst. Eng.*, **37**, 783 (2014).
8. Y.-P. Li, T.-J. Wang, W. Liang, C.-Z. Wu, *Energ. Fuel*, **24**, 1987 (2010).
9. A. -M. Al-Sabagh, M. -E. Mostafa, E. -M. -R. Noor, W. -R. Aly, *Egypt. J. Petrol.*, **20**, 17 (2011).
10. G. -R. Yu, J. -J. Zhao, D. -D. Song, *Ind. Eng. Chem. Res.*, **50**, 11690 (2011).
11. M. Lapuerta, O. Armas, R. García-Contreras, *Energ. Fuel*, **23**, 4343 (2009).
12. M.-V.-E. Santana, Q. Zhang, J.-R. Mihelcic, *Environ. Sci. Technol.*, **48**, 3084 (2014).
13. E.-B. Webb, C.-A. Koh, M.-W. Liberatore, *Ind. Eng. Chem. Res.*, DOI: 10.1021/ie5008954.
14. P.-B.-L. Fregolente, L.-V. Fregolente, M.-R.-W. Maciel, *J. Chem. Eng. Data*, **57**, 1817 (2012).
15. K.-Y. Lee, J.-J. Blaker, R. Murakami, J.-Y.-Y. Heng, A. Bismarck, *Langmuir*, 30, 452 (2014).
16. M. Li, L. -F.Xie, X. -H. Ju, F. -Q. Zhao, *Petrol. Chem.*, **53**, 431 (2013).
17. J.-M. Seminario, P. Politzer, Modern Density Functional Theory: A Tool for Chemistry, Elsevier: Amsterdam, 1995.
18. L.-F. Xie, C.-C. Ye, X.-H. Ju, F.-Q. Zhao, *J. Struct. Chem.*, **53**, 659 (2012).
19. M. Wang, J.-J. Geng, Z.-B. Wei, Z.-Y. Wang, *Chinese J. Struct. Chem.*, **32**, 890 (2013).
20. M.-J. Frisch, G.-W. Trucks, H. -B. Schlegel, Gaussian, Inc. Pittsburgh PA, 2003.

МЕХАНИЗЪМ НА ПРЕНОСА НА ВОДОРОД ОТ 1-МЕТИЛ-БУТИЛОВ ПЕРОКСИД КЪМ ХИДРОКСИЛЕН РАДИКАЛ

С. К. Жоу, Х. В. Куай, И. Х. Гу, В. Зоу, А. Р. Ли

Факултет по инженерна химия, Технологичен институт Хуайин, Хуаян, 223003, КНР

Постъпила на 4 ноември, 2014 г.; приета на 28 декември, 2015 г.

(Резюме)

Използван е DFT-методът за да се изследва механизма на преноса на водород от 1-метил-бутилов пероксид [*n*-$C_3H_7CH(CH_3)OOH$] към хидроксилен радикал. Използван е B3LYP-методът заедно с базисна мрежа 6-311++G**. Геометричната конфигурация на реагентите, продуктите и преходните състояния са оптимизирани на повърхностите на потенциалната енергия. Активиращите енергии на пренос на водорода са в интервала от 0.37 до 7.9 kJ/mol. Резултатите показват, че β-H е най-лесен за пренос от термодинамична и кинетична гледна точка. Обратно, преносът γ-H изисква по-големи активиращи енергии спрямо α- and β-H. Тези три типа пренос на водород се извършват по-лесно в присъствие на хидроксилни радикали, отколкото вътрешно-молекулния пренос, което е в добро съгласие с експерименталния факт, че емулсификацията на дизелово гориво във вода води до по-добри горивни качества.