J. At. Mol. Sci.
doi: 10.4208/jams.122810.011811a

Vol. **2**, No. 3, pp. 225-233
August 2011

Theoretical investigation of mechanism for the gas-phase reaction of OH radical and ethane

Xiao-Ping Hu[a], Bing-Xing Wang[a,*], Ying Gao[a,*], and Bing Yang[b]

[a] *College of Chemistry and Chemical Engineering, Harbin Normal University, Harbin 150025, China*
[b] *State Key Laboratory of Supramolecular Structure and Materials, Jilin University, Changchun 130012, China*

Received 28 December 2010; Accepted (in revised version) 18 January 2011

Abstract. Reaction mechanism of OH radical and ethane has been investigated by using *ab initio* (MP2) and hybrid DFT (B3LYP and BH&HLYP) methods with 6-311++G(d,p) basis set. The MP2 method can provide more reasonable geometrical structures than the B3LYP and BH&HLYP DFT functionals. The methodology does not significantly alter vibrational frequencies. Compared with previous reports, at MP2 level, large basis set is necessary to predict the barrier heights and reaction energies. Spin-projected MP2 energies with 6-311++G(d,p) basis set were adopted to construct the potential energy surface. Hydrogen abstraction channel exhibits most exothermicity and lowest barrier height. This channel is predominant thermodynamically and kinetically, and proceeds via an "early" transition state. The other channels are minor and their transition-state structures are neither reactant-like nor product-like.

PACS: 31.50.Bc, 82.30.Cf, 82.20.Kh

Key words: ethane, hydroxyl radical, reaction mechanism, PMP2, density functional theory (DFT)

---

1 Introduction

It is well known that hydroxyl radical plays a particularly important role in both combustion and atmospheric chemistry. With this recognition of the OH radical as a dominant reactive species in degradation of organic compounds in troposphere and combustion processes, kinetics and mechanisms of the OH radical reactions have been investigated experimentally and theoretically since 1961.

Atkinson has reviewed the previous work on the gas-phase reaction of the OH radical with organic compounds before 1985 [1]. The reactions with alkanes proceed obviously via H atom

---

[*] Corresponding author. *Email addresses:* `wangbx@dicp.ac.cn` (B. X. Wang); `yinggao99@126.com` (Y. Gao)

abstraction from C-H bond. The reaction with ethane is exothermic with 21 kcal/mol for the primary C–H bond. Hartree-Fock (HF) theory and second-order Møller-Plesset perturbation (MP2) theory with large basis set (adj2-cc-pVTZ) were employed to study the H abstraction reaction of ethane by the OH radical [2]. The results show that the electron correlation plays an important role in predicting the correct geometry of the transition state and calculating the vibrational frequencies. This large basis set can yield accurate barrier heights for both directions of the reaction. The forward barrier height was calculated to be 4.0 kcal/mol with MP2 method after spin projection. Including the zero-point energy correction reduces the barrier height to be 2.33 kcal/mol. This method produces reaction energy to be 19.24 kcal/mol. *Ab initio* calculations up to the (U)MP4/6-311+G(2d,p)//(U)MP2/6-31G(d,p) level theory have also been used to study the hydrogen atom abstraction by the OH radical from chloroethane and ethane [3]. The best results for the barrier heights and reaction enthalpies have been obtained by the MP2 theory with spin projection using the 6-311+G(2d,p) basis set. After the zero-point energy correction, the reaction enthalpy [ΔH(298 K)] and barrier height [ΔE_0(298 K)] are -18.76 and 3.02 kcal/mol, respectively. The basis set has a larger effect on the calculated barrier height than on the energies of reactants and products and the results are not strongly geometry dependent. Reactant and product complexes in the hydrogen abstraction reaction of the OH radical with ethane have been indentified at (U)MP2, (U)MP4 and (U)CCSD(T) level with aug-cc-pVDZ and aug-cc-pVTZ basis sets [4]. The transition-state structures are more sensitive to the electron correlation effect than the equilibrium structures. The barrier height and the reaction energy become smaller as the method improves. The effect of the basis set on the barrier height is not so significant. BH&HLYP method has previously been found to perform well in predicting the transition state structures and vibrational frequencies [5], and has been used to study the addition [6] of OH radical and the H atom abstraction [7,8]. In the reaction of OH with alkanes, the BH&HLYP structures could provide the better approach than the MP2 method [9]. Whereas, the differences of the optimized geometries with BH&HLYP, CCSD and QCISD method show very little in H transfer reaction [10]. On the other hand, it was found that the B3LYP method is also able to provide reasonable results in the hydrogen abstraction reactions [11,12].

In this paper, all possible channels of OH radical + ethane reaction were investigated by using various levels, *ab initio* (MP2) and hybrid DFT (B3LYP and BH&HLYP), with 6-311++G(d,p) basis set. The effect of methods on the structures, the barrier heights and the energy differences, was discussed. The reaction mechanism was investigated in detail.

2 Computational methods

All calculations were carried out by using the Gaussian 03 program package [13]. The geometrical structures of reactants, products and transition states (TSs) were optimized at the B3LYP, BH&HLYP and MP2 level, using the 6-311++G(d,p) basis set and the unrestricted formalism for the case of radicals. Vibrational frequencies and single point energies were obtained from the corresponding optimized structures. Analysis of the vibrational frequen-