

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

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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.

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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

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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 [$\Delta H(298\text{ K})$] and barrier height [$\Delta E_0(298\text{ K})$] 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-

cies was used to characterize local minima with real frequencies while a transition structure presents one imaginary frequency. The imaginary frequency corresponds to the transition vectors pointing in the direction of the specific reaction coordinate. Intrinsic reaction coordinate calculations (IRC) [14, 15] were performed to confirm that each TS connects reactants and products along the reaction coordinate.

The energy barrier and reaction energy represent the energy difference of the transition states and the products with respect to the reactants. Zero point energies were obtained from the corresponding vibrational frequencies and used to determine the barrier height and the reaction energy without scaling. When correlation corrections are included by unrestricted Møller-Plesset perturbation theory, the barrier height may be overestimated by up to 10 kcal/mol [16], owing to high spin contamination in the TS. Energies obtained after spin projection were believed to produce more reliable barrier heights which are in good agreement with experimental values [6, 17]. The barrier heights derived from the spin projected MP2 single point calculations provide the rate constants which are in accordance with the experimental values [6]. Therefore, the energies from the spin projected MP2 calculations were also adopted to estimate the reaction energies and barrier heights.

3 Results and discussion

A good agreement with the experimental data is necessary in order to prove the reliability of a theoretical prediction. Table 1 lists the geometrical parameters of ethane and ethanol calculated at B3LYP, BH&HLYP and MP2 levels with 6-311++G(*d,p*) basis set along with the available experimental data. The bond lengths and angles optimized at B3LYP and MP2 methods are in better agreement with the experimental values with average deviation to be 0.5% than that of BH&HLYP method with 1.1%. The largest deviation is observed in COH

Table 1: Optimized geometrical parameters of ethane and ethanol at various levels with 6-311++G(*d,p*) basis set, along with the available experimental data. Bond lengths are in Å and angles are in degrees.

Species	Parameter	B3LYP	BH&HLYP	MP2	Experimental ^a
Ethane	C-C	1.5308	1.5207	1.5291	1.5351
	C-H	1.0939	1.0861	1.0934	1.0940
	∠CCH	111.36	111.31	111.14	111.17
Ethanol	C-O	1.431	1.413	1.427	1.431
	O-H	0.962	0.950	0.961	0.971
	C2-H	1.10	1.09	1.10	1.10
	C1-H	1.09	1.09	1.09	1.09
	∠CCO	108.0	108.1	107.5	107.8
	∠COH	109	110	108	105
	∠C1C2H	110	110	110	111
∠C2C1H	110	110	110	110	

^a The experimental values are from Ref. [19].

of ethanol to be 3.8% and 2.9% at B3LYP and MP2 methods, respectively. Therefore, MP2 method can provide more reasonable geometrical structures than B3LYP method.

The computed vibrational frequencies for the equilibrium and transition-state structures are shown in Table 2, along with the available theoretical and experimental values. Due to the neglect of anharmonicity effects in the theoretical treatment, the computed results are typically larger than the fundamentals observed experimentally. According to Merrick *et al.*'s suggestion [18], the vibrational frequencies calculated at B3LYP, BH&HLYP and MP2 levels with 6-311++G(*d,p*) basis set were scaled by 0.9688, 0.9335 and 0.9523. The average deviations from the experimental values at B3LYP, BH&HLYP and MP2 levels with 6-311++G(*d,p*) basis set are 27, 33 and 37 cm^{-1} , respectively. The relative error is less than 3% except the lowest frequency of ethane and methyl, with the relative error up to 28% for the methyl. The methodology does not significantly alter the vibrational frequencies. Table 2 shows that the vibrational frequencies calculated at MP2/6-311++G(*d,p*) level are lower than those with 6-31G(*d,p*) [3] and adj-cc-pVTZ [2] basis sets and in better accordance with the experimental data. We can conclude that MP2/6-311++G(*d,p*) is a reasonable level to study the transition-

Table 2: Vibrational frequencies (cm^{-1}) of equilibrium and transition-state structures at various levels with 6-311++G(*d,p*) basis set, along with available calculated and experimental data.

Species	B3LYP	BH&HLYP	MP2	MP2 ^a	MP2 ^b	Experimental ^c
	/6-311++G(<i>d,p</i>)			/6-31G(<i>d,p</i>)	/adj-cc-pVTZ	
Ethane	301	295	312	337	343	275
	802	794	792	847	834	820
	965	967	984	1050	1038	993
	1180	1179	1180	1270	1239	1155
	1392	1359	1351	1460	1418	1375
	1380	1381	1376	1489	1441	1379
	1456	1451	1448	1567	1535	1460
	1458	1452	1448	1570	1536	1486
	2929	2904	2931	3138	3099	2899
	2929	2905	2932	3138	3101	2954
	2973	2950	3002	3221	3158	2963
H ₂ O	2996	2973	3023	3241	3180	2994
	1552	1542	1551	1683	1646	1595
	3700	3719	3700	3892	3847	3657
CH ₃	3802	3816	3812	4030	3963	3756
	520	492	437			606
	1358	1355	1378			1396
TS1	3181	3148	3203			3161
	212i	1464i	1385i	1761i	1409i	
	989i	1141i	1514i			
TS3	1332i	1477i	1615i			

^a The values calculated at MP2/6-31G(*d,p*) level are from Ref. [3].

^b The values calculated at MP2/adj-cc-pVTZ level are from Ref. [2].

^c The experimental values are from Ref. [20] (for ethane), Ref. [19] (for H₂O and CH₃).

state region of the title reaction.

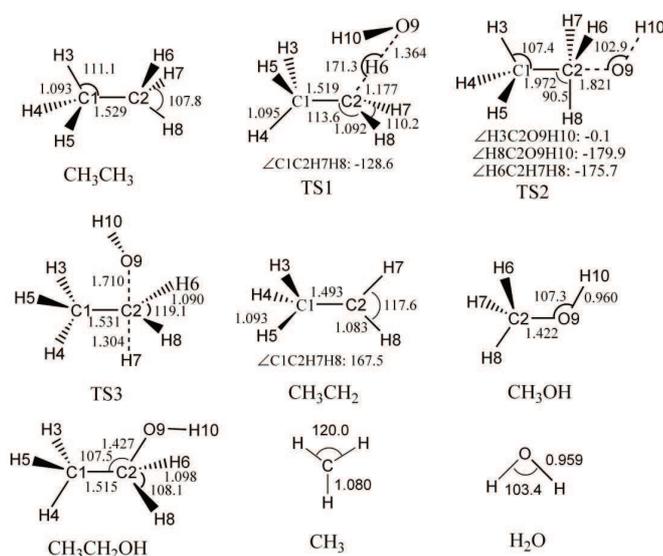


Figure 1: Optimized geometries of the reactants, transition states and products involved in OH + CH₃CH₃ reaction at MP2/6-311++G(d,p) level. Bond lengths are in Å and bond angles in degree.

The optimized structures calculated at MP2/6-311++G(d,p) level are displayed for the reactants, products and TSs in Fig. 1. The OH radical can react with ethane by hydrogen abstraction, hydrogen and methyl substitution. Three transition state structures (denoted as TS1-3) have been located along different reaction channels. The calculated Hessian matrix for these structures possesses only one imaginary eigenvalue. The total and relative energies (with respect to the reactants) calculated at corresponding geometrical structures are collected in Table 3. Contamination with higher spin states is a big problem in the application of unrestricted spin formalisms. In most cases, spin contamination would lead the increase of the energies since a higher-energy state is mixed in [21]. If there is no spin contamination, the expectation value of the total spin S^2 , should be equal to $S(S+1)$, where $S = 1/2$ times the number of unpaired electrons. For a doublet state, the accurate expectation value $S^2 = 0.75$. Thus, the S^2 values were monitored at various levels and also collected in Table 3. Spin contamination was considered to be minor in density functional theory [22]. Table 3 shows that the two density functionals (B3LYP and BH&HLYP) give the S^2 values from 0.75 to 0.81 for all species. For the MP2 method, the S^2 values are up to 0.87. After spin projection, the spin contamination is negligible. For open-shell species, since the energy differences derived from spin-projected MP2 values (PMP2) are in agreement with experimental values, the PMP2 energies were also adopted and given in Table 3. The spin projection has more effect on the energy barriers than on the reaction energies. The barrier heights derived after the spin projection correction are about 2-10 kcal/mol below the non-projected values, which is

Table 3: Total (E , Hartree) and relative^a (E_r , kcal/mol) energies including the ZPE correction.

Species	B3LYP		BH&HLYP		MP2			PMP2	
	E_r	S^2	E_r	S^2	E	E_r^b	S^2	E	E_r^b
Reactant (C ₂ H ₆ + OH)	0	0, 0.75	0	0, 0.75	-155.0671	0	0, 0.76	-155.0687	0
TS1	-1.00	0.76	5.37	0.77	-155.0574	6.10(4.14)	0.78	-155.0620	4.19(2.33)
TS2	38.59	0.77	49.35	0.81	-154.9850	51.53	0.87	-155.0004	2.86
TS3	41.74	0.77	52.42	0.79	-154.9876	49.86	0.84	-154.9979	44.42
P1(H ₂ O + CH ₃ CH ₂)	-17.00	0, 0.75	-13.26	0, 0.76	-155.0976	-19.18(-19.02)	0, 0.76	-155.0997	-19.46(-19.24)
P2(CH ₃ OH + CH ₃)	-2.06	0, 0.75	1.32	0, 0.75	-155.0715	-2.79	0, 0.76	-155.0734	-2.94
P3(CH ₃ CH ₂ OH + H)	11.52	0, 0.75	15.44	0, 0.75	-155.0645	1.62	0, 0.75	-155.0645	2.66

^a The relative energies are with respect to the reactants, ethane + OH radical.

^b Values in parentheses are the zero-point energy corrected values at MP2/adj-cc-pVTZ level from Ref. [2].

similar to the previous observation [2].

The schematic potential energy surface on the PMP2/6-311++G(d,p) energies for all possible reaction channels is illustrated in Fig. 2. According to various attack positions, we will discuss all possible reaction channels below.

3.1 Hydrogen abstraction channel

The OH radical can attack directly and abstract the hydrogen atom from the ethane

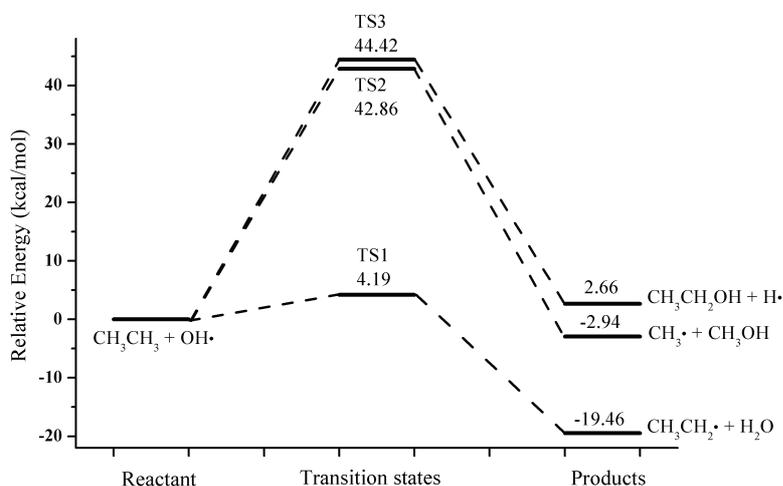
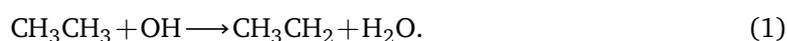


Figure 2: Schematic potential energy surface calculate at the MP2/6-311++G(d,p) level after spin projection.

The transition state structure for this channel is identified and denoted as TS1. Only one imaginary frequency is found to be 212i, 1464i, and 1385i cm^{-1} , respectively, at B3LYP, BH&HLYP and MP2 levels, as shown in Table 2. The imaginary frequency we obtained at B3LYP level is 212i cm^{-1} , which is much lower than the other levels and likely incorrect. Except the B3LYP, the MP2/6-311++G(d,p) vibrational frequencies are lower than that at the BH&HLYP level and than that with other basis sets. Chandra and Uchimaru have suggested that the B3LYP method does not produce good results for the hydrogen abstraction reactions [23]. In TS1, the breaking bond C2–H6 is 0.084 Å longer than the C–H bond length of the reactant, and the forming bond O9–H6 is 0.405 Å longer than the O–H bond length of the water molecule. Compared with the geometrical structure of the reactant, the geometrical parameters of TS1 change little (Fig. 1). Therefore, the TS1 shows reactant-like structure. As previous statement [23], the B3LYP method produces negative barrier height in this channel, which is not in accordance with the experimental observation. In Table 3, the barrier height and reaction energy calculated at PMP2/6-311++G(d,p) level are close to those with large basis set (adjcc-pVTZ), which is in more agreement with the experimental value [2]. This suggests that the larger basis set is necessary in the single point calculation to predict the energies. The hydrogen abstraction channel has lowest barrier height with 4.19 kcal/mol and most exothermicity with 19.49 kcal/mol (Fig. 2). According to Hammond's postulate [24], the exothermicity also indicates the reactant-like structure of TS1. Thus this channel is predominant kinetically and thermodynamically.

3.2 Methyl substitution channel

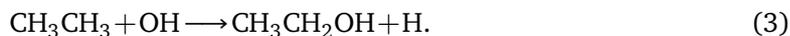
When the hydroxyl radical attacks the C–C bond from the end-on, the OH radical is oriented, where H3C1C2 and H8O9H10 are almost coplanar, as shown in Fig. 1. The opposite methyl can be substituted by the OH radical to produce methanol



In the TS2, the breaking and forming bonds are 0.443 and 0.399 Å longer than the corresponding bonds of the ethane and the methanol, respectively. This implies that the TS2 is neither reactant-like nor product-like. The slight exothermicity of this channel with 2.94 kcal/mol at PMP2 level also supports this implication. Table 3 displays the reaction energies at different calculation level. The results show that the reaction energies are few, no matter exothermic or endothermic. Due to the approach of the OH radical, the tetrahedral structure formed by C2H76H7H8 is converted into a coplanar one, which is perpendicular to the C1–C2 bond. Vibrational analysis shows only one imaginary frequency, corresponding to the to-and-fro turnover of CH₃ group. At MP2 level, the imaginary frequency is 1514i cm^{-1} , larger than that at B3LYP and BH&HLYP level, as listed in Table 2. The barrier height calculated for this channel is up to 42.86 kcal/mol at PMP2 level. The BH&HLYP result shows this channel is endothermic, whereas the other methods exhibit it is exothermic. The contribution of this channel is of no importance and can be negligible.

3.3 Hydrogen substitution channel

The hydroxyl radical can also attack the C2 position, perpendicularly to the C1–C2 bond and opposite the H8 atom



The transition state structure for this channel is shown in Fig. 1 and denoted as TS3. The breaking C2–H7 bond is elongated by 0.211 Å and the forming C2–O9 bond is 0.283 Å longer than that of the methanol. The TS3 structure also resembles neither the reactant nor the product. The reaction energy calculated at PMP2 level is -2.66 kcal/mol, about 10 kcal/mol fewer than that at B3LYP and BH&HLYP level, which, according to Hammond's postulate, also supports the statement. The vibrational mode of the imaginary frequency (with 1615i cm⁻¹ at MP2 level) corresponds to the rupture of the C2–H7 bond and the formation of the C2–O9 bond. The intrinsic reaction coordinate (IRC) is calculated to confirm the right connection along the reaction path. The energies calculated for this channel at PMP2 level give high barrier with 44.42 kcal/mol, lower than the results at BH&HLYP and MP2 methods. Therefore, the hydrogen substitution in OH + ethane reaction cannot occur to any extent.

4 Conclusions

The reaction mechanism of ethane with the hydroxyl radical has been investigated in detail at *ab initio* (MP2) and DFT (B3LYP and BH&HLYP) method 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 the vibrational frequencies. By using MP2 method, 6-311++G(*d,p*) basis set is more suitable for frequency calculation than the other basis sets. Comparison of reaction energies with various basis sets indicates that large basis set is necessary for single point energy calculation. Due to the spin contamination of MP2 method, spin-projected MP2 energies were adopted to construct the potential energy surface. The results show that the hydrogen abstraction channel is favored kinetically and thermodynamically. The other channels have high barrier and are not feasible. The hydrogen abstraction channel proceeds via an "early" transition state and the transition-state structures for the other channels are neither reactant-like nor product-like.

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