

Ab initio calculations: a significant route to identify the transition states, entrance and exit channel complexes, and activation energies

حسابات نظرية لتفاعل استخلاص الهيدروجين من الميثان بواسطة جذر الهيدروكسيل

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Abstract

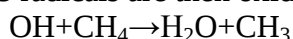
Ab initio calculations have been used to identify the potential energy minimum of the entrance and exit channel complexes and transition state structure in the hydrogen abstraction reaction of CH₄ with OH radical, as well as activation energy and reaction enthalpy were computed. MP2/6-31G** and HF/6-31G** levels have been used to optimized geometries and harmonic vibrational frequencies. The product complex is at a lower energy level than reactant complex (-304193.2414 KJ/MOL vs -304144.0172 KJ/MOL) at MP2 level, so the exit channel complex is more stable than entrance complex. The activation barrier is 45.9161 KJ/MOL and the enthalpy change is -49.2242 KJ/MOL at MP2 level.

الملخص

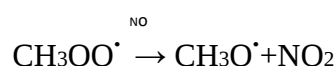
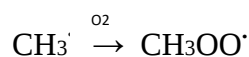
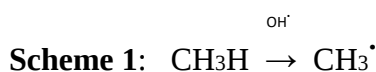
تم استخدام بعض طرق الميكانيك الكمي (*Ab initio*) لحساب اقل طاقة جهد لمعقدات النواتج والمفاعلات (entrance and exit complex) وتركيب حاله الانتقال لتفاعل جزيئه الميثان مع جذر الهيدروكسيل, بالاضافه الى حساب طاقه التنشيط وانتالييه التفاعل. في هذه الدراسه تم استخدام المستويات النظرية MP2/6-31G** و HF/6-31G** لتحديد التركيب الهندسي والتردد الاهتزازي. وقد اوضحت النتائج ان معقد النواتج يمتلك طاقه (-304193.2414 KJ/MOL) اقل من معقد المفاعلات (-304144.0172 KJ/MOL) عند المستوى MP2, وهذا يعني انه اكثر استقرارا من معقد المفاعلات. حاجز التنشيط لهذا التفاعل = 45.9161 KJ/MOL وانتالي التفاعل = -49.2242 عند مستوى MP2.

Introduction

Over the past 30 years the reaction of Methane with hydroxyl radical has been intensively studied. This is due to the fact that this reaction is considered as an important step in the combustion process of fossil fuels because in this reaction methane molecular react with hydroxyl radical through direct hydrogen abstraction mechanism, water and CH₃ radical are produced through it, CH₃ radicals are then oxidized to CO and CO₂ during a chain reaction mechanism^{1,2}.



Furthermore, this hydrogen abstraction reaction might affect the levels of tropospheric's ozone because the initially formed Methyl radical may react with oxygen molecular rapidly to produce new radical (CH₃OO·) which may oxidize NO to NO₂ and leads to shift the balance of atmospheric NO_x as shown below in scheme (1)³.



Finally, another importance of hydrogen abstraction reaction is that in the atmosphere methane is degraded and regulates the steady- state concentration of OH radicals⁽¹⁾. Thus, the oxidation of methane in the upper atmosphere provides a large amount of water vapour to the stratosphere. This project will test the ability of *ab initio* quantum mechanical methods to calculate the energy minimum of the entrance and exit channels complexes, transition state structure, in addition to calculate the activation energy for the above reaction.

Computational Details

The GAUSSIAN 03 system of programs ⁴ was used in this project to perform the *ab initio* calculations. Harmonic vibrational frequencies, zero-point correction energies and optimized geometries for the entrance and exit channel complexes and proposed transition state structure were carried out at the second-order Møller- Plesset perturbation theory (MP2) and Hartree Fock theory (HF). The 6-31G** basis set was used for the hydrogen abstraction reaction, and this basis set includes two stars (**) to consider the hydrogen atom in the reaction (in other words, for heavy atoms one d polarization functions should be added and for H atom one p polarization functions should be added) . As well as, the Intrinsic Reaction Coordinate (IRC) of this reaction was calculated at the MP2 level with 6-31G** basis set using the geometries of transition state which are optimized at that level.

Results and Discussion

In this study, the optimized geometries of the reactants and products for the hydrogen abstraction reaction were calculated at MP2/6-31G** and HF/6-31G** levels. The structure of optimized methane shows that CH₄ is a non-polar molecule with four equivalent C-H single bonds, it belongs to the T_d point group and the bond angle (H-C-H) is 109.471° at both MP2 and HF levels. Table (1) shows that our results which were obtained at MP2/6-31G** are in a good agreement with the experimental value than at HF/6-31G**, also they agree with those that were obtained by Siyu and Ruozhuang ⁵ at high- level *ab initio* method: QCISD/cc-pVTZ. Overall the calculated bond length at HF level shorter than at MP2 level.

Table (1): The bond lengths of the reactants and products (Å°)

Methods	CH ₄ (T _d)	OH(C _{∞v})	CH ₃ (D _{3h})	H ₂ O(C _{2v})
	C-H	O-H	C-H	O-H
MP2/6-31G**	1.08504	0.97184	1.07441	0.96144
HF/6-31G**	1.08354	0.95489	1.07279	0.94314
Expt. (a)	1.091	0.971	1.079	0.958
QCISD/cc-pVTZ (b)	1.085	0.967	1.074	0.956

a: experimental data ⁶ · b: theoretical data ⁵

Ab initio calculations have been used to compute the harmonic vibrational frequencies. So, from these calculations we are able to compare between the vibrational frequencies for methane molecular and hydroxyl radical with the experimental values.

As can be seen from table (2), the *ab initio* frequencies are larger than the experimental values, and the MP2/6-31G** gives result nearest to experimental result than HF/6-31G** (HF calculation typically overestimate frequencies), and these differences can be decreased by using large basis sets and advanced methods which correctly treated the electron correlation.

So, according to previous study which was done by Lasaga and Gibbs, when they used large basis set (MP2/6-311G**) they obtained vibrational frequencies closely agree with the experimental results ⁷.

Table (2): Vibrational frequencies for the reactants (CH₄+OH) in cm⁻¹

Methods	Methane				Hydroxyl
	v1(T)	v2(E)	v3 (A)	v4(T)	v (SG)
MP2/6-31G**	1403.71	1623.85	3136.07	3282.32	3841.83
HF/6-31G**	1469.01	1685.49	3174.41	3285.24	4053.88
Expt. (a,b)	1357	1567	3137	3158	3738
MP2/6-311G**(c)	1362	1579	3083	3222	3862

a: experimental data for methane ⁸

b: experimental data for Hydroxyl ⁷

c: theoretical data for both CH₄ and OH ⁷

Two different methods HF and MP2 level of theory have been used to calculate the minimum potential energy at the entrance and exit channels of the reaction. From the geometry of the weakly bound CH₄...OH complex which is formed in the shallow well at the entrance channel fig (1), the distance between oxygen atom and the nearest hydrogen atom of CH₄ is 2.65488 Å at MP2/6-31G** level of approximation and this is very close to that one was calculated at UMP2/aug-cc-pVDZ (2.647 Å)², but at HF/6-31G** the oxygen atom is located at 2.85157 Å away from the hydrogen atom. As well as the C1, H2, O6 and H7 atoms are not collinear because the bond angle of C1-H2-O6 and H2-O6-H1 are not 180°.

The zero-point correction energy at the entrance channel is -304144.0172 KJ/MOL at MP2, it is lower than the zero-point correction energy at the HF level -303333.2255 kJ/MOL. Furthermore, the reactant complex is more stable than the reactants, because the energy of the formal is -304144.0172 KJ/MOL while for the latter is -105855.055 KJ/MOL for methane molecule and -198286.510266 KJ/MOL for hydroxyl at MP2 (-197907.8173 KJ/MOL for OH and -105425.1157 KJ/MOL for CH₄ at HF method).

As can be seen from table (3) the bond length for hydroxyl radical is slightly small than that of entrance complex, while The C-H bond of the entrance channel complex is smaller than for methane at both methods as well as the bond lengths at MP2 level are longer than at HF level.

The molecular structure of the product complex CH₃...H₂O in the exit valley of the potential energy surface has been studied in this project and as can be seen from fig (1), the H5 atom of H₂O is located at 2.48297 Å away from the carbon atom of methyl radical at MP2 and it is shorter than at HF (2.69101Å⁰). There is a slight similarity to the product complex which was found by Hashimoto and Iwata ², they found the bond length H5-C1 is 2.433Å⁰ at UMP2/aug-cc-PVDZ. The

C1, H5, O6 and H7 atoms are still located at the same plane and not collinear. In addition, there is a slight difference between the products and exit complex, the bond length of the two O-H for the H₂O in the exit complex is not equal, (O6-H5) is 0.96325 Å and the (O6-H7) is 0.96127 Å, while for H₂O molecular is equivalent (0.96144Å) at MP2 level and this result agrees with Hashimoto and Iwata study(at UMP2/aug-cc-PVTZ level the (O6-H5) is 0.965 Å and the (O6-H7) is 0.961 Å)². Therefore, this geometry leads to forming a strong binding compared with the reactant complex.

The most important point is the zero-point correction energy of the exit channel complex (-304193.2414 KJ/MOL at MP2 level and -303334.5882 KJ/MOL at HF level of theory) is smaller than for the entrance complex, so this leads to making the reaction exothermic. Also this means that the exit channel complex is more stable compare with entrance channel complex. Table (4) gives the bond lengths of the products (CH₃ and H₂O) and the exit complex, all the bond lengths of the exit complex are larger than the products at both MP2 and HF levels.

Another important point is that all the harmonic vibrational frequencies for the entrance and exit complexes which are computed at the MP2/6-31G** and HF/6-31G** levels are real [the eigenvalues of the Hessian (second derivative) matrix are positive], so the structure is a true potential energy minimum. Furthermore, the project's results show that all the harmonic vibrational frequencies of reactants, products and complexes which are calculated at HF/6-31G** is larger than at MP2/6-31G** levels, and this is in a good agreement with the study of Gonzalez et al., also they found that frequencies at UMP2 are lower than at HF⁹. Overall, by using MP2/6-31G** level the vibrational frequencies are higher than the experimental results; this is due to the basis sets impacts and neglect of anharmonicity¹⁰.

Table (3): bond lengths (Å) of the reactants and entrance channel complex

Methods	(C-H) for methane	(C-H) entrance complex	(O-H) for hydroxyl	(O-H)entrance complex
MP2/6-31G**	1.08504	1.08487	0.97184	0.97243
HF/6-31G**	1.08354	1.08303	0.95489	0.95502

Table (4): bond lengths (Å) of the products and exit channel complex

Methods	(C-H) for methyl	(C-H) exit complex	(O-H) for water	(O-H5) exit complex
MP2/6-31G**	1.07441	1.07549	0.96144	0.96325
HF/6-31G**	1.07279	1.07347	0.94314	0.94400

In term of transition state, *ab initio* methods have utilized to optimize the transition structure which is separate the reactants and the products, and has higher potential energy compare with the equilibrium structures along the reaction path. The geometry of molecular configuration at this point provides a significant piece of information to describe the mechanism of the reaction. In this project transition state for hydrogen abstraction reaction was computed at the MP2/6-31G** and HF/6-31G** levels. Two recipes have been used to compute the transition state structure: First one depends on guess the structure of transition state and then optimises it; this recipe is suitable for simple reactions. The *ab initio* calculations for this guessing transition structure show that all the vibrational frequencies are real just one is imaginary (- 2061.23cm⁻¹ at MP2 level, it is roughly nearest to that one which was found in previous study -2055 cm⁻¹ at UMP2/6-31G** level⁹). This is because the transition state is considered mathematically as a saddle point on the potential energy surface, and the first derivative of the potential energy of this point is zero with respect to any nuclear coordinate, while the second derivative for all is positive just one coordinate. So, on the

potential energy surface this point appears minimum in every direction just in one. As a result, optimizing the geometry of the transition structure is slightly difficult because there are lots of saddle point structures on the potential energy surface, also another challenge which faces the calculation of correct transition state is that at the transition structure the potential energy surface is more flat compare with the surface around the equilibrium structure.

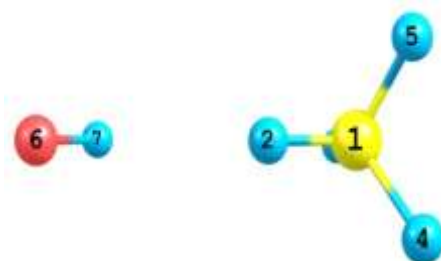
In this work several tries were done until the correct transition structure of the hydrogen abstraction reaction was obtained. The transition state in this project is formed when the hydroxyl radical attach linearly hydrogen atom of methane molecule. Fig (1) shows that the distant between the oxygen atom of the hydroxyl radical and the hydrogen atom of methane is roughly $1.28144\text{\AA}$ and the angle H5-O6-H7 of the transition structure is approximately 98.52° at MP2. However, at HF level the length between O6...H5 is $1.20577\text{\AA}$ and the angle H5-O6-H7 is 99.902° .

The result at MP2 is close to the geometry of the transition structure that was calculated by Aliagas and Gronert³, they found that the distance between O6...H5 is $1.283\text{\AA}$ and the angle is 98.5° at MP2/6-31G(d, p) level. Also, the geometry of the transition state at HF is similar to another one which was done by Gonzales et al.⁹, the distance between CH₄ and OH radical is $1.206\text{\AA}$ and H5-O6-H7 angle is 99.94° at HF/6-31G**. So from the *ab initio* calculations, we are able to know that the transition state structure is occurring at the beginning of the reaction. In other words, transition state is expected to be close to the reactants rather than to the products at MP2/6-31G** because the bond length of C1-H5 is smaller than the O6-H5 ($1.20547\text{\AA}$ vs $1.28144\text{\AA}$) and this is the same with the transition state which was found by Gonzales et al. (C-H is 1.204 and O-H is 1.281 at UMP2\6-31G**)⁹. However, the situation is reversed at the HF level ($1.29843\text{\AA}$ vs $1.20577\text{\AA}$) and this is similar to the previous study at HF level ($1.298\text{\AA}$ vs $1.206\text{\AA}$)⁹.

Moreover, the zero-point correction energy of transition state is $-304098.1011\text{ KJ/MOL}$ at MP2 level and its lower than at HF method ($-303217.4756\text{ KJ/MOL}$), this significant difference in energy between the two methods could be because Hartree Fock theory is incorrectly treated the electron correlation, it allows electrons to come close to each other than they would be in reality, so this leads to overestimated the total electronic energy.

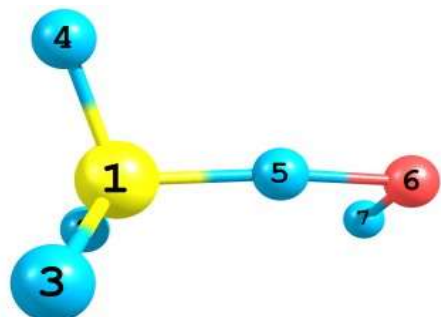
Entrance complex

Distance between O6 and H2 = $2.65488\text{\AA}$



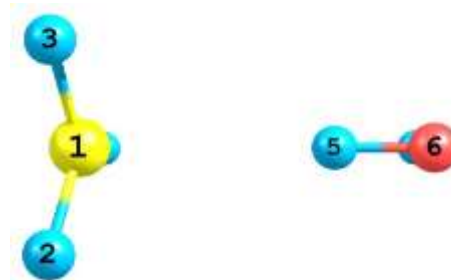
Transition state

Distance between O6 and H5 = $1.28144\text{\AA}$



Exit complex

Distance between O6 and H5 = 0.96325 Å



Figure(1): Optimized structures of the entrance and exit channels complexes and the transition state in the reaction of $\text{CH}_4 + \text{OH} \rightarrow \text{CH}_3 + \text{H}_2\text{O}$ at the MP2/6 31G**level.

Furthermore, according to Hashimoto and Iwata², the transition state structure is very sensitive to the effect of electron correlation compare with the equilibrium structure, so the transition state that is calculated at the MP2 is better than HF level as MP2 recovers the electron correlation and the first and second derivatives can be evaluated easily at this method.

The second recipe is depending on using Synchronous Transit-Guided Quasi-Newton Methods (STQN) to optimize the transition state for complicated reactions. It involves two methods: QST2 and QST3. The transition state was calculated by using QST2 method (requires the molecule specifications for reactants and products) does not giving correct transition structure. On the other hands, QST3 method (requires the molecule specifications for initial guess transition state structures, reactants and products) has used to compute the transition state and it gives results (energy and geometrical parameters) too close to that one was calculated in the first recipe ($E = -304098.1014$ KJ/MOL vs -304098.1011 KJ/MOL at MP2 level), and slight difference to that one calculated at HF method (-303218.1509 KJ/MOL vs -303217.4756 KJ/MOL). These methods are better than the first one as there is no need to the second derivative matrix.

As regard to activation energy, in this project *ab initio* methods have been used to determine the activation energy for the reaction between methane and hydroxyl radical. Activation energy is the difference between the transition state energy and the energy of the reactants fig (2), so the activation energy for this reaction is 45.9161 KJ/MOL at MP2 level and at HF level is 115.7499 KJ/MOL.

As pointed out by Lasage and Gibbs⁷, high activation energy can obtain by using SCF Hartree-Fock calculation, while by using higher level methods which are treated the electron correlation with large bases sets, the activation energy reduces and becomes close to the experimental data. Sana et al.¹¹ found that the activation energy results for SCF is 129.704 KJ/MOL, while with the electron correlation methods the activation energy is 47.6976 KJ/MOL. Thus, the result of this project is slightly different to that one which was calculated by Lasage and Gibbs⁷, when they used MP2/6-311G**level of theory the activation energy is 37.024216 KJ/MOL and it is far away from another one which was done by Gonzales et al.⁸, they produced lower activation energy (30.71056 KJ/MOL) when they used PMP4/6-311G**//UMP2/6-31G** because they used electron correlation methods with large bases set.

From the experimental result of $\text{CH}_4 + \text{OH}$ reaction, the activation energy range value is in between 8.368- 20.92 KJ/MOL⁷ and the actual value is between 12.552-16.736 KJ/MOL¹², while the experimental range found by Gonzales et al. is 16.736-29.288 KJ/MOL⁸. Moreover, the enthalpy change for $\text{CH}_4 + \text{OH}$ reaction has been calculated by using *ab initio* methods. As can be seen from fig (2) the enthalpy change is the difference between the products energy and the reactants energy.

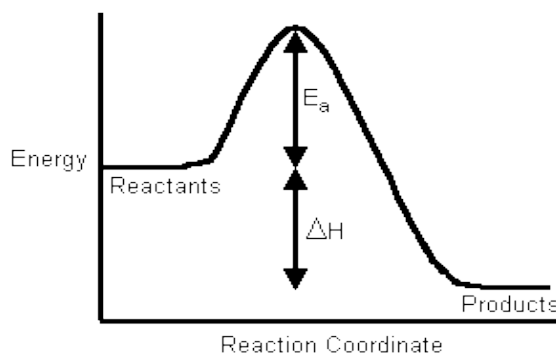


Figure (2): activation energy & enthalpy change

In the present work the enthalpy change is calculated at the MP2/6-31G** level of theory is equal to -49.2242 KJ/MOL, while by using HF/6-31G** enthalpy change is - 1.3627 KJ/MOL. As a result, calculate the enthalpy change for the reaction is often used to measure the quality of the calculations³, and the value of ΔH can reduce by using more accurate methods.

Last part in this project shows that *ab initio* calculations can be used to explore the potential energy pathways for the above hydrogen abstraction reaction through using intrinsic reaction coordinate (IRC). According to Fukui, the IRC is "the descent pathway in mass-weighted coordinates starting from a transition state (TS) and ending in a local minimum on a potential energy surface (PES)"¹³. Thus, reaction pathway plays an essential role in the study of PES for chemical reaction.

Figure (3) shows the IRC for $\text{OH} + \text{CH}_4 \rightarrow \text{H}_2\text{O} + \text{CH}_3$ reaction at MP2/6-31G** level with Max Points=18 and Step Size=5. The entrance channel complex from IRC is slightly different from the calculated entrance channel complex, which has minimum energy -304286.9685848 KJ/MOL, the distance between O...H2 is $2.33414 \text{ \AA}$ and C-H2 is $1.08134 \text{ \AA}$. But, there is not fully understood why the energy of TS from IRC is lower than the calculated TS.

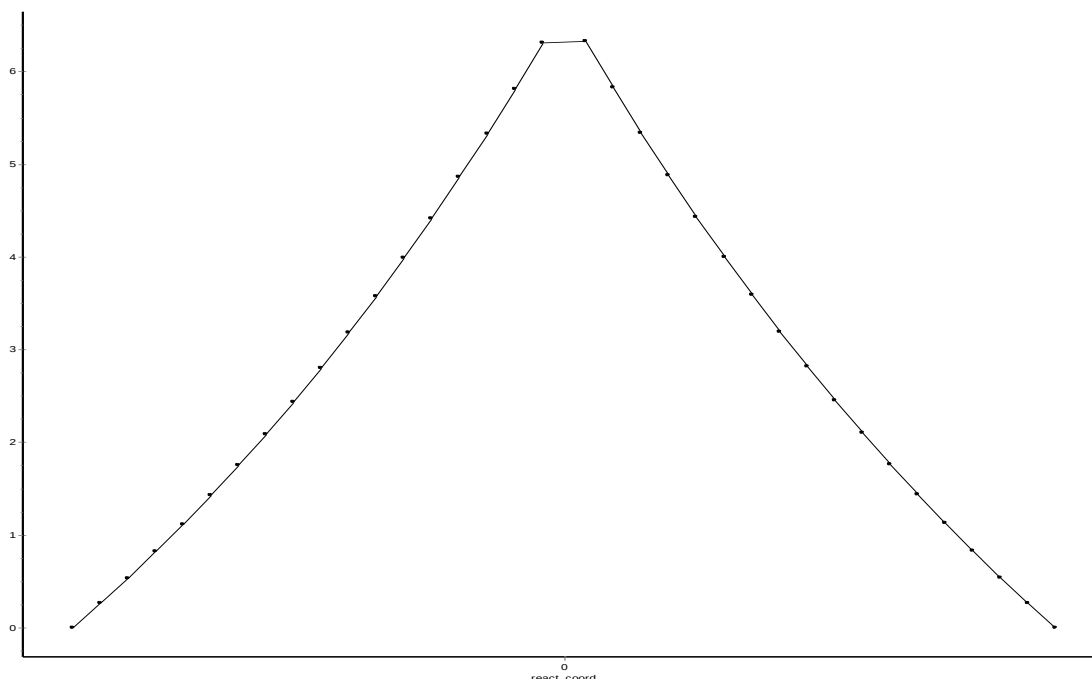


Figure (3): The Geometry of Transition States Structures of $\text{CH}_4 + \text{OH}$ from IRC calculation

Conclusion

This project indicates that *ab initio* methods can be used as a sophisticated tool to explore the potential energy pathways for the reaction of methane and hydroxyl radical. By using high level of theory which involves electron correlations such as MP2 accurate quantum mechanical results are obtained. The activation energy for CH₄+OH reaction is 45.9161 KJ/MOL at MP2 level, to bring it to the experimental value, high level methods with large basis sets should be used. Hartree- Fock methods typically overestimate vibrational frequencies, minimum potential energies and the activation barrier, but it gives short bond length. Finally, MP2 method is more reasonable than HF method to calculate the potential energy minimum for equilibrium and transition structures and it is perfect for vibrational frequencies and geometry optimisation calculations as it recovers the majority of electron correlation.

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