

Theoretical investigation on mechanism reaction of methane gas with hydroxyl free radical

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Abstract

Potential energy surface have been performed to estimate the reaction mechanism of methane with hydroxyl radical in vacuum using modern quantum mechanics calculation methods that's package on hyperchem8.02 program. Optimized structures and structural reactivates have been studied through bond stability and angles using DFT calculation based on the basis set 6-31G**. Energetic properties have been calculated like total energy, Gibbs free energy, entropy, heat of formation, and rate constant for all chemical species that's participate in the suggested reaction mechanism. Reaction mechanism and rate determining step had been suggested according to calculation of energy barrier values and compares between the suggested competitive reactions for each probable reaction step. Suggested structures and the probable transition states have been studied.

Key words: free radicals, reaction mechanism, theoretical chemistry, quantum mechanics, rate determining step.

Introduction:

The free radical reactions are rapid faster reaction rates than other reaction types with high values of rate constants and the life

of chemical species may reach into 10^{-12} s, therefore this reaction needed special high expensive technique to study out the mechanism (Westerberg and Blomberg 1998). Theoretical methods depending on calculation

methods of modern quantum mechanics are using to study of the different complicated reaction types to reduced the spend time of calculations, risk, and the economic value ,also the result will have ± 20 kJ/mol respective to the practical results (Gordon *et al.* 1988, and leach 2001). Calculation methods have been packaged on programs according to different levels of accuracy related to the nature of chemical system and the molecular formula that's needed required time to complete the process of calculation into suitable computer processor (Kratzer *et al.* 1996, Dorsett and White 2000). Human have been used natural products from a long period of time in industries to get out different products, petroleum gas (natural gas) is an important source for methane that's been used in different industries. Methane gas can be inter into different chemical process to produced different chemical products through free radical determination step that's consisting the concentrations and pressures or reactant species in this slow step (HyperChem 8.02, 2007). The transition states calculations can be used to proved the suggested mechanisms, since the transition state is characterized by only one imaginary frequency. The assembly of atoms at the transition state has been called an activated complex. The calculated potential-energy surfaces refer to the potential energy at the saddle point, as this is the only point for which the requisite for transition state

coordinates to be assumed (HyperChem Release 7, 2002). Density Functional Theory (DFT) and ab-initio calculations have been performed for tropospheric ozone with light hydrocarbons (methane, ethane, and propane gas) which are known to be important in atmospheric chemistry. Reactants, transition states, intermediate species and products are optimized at DFT (B3LYP) and MP2 level of theory using different basis sets .Thermodynamic properties ΔH° , ΔS° , and ΔG° have been calculated for replacement reactions, abstraction reactions, and hydroxylation reactions, since energy barriers values are calculated for this competitive reactions (Bahjat and Muhyedeen 2007, and Hashimoto *et al.* 2001).

In this work, the hydroxyl radical are producing through photolysis of hydrogen peroxide to induce with methane in simulated reaction mechanism. Different methods of quantum mechanics have been interested to estimate the optimized structures of chemical species, that's participate in the reaction mechanism of methane in vacuum. The suggested structures for chemical moieties are getting on through potential energy surface. Final equation of reaction mechanism investigation comes out depending on energy barrier calculated values for different reaction probabilities and zero point energy with first imaginary frequencies for transition states. Enthalpy formation of reaction for all most

probable subsequent steps are carried out to indicate the summation of enthalpy change value to final reaction .rate determination step investigated depending on the rate constant value for the most probable reaction steps in free radical mechanism.

Description of calculations

All theoretical calculations in this work were performed using the computational implemented in the Hyperchem package 8.02 (HyperChem 8.02, 2007). All suggested structures of free radicals reactions mechanisms have been optimized by DFT, 6-31G(d), 6-31++G(d,p), and MP2 levels of theory (Maas and Calzaferri 2002, Tsatsaronis and Park 1999). Frequencies of proposed transition state structures have been calculated at UHF/RHF/configuration interaction microstate (4X4) semi-empirical for characterization of the nature of stationary points and zero point energy (ZPE) calculations to compute the quantum energies of these reactions. Rate constant values for the most probable reactions have been calculated by DFT, 6-31G**to estimate the rate determination step for methane gas with hydroxyl radical.

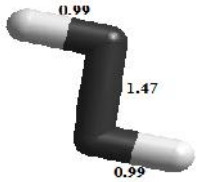
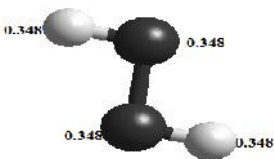


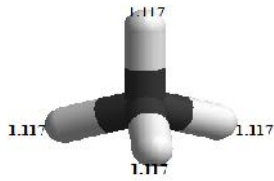
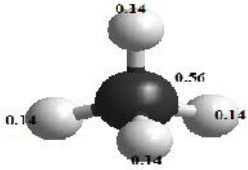
Results and Discussion

Optimized structures of reactant species

Photolysis of gaseous hydrogen peroxide occurs at wave length shorter than 320 nm. Figure 1 shows the structural and electronic

properties of reactant molecules. The bond lengths of O-H and O-O bond are 0.99&1.47Å respectively in hydrogen peroxide molecule. The bond angle of O-O-H bond is 97.5° with torsion angle equal to 180°. The distribution of electronic density are homogenously on the atoms, where the both of oxygen atoms have negative density provided with black color ,while the hydrogen atoms have positive density provided with white color. Hydrogen peroxide belongs to the C₂ point group. H₂O₂ has five fundamental vibrations. The active IR modes are including the symmetric O-H stretching vibrations, asymmetric O-H stretching vibrations, asymmetric O-H bending vibration and torsion (ν_1, ν_5, ν_4) respectively, but the infrared in active modes are including the symmetric O-H bending (ν_2)and O-O stretching (ν_3) vibration (Pehkonen 2008), as shown in table 1. The negative charged side concentrated on oxygen atom provided with black color and positive charged side concentrated on hydrogen atom provided with white color. This radical has short live time due the highly reactivity toward reaction to released the energy into the more comfortable reaction product.

Optimized methane structure show non polar molecule with symmetrical characteristic four C-H bonds. The positive side of electronic density is focused into hydrogen atoms provided with white color and negative side of electronic density is focused into carbon atoms provided with black color.

		
Tube view with bond lengths (Å) of hydrogen peroxide.	Ball and cylinder with atomic charge of hydrogen peroxide.	Atomic charge of hydroxyl radical.
		
Tube view with bond lengths (Å) and Basis set of hydroxyl radical.	Tube view with bond lengths (Å) of methane.	Ball and cylinder with atomic charge of methane.

Mole- cule	Basis set	Total energy	Free energy at 298 K°	Entropy at 298 K°	Heat of formation at 298 K°	IR- Freq. (cm ⁻¹)	IR- Int. (km/mol)
H ₂ O ₂	6-31G*	-93639.33	-93653.4	0.053	-93637.61	938.21 1189.29 1483.27 3499.17 3514.7	2.19 139.60 0.327 0.591 45.175
	6-31G**	-93644.97	-93659.1	0.053	-93643.31	936.37 1170.61 1459.13 3549.26 3562.54	0.014 139.44 0.128 0.469 47.56
·OH	6-31G*	-46782.34	-46792.8	0.04	-46780.88	3985.41	24.0
	6-31G**	-46785.21	-46795	0.04	-46783.03	3821.71	21.51
CH ₄	6-31G*	-24791.16	-24803.7	0.048	-24789.4	2311.44 4457.77 4458.16 4458.44	1846.47 5184.82 5185.01 5184.39
	6-31G**	-24794.09	-24806.7	0.048	-24792.4	2247.56 3647.96 3704.82 3705.25	546.23 0.116 326.06 326.051

Dissociation reaction of peroxide in gas phase occurs with energy barrier equal to 67 kCal/mol calculated at DFT through 6-31G** full MP2 to yielded two moles of hydroxyl radical as initiator of methane radical mechanism. Potential energy stability (PES) has been investigated for the two bonds of peroxide to estimate the reactivity toward photolysis reaction. Figure 2 illustrates the

stability energy curve of bonds. The figure illustrate that O-O is more active than O-H bond. The O-O bond is broken down at 2.97 Å (-93516.08kCal/mol), but O-H bond is broken down at 2.49 Å (-93494kCal/mol). At the same time figure shows the C—H bond is break down at 2.5Å with bond dissociation energy equal to 111 kCal/ mol.

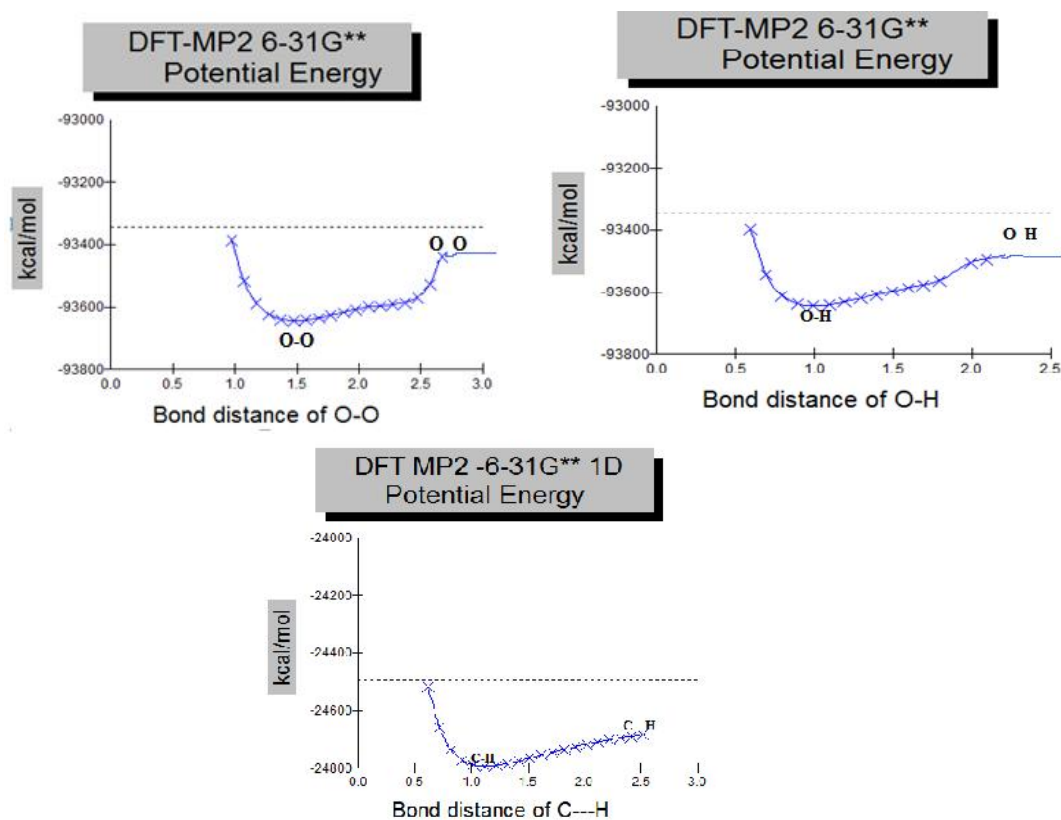


Figure (2) Potential energy stability curve of hydrogen peroxide's bonds and methane's bonds which calculated at DFT through 6-31G** full MP2.

Transition state of the reaction

Investigation of transition state for the reaction of methane with hydroxyl radical can be occurs in two different suggested path

ways, since the positive side attached to negative side. The suggestions involve, the first probable included the attaching of ·OH with carbon of methane to give TS₁. The second probable included the attaching of ·OH

with Hydrogen atom to give TS₂. Figure 3 show the geometry optimized of these transition states. Table 2 shows the energetic properties of TS₁ and TS₂. That's only one of these give up the real path for initiation step. TS₂ is represent real path for initiation step because TS₂ has lowest value of energy

barrier (14.73 kCal/mol) and the largest zero energy value (12.5 kCal/mol) rather than TS₁ (34.36 kcal/mol and 5.12 kcal/mol)respectively. This meaning that TS₂ needed lowest value of activation energy to give the reaction product (Drea 2010a).

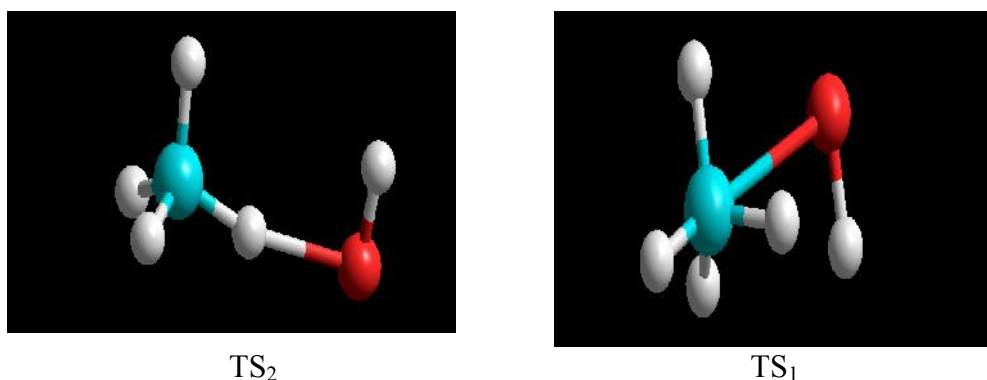


Figure (3) Ball and Cylinder view of suggested transition states calculated at DFT through 6-31G** full MP2 /UHF.

Table (2) Energetic values of proposed Transition states calculated at 298 K° by DFT through 6-31G full MP2 /UHF by kcal/mol units.**

TS	Total energy	IR Frequency	Zero point energy	Energy barrier	Enthalpies	Free Energy	Entropy
TS ₁	-63514.91	-	5.12	34.36	-63512.62	-63529.9	0.058
TS ₂	-63517.89	-	12.5	14.73	-63516.42	-63533.7	0.058

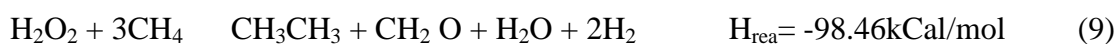
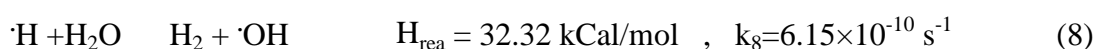
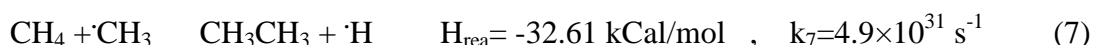
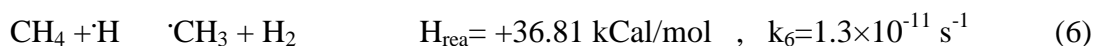
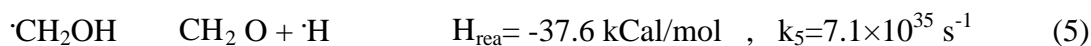
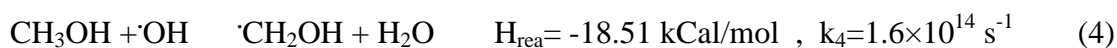
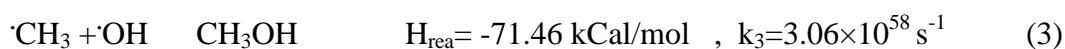
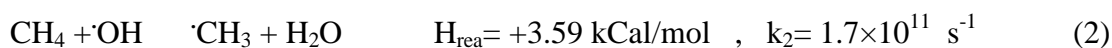
The suggested reaction of methane gas with hydroxyl free Radical

The chemical reaction of methane gas with hydroxyl radical can be taking out into several probable free radical reactions to obtain the net equation for the suggested mechanism of methane gas with hydroxyl radical. Table 3 shows the energetic values of chemical species that's participating in the reaction mechanism Table 4 shows compares between different competitive probable reactions according to the energy barrier value of reaction, the lowest energy barrier

reaction is the most probable than other competitive reactions. The several respected probabilities, which's have low value of energy barrier consisted the suggested mechanism of reaction (Drea 2010b). Scheme 1 how the suggested mechanism reaction of methane with hydroxyl radical. The net equation consisted from one mol of hydrogen peroxide reacted with three mol of methane gas to produced one mol of ethane , water and two mol of hydrogen gas . The reaction is exothermic to give up $H_{rea} = - 98.46$ kCal/mol of energy that's also can be used to done useful work.

Table (3) Energetic values of suggested chemical species that's participate in the reaction mechanism calculated at 298K° DFT through 6-31G full MP2 /UHF by kCal/mol units.**

Reaction compounds	Total Energy	Zero point Energy	IR - Frequency	Heat of formation	Free energy	Entropy
$\cdot\text{OH}$	-42141.25	3.1	+	-42146.58	-42158.8	0.041
$\cdot\text{CH}_3$	-21152.5	8.48	-	-21150.6	-21165.2	0.049
CH_3CH_3	-42373.3	24	+	-42371.61	-42388.3	0.056
CH_3OH	63371.46	15.5	+	-63368.72	-63386.3	0.059
$\text{CH}_3\text{O}\cdot$	-63167.11	2.29	-	-63166.61	-63183	0.055
$\cdot\text{CH}_2\text{OH}$	-63179.05	8.98	-	-63177.43	-63193.82	0.055
CH_2O	-63033.36	7.67	+	-63031.31	-63047.4	0.054
H_2O	-42354.37	5.66	+	-42352.79	-42366.8	0.047
$\cdot\text{H}$	-132.54	-	-		-	-
H_2	-347.5	3.2	+	-345.89	-355.72	0.033



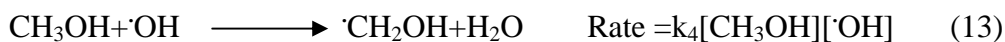
Scheme (1) The net equation of free radical steps for methane in vacuum.

Table (4) Reaction probabilities of free radical sequences mechanism calculated at DFT 6-31Gfull MP2/UHF by kCal/mol units.**

Reactant	Product	Energy Barrier	Heat change of reaction
H ₂ O ₂	2·OH	67.97	-11
CH ₄ +·OH	·CH ₃ +H ₂ O	29.14	+3.59
·CH ₃ +CH ₄	CH ₃ CH ₃ +·H	306.56	-26.32
·CH ₃ +·OH	CH ₃ OH	116.98	-71.46
CH ₃ OH+·OH	CH ₃ O·+H ₂ O	237.35	-4.1
	·CH ₂ OH+H ₂ O	34.03	-14.92
CH ₃ OH+·CH ₃	CH ₃ O·+CH ₄	65.97	-7.69
	·CH ₂ OH+CH ₄	60.49	-18.51
·CH ₂ OH	CH ₂ O+·H	14.54	-37.6
·H+CH ₄	·CH ₃ +H ₂	-0.03	+36.81
·CH ₃ +CH ₄	CH ₃ CH ₃ +·H	306.56	-32.61
·CH ₃ +·CH ₃	CH ₃ CH ₃	1420	-48.35
·H+H ₂ O	H ₂ +·OH	96.3	+32.32

According to rate constant values, the rate determining step have been suggested depending on the steady state approximation. Scheme 2 represent the determination of the effective concentration on the reaction rate,

they appear that's hydrogen peroxide concentrations is very important in the initiation of methane's reactions by the equation formula



The reaction rate law for the investigated mechanism can be derived according to the steady-state approximation; the net rate of

change of the intermediates may be set equal to zero (Stein and Sauer 1997).

$$\begin{aligned} d[\cdot\text{OH}]/dt = k_1[\text{H}_2\text{O}_2] - k_2[\cdot\text{OH}][\text{CH}_4] - k_3[\cdot\text{CH}_3][\cdot\text{OH}] - \\ k_4[\text{CH}_3\text{OH}][\cdot\text{OH}] = 0 \end{aligned} \quad (17)$$

$$\begin{aligned} d[\cdot\text{CH}_3]/dt = k_2[\cdot\text{OH}][\text{CH}_4] - k_3[\cdot\text{CH}_3][\cdot\text{OH}] + k_6[\cdot\text{H}][\text{CH}_4] - k_7 \\ [\cdot\text{CH}_3][\text{CH}_4] = 0 \end{aligned} \quad (18)$$

$$d[\cdot\text{H}]/dt = k_5[\cdot\text{CH}_2\text{OH}] - k_6[\cdot\text{H}][\text{CH}_4] + k_7[\cdot\text{CH}_3][\text{CH}_4] = 0 \quad (19)$$

$$d[\cdot\text{CH}_2\text{OH}]/dt = k_4[\text{CH}_3\text{OH}][\cdot\text{OH}] - k_5[\cdot\text{CH}_2\text{OH}] = 0 \quad (20)$$

$$k_5[\cdot\text{CH}_2\text{OH}] = k_4[\text{CH}_3\text{OH}][\cdot\text{OH}] \quad (21)$$

Substitute equation (21) in equation (19)

$$k_4[\text{CH}_3\text{OH}][\cdot\text{OH}] - k_6[\cdot\text{H}][\text{CH}_4] + k_7[\cdot\text{CH}_3][\text{CH}_4] = 0 \quad (22)$$

$$[\cdot\text{H}] = (k_4[\text{CH}_3\text{OH}][\cdot\text{OH}] + k_7[\cdot\text{CH}_3][\text{CH}_4]) / k_6[\text{CH}_4] \quad (23)$$

The summation of the two equations (17), (18) to produce:

$$k_1[\text{H}_2\text{O}_2] - 2k_3[\cdot\text{CH}_3][\cdot\text{OH}] - k_4[\text{CH}_3\text{OH}][\cdot\text{OH}] + k_6[\cdot\text{H}][\text{CH}_4] - k_7[\cdot\text{CH}_3][\text{CH}_4] = 0 \quad (24)$$

Substitute equation (23) in equation (24) and ignore all symmetrical terms

$$k_1[\text{H}_2\text{O}_2] - 2k_3[\cdot\text{CH}_3][\cdot\text{OH}] - k_4[\text{CH}_3\text{OH}][\cdot\text{OH}] + k_6[\text{CH}_4] \left(\frac{k_4[\text{CH}_3\text{OH}][\cdot\text{OH}] + k_7[\cdot\text{CH}_3][\text{CH}_4]}{k_6[\text{CH}_4]} \right) - k_7[\cdot\text{CH}_3][\text{CH}_4] = 0 \quad (25)$$

$$k_3[\cdot\text{CH}_3][\cdot\text{OH}] = 1/2 k_1[\text{H}_2\text{O}_2] \quad (26)$$

Substitute equation (26) in equation (17)

$$k_1[\text{H}_2\text{O}_2] - k_2[\cdot\text{OH}][\text{CH}_4] - 1/2[\text{H}_2\text{O}_2] - k_4[\text{CH}_3\text{OH}][\cdot\text{OH}] \quad (27)$$

$$[\cdot\text{OH}] = k_1[\text{H}_2\text{O}_2] / 2(k_2[\text{CH}_4] + k_4[\text{CH}_3\text{OH}]) \quad (28)$$

since the rate determined step is $\text{Rate} = k_2[\cdot\text{OH}][\text{CH}_4] \quad (29)$

therefore can be substituted equation (28) in equation (29) to obtain the rate of the determined step according to steady state approximation.

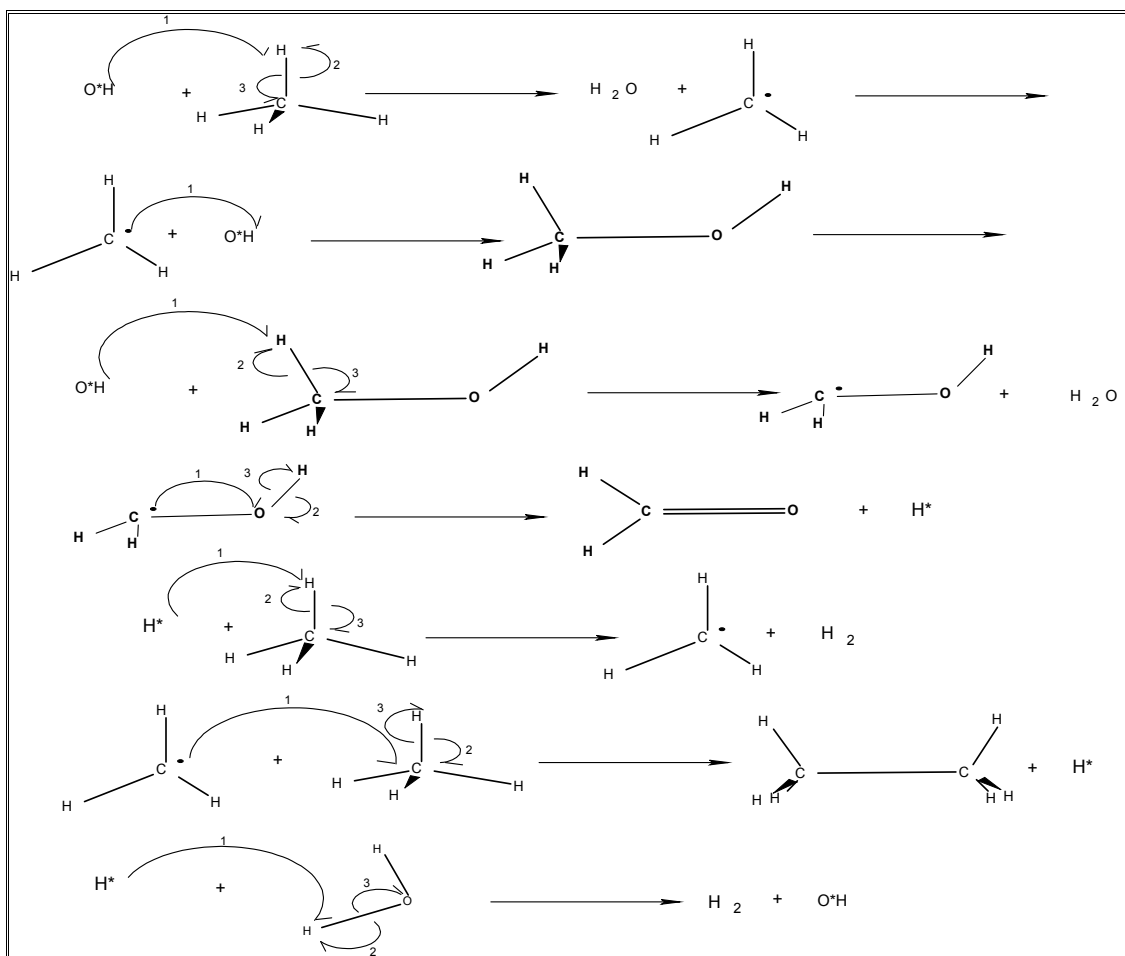
$$\text{Rate} = k_1[\text{H}_2\text{O}_2] k_2[\text{CH}_4] / 2(k_2[\text{CH}_4] + k_4[\text{CH}_3\text{OH}]) \quad (30)$$

At the beginning of the reaction, methanol concentration is very small and unaffected on the reaction rate, therefore it can be ignored, or $k_2[\text{CH}_4] + k_4[\text{CH}_3\text{OH}] \approx 2k_2[\text{CH}_4]$

At this time equation 31 becomes as

$$\text{Rate} = k_1/2k_2[\text{H}_2\text{O}_2] \Rightarrow \text{Rate} = k'[\text{H}_2\text{O}_2], \text{ since } k' = 2.882 \times 10^{-14} \text{ s}^{-1} \quad (31)$$

According to the previous investigation, it can be suggested that the orientation of the reaction mechanism of free radicals is as shown in scheme 3.



Scheme (3) Suggested mechanism of methane in vacuum using hydroxyl radical.

Conclusions

- The photolysis reaction of peroxide in gas phase occurs with energy barrier equal to 67 kCal/mol.
- The predominant formula of methane structure is tetrahedral (sp^3 hybridized) the stabilized structure comes out by total energy that's equal to -24794.09 kCal/mol.
- The direct reaction of methane with hydroxyl radical occurs through the second probable transition state with lowest value of energy barrier (14.73 kCal/mol) and the largest zero energy value (12.5 kCal/mol).
- The net equation of the suggested mechanism reaction of methane with hydroxyl radical consisted from one mol of hydrogen peroxide and three mol of methane to produced one mol of ethane , water ,and two mol of hydrogen gas .the reaction is

exothermic to give up $H_{\text{rea}} = -98.46 \text{ kCal/mol}$.

- The rate determinate step depending on the photolysis rate of peroxide molecules to initiate the sequence free radical reaction of methane by rate constant equal to $k' = 2.882 \times 10^{14} \text{ s}^{-1}$.

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التحقق النظري لآلية تفاعل غاز الميثان مع جذر الهيدروكسيل الحر

نادية عزت و عباس عبد علي دريع

كلية التربية للبنات ، كلية العلوم قسم الكيمياء

الخلاصة

جهد السطح لمحاكاة آلية تفاعل الميثان مع جذر الهيدروكسيل فراغيا بواسطة طرق حسابات ميكانيك الكم الحديث المحملة ضمن برنامج الهايبركم 8.02. تم دراسة التراكيب الفراغية المثلى والفعاليت التركيبية من خلال استقرار أطوال الأواصر وزواياها بواسطة طريقة دالة الكثافة الوظيفية المعتمدة على القاعدة 6-31G**. احتسبت الخواص الطاقية والتي تتمثل بالطاقة الكلية وطاقة كبس الحرة والانتروبي والمحتوى الحراري للتكون وثوابت السرعة لجميع الأصناف الكيميائية المساهمة في آلية التفاعل المقترحة. تم اقتراح آلية التفاعل واستنتاج الخطوة الضابطة لسرعة التفاعل وذلك بالاعتماد على المقارنة بين تفاعلات الجذور الحرة المتنافسة المحتمل حدوثها وقيم حواجز الطاقة العائدة لها. تم احتساب ودراسة التراكيب الفراغية والحالات الانتقالية 6-31G**.

إلية التفاعل الكيمياء النظرية ميكانيك الكم

الكلمات المفتاحية: