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Reaction Rate calculations for reactions between Methanol and Hydrogen

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Abstract
In this work, we calculate the reaction of methanol (CH_3OH) and Hydrogen atoms to explore reaction pathways. Three different products were found, forming $CH_3O + H_2$, $CH_4 + OH$ and $CH_3 + H_2O$. The APUAMA code was used to calculate de reaction rate over the temperature range of 200-4000K. Results are compared with reference data and are in good agreement for the first pathway.

Introduction
As far as research goes, it's well known that methanol is one of the most abundant organic gases in the atmosphere [1]. With the current use of this gas as a form of fuel additive and other organic purposes, concentration in the atmosphere of its products tends to increase [2]. Hence, a theoretical approach to this matter shows its value for chemistry when we are able to further investigate their interactions with other species, such as the hydrogen, that may be present in the atmosphere through data gathered from these reactions.

To make further progress on the subject of reaction rate studies, the interactivity of the hydrogen specie with methanol in a temperature arrangement (200K -4000K) exposing groups formed by this reaction, with analysis on their kinetics through the reaction rate calculations and thermodynamic properties.

Three different pathways were found:

$$CH_3OH + H \begin{cases} CH_3O + H_2 & (R1) \\ CH_4 + OH & (R2) \\ CH_3 + H_2O & (R3) \end{cases}$$

The first pathway is derived from the H-abstraction in the methanol hydroxyl group, and second one is obtained by incorporation of H in the CH_3 group to form CH_4, while the latter forms water (H_2O) and methyl (CH_3).

Methodology
The ab initio calculation is carried out by Gaussian software [3]. The B3LYP with 6-311(2d,d,p) basis set was used to optimize the geometries and calculate the frequencies, while the energies where determined at CBS-QB3. Information on optimized geometry, frequencies and energy for reactants, products, and transition states are later used on APUAMA [4] for the kinetics calculations and transition state theory. Each transition state had only one imaginary frequency (negative), while reactants and products did not.

On APUAMA [4], a software tool developed to easily calculate and separate information on reaction rate and thermodynamic properties for molecular reactions, we were able to gather all the desired data for the reaction, ranging from 200K-4000K in temperature.

Results and Discussion
Figure 1 compares the geometries of reactant, products and transition state with reference data [5]. In general, the error among calculates and reference data are less than 0.1Å in distance and 1° in angle. To

confirm that the transition state really connects with products, the intrinsic reaction coordinate (IRC) [6] calculations were performed.

Figure 2 shows the IRC calculation. In Fig. 2(a) it is possible to observe the shorting of the distance HH and an increase of distance OH, meaning the formation of H_2 and the break of bond OH of CH_3OH. Fig. 2(b) the bond CO from the methanol molecule increases as the distance CH gets lower, towards the formation of CH_4. Lastly, in Fig. 2(c), again the CO bond distance of CH_3OH gets higher as the hydroxyl group bonds with the hydrogen reactant, reducing the HO distance, to form H_2O.

Figure 3 presents the reaction rate and branching rate. Fig. 3(a) compares the reaction rate for the first pathway with reference data, while Fig. 3(b) for the third pathway. To our knowledge there is not reference data for the second pathway. Fig. 3(c) compares the reaction rate for the three pathways

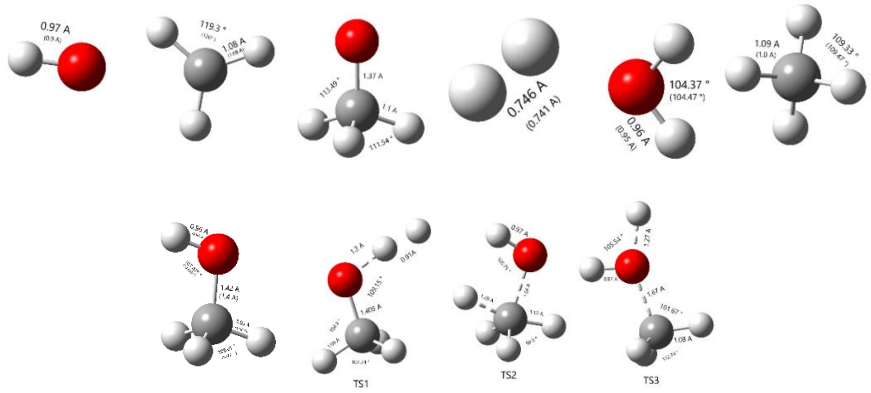
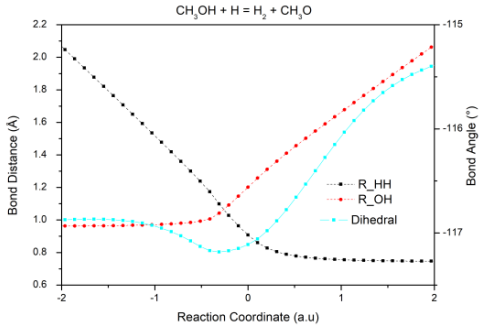
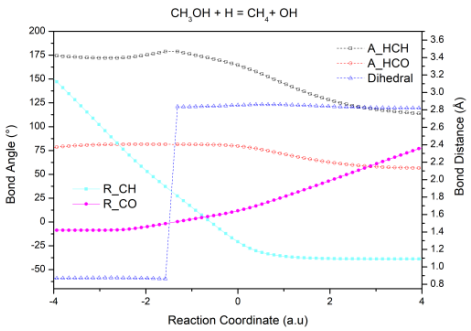


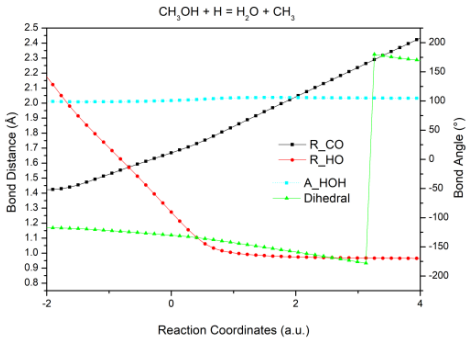
Figure 1: Optimized geometries



(a)



(b)



(c)

Figure 2: IRC calcution of CH_3OH+H: (a) CH_3O+H_2, (b) CH_4+OH, (c) CH_3+H_2O

Reaction (R1) shows a higher chance of happening up to 99-100 %, for all range of temperature, as observed on the Fig. 3(d). The other two channels have very low branching rate, less than 1%. It is possible to observe an increase in the branching rate for reaction (R2) up to 500K and for reaction (R3) up to 2000K.

Conclusion

We had presented the three pathways for CH_3OH+ reaction. The reaction rate is given as:

$$k_{R1} = 3.79 \times 10^{8} T^{1.78} \exp(-110.1/RT)$$

$$k_{R2} = 9.30 \times 10^{8}\ T^{1.54} \exp(-44.8/RT)$$

$$k_{R3} = 7.58 \times 10^{8}\ T^{1.69} \exp(-222.6/RT)$$

Determined through APUAMA code using small curvature transmission coefficient (SCT), the rate is given in $cm^3\ s^{-1}\ mol^{-1}$, and the activation energy in kcal mol^{-1}.

Acknowledgements

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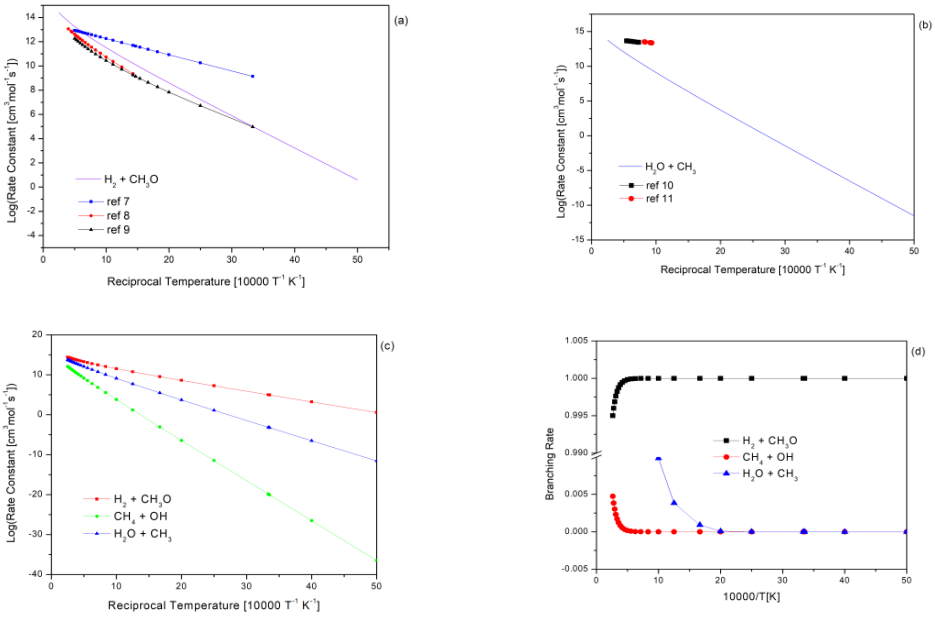

Figura 4: (a) rate constant for $CH_3OH + H = CH_3O + H_2$ [7-9], (b) rate constant for $CH_3OH + H = CH_3 + H_2O$ [10-11], (c) rate constant for $CH_3OH + H$=products (d) branching rate for $CH_3OH + H$ = products.