

Reaction Rate calculations for reactions between Methanol and Hydrogen

João Pedro Marretto Helmeister¹ and Patricia R. P Barreto².

¹Universidade Estadual de Campinas, Faculdade de Ciências Aplicadas, Limeira, SP CEP 13484-350, Brazil.

²Laboratório Associado de Plasma, Instituto Nacional de Pesquisas Espaciais, CP515, São Jose dos Campos, SP CEP 12247-970, Brazil;

j174564@dac.unicamp.br

Keywords: Methanol, Hydrogen, TST, Reaction DFT

Abstract

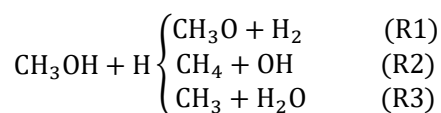
In this work, we calculate the reaction of methanol (CH₃OH) and Hydrogen atoms to explore reaction pathways. Three different products were found, forming CH₃O + H₂, CH₄ + OH and CH₃ + H₂O. The APUAMA code was used to calculate the reaction rate over the temperature range of 200-4000K. Results are compared 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:



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 CH₃ group to form CH₄, while the latter forms water (H₂O) and methyl (CH₃).

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 were 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 calculated 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 H₂ and the break of bond OH of CH₃OH. Fig. 2(b) the bond CO from the methanol molecule increases as the distance CH gets lower, towards the formation of CH₄. Lastly, in Fig. 2(c), again the CO bond distance of

CH₃OH gets higher as the hydroxyl group bonds with the hydrogen reactant, reducing the HO distance, to form H₂O.

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

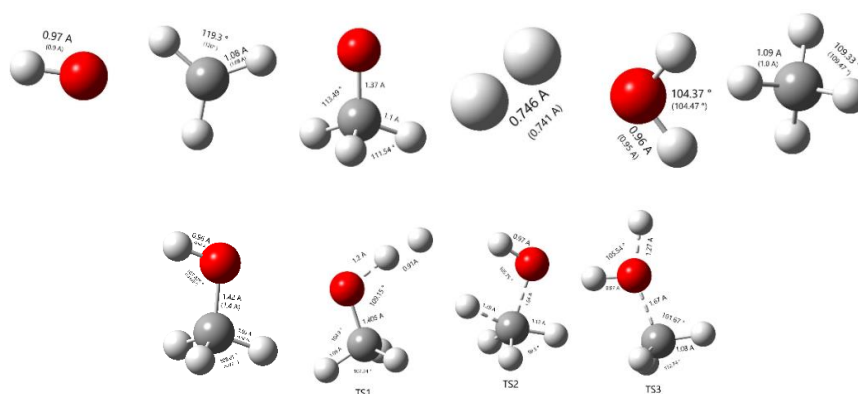


Figure 1: Optimized geometries

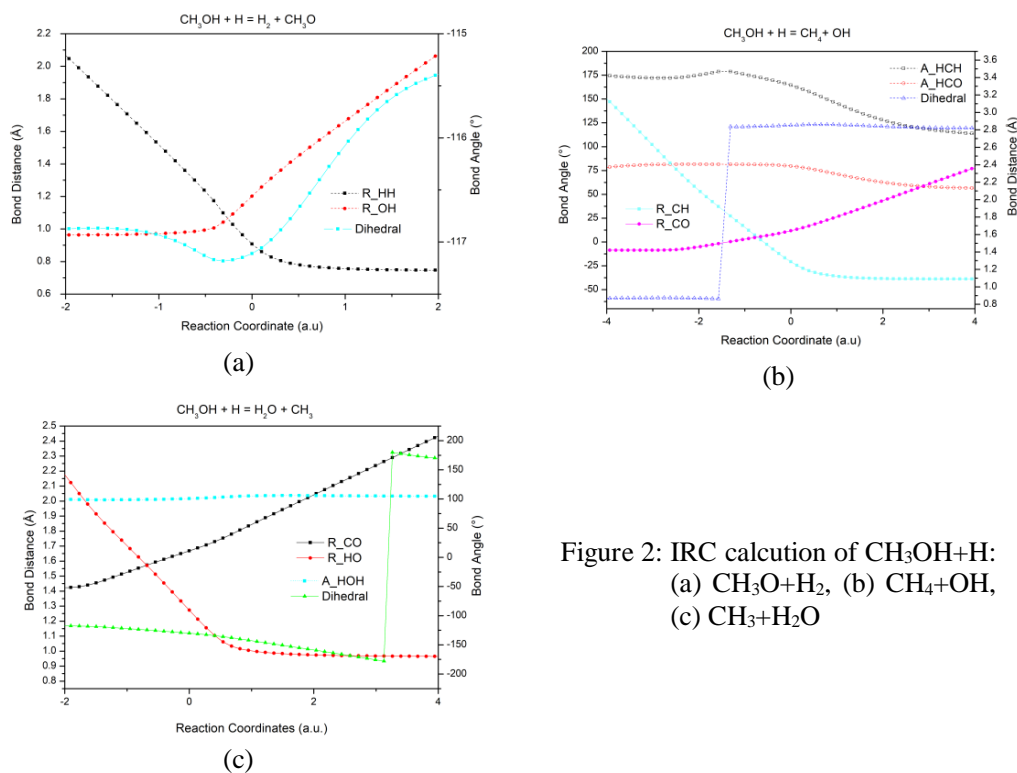


Figure 2: IRC calculation of CH₃OH+H: (a) CH₃O+H₂, (b) CH₄+OH, (c) CH₃+H₂O

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 CH₃OH+ 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 cm³ s⁻¹ mol⁻¹, and the activation energy in kcal mol⁻¹.

Acknowledgements

I'm thankful to CNPq/PIBIC for the financial support to the realization of this research.

References

- [1] Kelvin H. Bates et. Al. The Global Budget of Atmospheric Methanol: New Constraints on Secondary, Oceanic and Terrestrial sources. 2021.
- [2] Daniel J. Jacob, et. Al. The Global Budget of Atmospheric Methanol: Constraints from atmospheric observations. 2005.
- [3] M. J. Frisch, et. Al. Gaussian 09, Revision A.02-SMP. 2016. Gaussian.
- [4] Euclides HO, Barreto PRP (2017) J Mol Model 23:176
- [5] <http://cccbdb.nist.gov/>
- [6] K. Raghavachari et. Al. Chem Phys. Lett. 157 (1989) 479.
- [7] Warnatz, J. Rate coefficients in the C/H/O system. Combustion Chemistry. 1984.
- [8] Meana-Paneda, R et. Al. High-level direct-dynamics variational transition state theory calculations including multidimensional tunneling of the thermal rate constants, branching ratios, and kinetic isotope effects of the hydrogen abstraction reactions from methanol by atomic hydrogen. J. Chem Phys. 2011.
- [9] Jodkowski, J. et. Al. Theoretical Study of the Kinetics of the Hydrogen Abstraction from Methanol. 3. Reaction of Methanol with Hydrogen Atom, Methyl, and Hydroxyl Radicals. J. Phys. Chem. A. 1999.
- [10] Hidaka, Y. et. Al. Thermal decomposition of methanol in shock waves. J. Phys. Chem. 93. 1989.
- [11] Aronowitz, D. et. Al. Kinetics of the pyrolysis of methanol. J. Phys. Chem. 81. 1977

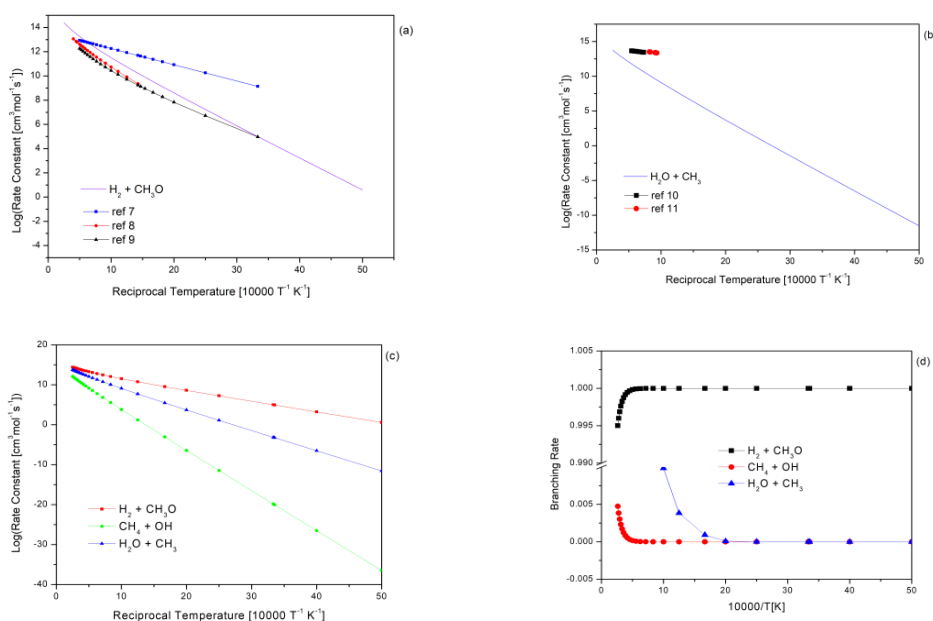


Figura 4: (a) rate constant for CH₃OH + H = CH₃O + H₂ [7-9], (b) rate constant for CH₃OH + H = CH₃ + H₂O [10-11], (c) rate constant for CH₃OH + H=products (d) branching rate for CH₃OH + H = products.