

Modeling combustions: the $O(^3P) + CH_3OH$ reaction

L. Pacifici¹, F. Talotta¹, N. Balucani¹ and A. Laganà¹

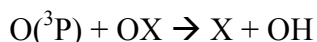
1. Department of Chemistry, Biology and Biotechnologies, University of Perugia, via elce di sotto, 8 06125 Perugia

Among bio-alcohols, methanol is considered a very promising alternative fuel: in fact, it can be used in modern internal combustion engines as well as in fuel cells thanks to a catalytic electrolytic chemical process. In the last years, several experiments and theoretical calculations [1,2] were carried out in order to evaluate its combustion properties, such as those important for the environment: heat release, CO_2 emission and efficiency as fuel. Moreover, the oxidation of methanol represents a challenge from a theoretical point of view due to the fact that the system is too large for applying a full quantum treatment but too small to build a semi empirical ab initio potential energy surface (PES) to be used in quantum reactive scattering calculations. It is a matter of fact that most of the previous studies on the oxidation of methanol do not make use of quantum dynamics techniques. Therefore, this preliminary work on the title reaction focuses on the assemblage of a suitable PES on which quantum calculations are being carried out in order to work out dynamical observables to be compared with existing experimental information.

The methanol oxidation proceeds via many elementary reactions. The most important are listed below:

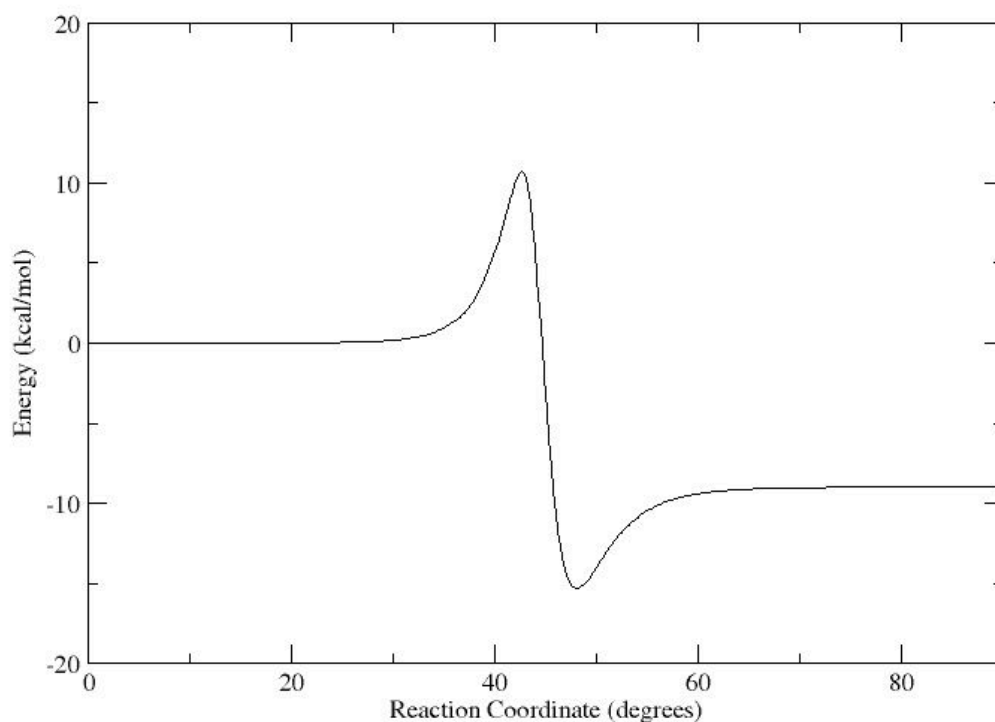
- 1- $O(^3P) + CH_3OH \rightarrow CH_3O + OH$
- 2- $O(^3P) + CH_3OH \rightarrow CH_2OH + OH$
- 3- $O(^3P) + CH_3OH \rightarrow HO_2 + CH_3$

In order to build the PES we focus on channel 2, because it is characterized by a small reaction barrier (7.6 Kcal/mol [1]) and it is about ~ 7 Kcal/mol exoergic [1]. Moreover, we consider the CH_2OH fragment as a single body, hereinafter called X. In this way the reaction becomes



with X having a mass equal to the sum of the constituent atoms. The PES is formulated as a LEPS semiempirical functional form [3]. For the purpose of optimizing the LEPS parameters, we first carried out DFT calculations in order to characterize the stationary points (reactants, transition state and products) and to work out harmonic vibrational frequencies in order to check the nature of the stationary points. Calculated frequencies are also used to determine diatomic curves. The energy of the stationary points was refined at the CCSD(T) level of theory and calculated values were used as estimates of the exoergicity of the considered channel and of the barrier to reaction. This allows us to estimate the optimum Sato parameters. The Minimum Energy Path (MEP) of the reaction is shown in Fig. 1.

The MEP singles out a barrier to reaction of about 10 Kcal/mol, followed by a relatively small well of 15.4 Kcal/mol. The ΔH_{298}^0 is -9.01 Kcal/mol.



On such LEPS PES we have started quantum reactive scattering calculations of the state specific probabilities using both the MCTDH (Multi Configurational Time Dependent Hartree) method and the Time Independent one. By running calculations at different values of the total angular momentum we shall calculate the thermal rate coefficient of the process for improving the data base used by combustion simulations.

REFERENCES

- [1] M. M. Alves, E. F. V. Carvalho, F. B. C. Machado, O. Roberto-Neto, Int. Journal of Quantum Chemistry, **110**, 2037 (2010)
- [2] Chih-Wei Lu, Shen-Long Chou, Yuan-Pern Lee, Shucheng Xu, Z. F. Xu, and M. C. Lin, J. Chem. Phys. **122**, 244314 (2005)
- [3] S. Sato, J. Chem. Phys. **23**, 592 (1955); S. Sato, J. Chem. Phys. **23**, 2465 (1955)