

HO + CH₄: *ab initio* Rate Constants and Kinetic Isotope Effects from Semi-Classical Transition State Theory and HEAT

Mohamad Akbar Ali,¹ J. A. Sonk,¹ C. G. L. Li,¹ J. R. Barker^{1,*}, T. L. Nguyen,² and J. F. Stanton,²

¹ Climate and Space Science & Engineering, University of Michigan, Ann Arbor, MI, USA

² Department of Chemistry and Biochemistry, The University of Texas, Austin, TX, USA

* Corresponding author: jrbarker@umich.edu

Calculations were performed for a number of isotopologues of the title reaction with various combinations of ¹⁶O, H, D, ¹²C, ¹³C, and ¹⁴C. The computed rate constants are based on harmonic vibrational frequencies and X_{ij} vibrational anharmonicity coefficients calculated at the CCSD(T)/aug-cc-pcVTZ level of theory. The reaction thermochemistry was calculated using the high accuracy extrapolated *ab initio* thermochemistry protocol (HEAT-345Q),¹ which includes a very high level treatment of electron correlation effects, extending up to CCSDT(Q). In addition, other small corrections are made, including the anharmonic zero-point vibrational energy, a scalar relativistic correction, first-order spin-orbit effects, and the diagonal Born-Oppenheimer correction. Rate constants were calculated using Semi-Classical Transition State Theory (SCTST), which was originally formulated by W. H. Miller and colleagues.² SCTST includes non-separable coupling among all vibrational degrees of freedom and multi-dimensional quantum mechanical tunneling along the curved reaction path in hyperspace. It has been used with good success on a number of reaction systems.³ In this presentation, we will describe our implementation⁴ of SCTST and how the calculations were performed using modules in the MultiWell Program Suite.⁵ In the present work, the hindered internal rotation was treated as separable. We will compare the computed rate constants and kinetic isotope effects with experimental data and other theories, and then discuss the implications of our results.

References

1. (a) Tajti, A.; Szalay, P. G.; Csaszar, A. G.; Kallay, M.; Gauss, J.; Valeev, E. F.; Flowers, B. A.; Vazquez, J.; Stanton, J. F., *J. Chem. Phys.* **2004**, *121* (23), 11599-11613; (b) Bomble, Y. J.; Vazquez, J.; Kallay, M.; Michauk, C.; Szalay, P. G.; Csaszar, A. G.; Gauss, J.; Stanton, J. F., *J. Chem. Phys.* **2006**, *125*, 064108; (c) Harding, M. E.; Vazquez, J.; Ruscic, B.; Wilson, A. K.; Gauss, J.; Stanton, J. F., *J. Chem. Phys.* **2008**, *128*, 114111.
2. (a) Miller, W. H., *J. Chem. Phys.* **1975**, *62*, 1899-1906; (b) Miller, W. H., Semi-Classical *Faraday Discuss. Chem. Soc.* **1977**, *62*, 40-46; (c) Miller, W. H.; Hernandez, R.; Handy, N. C.; Jayatilaka, D.; Willets, A., *Chem. Phys. Letters* **1990**, *172*, 62-68; (d) Hernandez, R.; Miller, W. H., *Chem. Phys. Lett.* **1993**, *214* (2), 129-136.
3. Nguyen, T. L.; Barker, J. R.; Stanton, J. F., Atmospheric Reaction Rate Constants and Kinetic Isotope Effects Computed Using the HEAT Protocol and Semi-Classical Transition State Theory. In *Advances in Atmospheric Chemistry*, Barker, J. R.; Steiner, A. E.; Wallington, T. J., Eds. World Scientific: Singapore, 2016; Vol. 1 (In Press).
4. (a) Nguyen, T. L.; Stanton, J. F.; Barker, J. R., *Chem. Phys. Letters* **2010**, *499*, 9-15; (b) Nguyen, T. L.; Stanton, J. F.; Barker, J. R., *J. Phys. Chem. A* **2011**, *115*, 5118-5126.
5. Barker, J. R.; Nguyen, T. L.; Stanton, J. F.; Aieta, C.; Ceotto, M.; Gabas, F.; Kumar, T. J. D.; Li, C. G. L.; Lohr, L. L.; Maranzana, A.; Ortiz, N. F.; Preses, J. M.; Stimac, P. J. *MultiWell-2016 Software Suite*, University of Michigan: Ann Arbor, Michigan, USA, 2016.