Modeling the thermal decomposition of methyl acetate: a study in combustion

James H. Thorpe[1], Thanh Lam Nguyen[1], G. Barney Ellison[2], John F. Stanton[1]

[1]*University of Florida, Quantum Theory Project, Gainesville, FL, 32611 (USA).*

[2]*University of Colorado, Department of Chemistry & Biochemistry, Boulder, CO, 80309 (USA)*

In this work, we have modeled the pyrolysis of methyl acetate, CH_3COOCH_3, as a prototype for fatty-acid combustion. We previously studied this molecule in the context of the experimental work of Porterfield *et al.* [1], and now focus on a high-level kinetics analysis of the chemically significant pathways discussed in that paper.

The potential energy surface of this decomposition features loose transition states, products with complicated electronic structures, and competing pathways. To meet these challenges we employed the mHEAT protocol, which yields heats of formation to within ± 2 kJ/mol and has successfully described gas phase reactions before [2]. We then used a two-dimensional master equation program (TDME) to explore the product branching ratios and rate coefficients of this system at temperatures of 1000-2000 K and pressures of 0.1-100 atm.

Our predicted primary products are CH_3OH and CH_2CO formed via two competing pathways, with $2CH_3$ and CO_2 as significant, but temperature dependent, secondary products that result from the decomposition of CH_3 and CH_3CO_2/CH_3OCO. Additionally, we see negligibly small quantities of CH_2O and CH_3CHO. Our analysis is consistent with the experimental results [1]. Interestingly, the formation of methanol and ketene defies the usual intuition and proceeds via a non-minimum route due to sum of states differences between the competing transition states, validating the use of high-level analysis.

[1] J. P. Porterfield, D. H Bross, B. Russic, J. H. Thorpe, T. L. Nguyen, J. H. Baraban, J. F. Stanton, J. W. Daily, G. B. Ellision, *J. Phys. Chem. A*, **121**, 4658-4677 (2016).

[2] T. L. Nguyen, L. McCaslin, M. C. Carthy, J. F. Stanton, *J. Chem. Phys.*, **145**, 131102 (2016).