

Novel Reactions in Low Temperature Hydrocarbon Oxidation: A High-Level Computational Investigation of the Kinetics and Thermochemistry of 2-Formyl Ethylhydroperoxide

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The reactions of peroxy radicals derived from fuels comprise a class of important but technically challenging reactions in fuel chemistry. The quantitative understanding of these reactions is essential for accurately modeling and predicting the chemistry that occurs in combustion engines; however, because of the experimental limitations associated with generating and detecting these species and the theoretical challenges with modeling the strongly coupled torsions they possess, the kinetics and thermochemistry of these complex reaction systems is largely unknown. Ketohydroperoxides (HOOQ=O) have long been proposed as important intermediates in low temperature hydrocarbon oxidation.¹ Recent gas phase experiments² have corroborated the formation of ketohydroperoxide in low temperature oxidation; however, the formation of products which cannot be readily explained by existing pathways—such as carboxylic acids, ketones, aldehydes, and diketones—was also observed.

Based on evidence obtained over thirty years ago in liquid phase oxidation experiments, we have recently discovered new pathways that lead to the formation of acids and carbonyl compounds starting from the HOOQ=O species. In this work, high-level CCSD(T)-F12/VTZ-F12//M06-2X/MG3S quantum chemistry calculations have been employed to characterize the stationary points along the new reaction pathways using 2-formyl ethylhydroperoxide as a prototypical compound. Conformationally-averaged partition functions for all species were computed using the MS-T method⁴ which also accounts for torsional anharmonicity. These were integrated with transition state theory and asymmetric Eckart tunneling coefficients to explore the kinetics of the new reactions. Calculations with other more affordable electronic structure methods were performed to test their applicability in studying similar reactions for larger systems. Results from this effort offer insight into the energetics of the new reactions and on the choice of model chemistry to capture the dominant effects. A more comprehensive study of the newly discovered reaction classes is in progress and will be useful in low temperature oxidation models relevant to combustion, atmospheric and autoxidation chemistry.

References

- (1) Zádor, J.; Taatjes, C. A.; Fernandes, R. X. *Progress in Energy and Combustion Science* **2011**, *37*, 371.
- (2) Herbinet, O.; Battin-Leclerc, F.; Bax, S.; Gall, H. L.; Glaude, P.-A.; Fournet, R.; Zhou, Z.; Deng, L.; Guo, H.; Xie, M.; Qi, F. *Physical Chemistry Chemical Physics* **2011**, *13*.
- (3) Jensen, R. K.; Korcek, S.; Mahoney, L. R.; Zinbo, M. *Journal of the American Chemical Society* **1981**, *103*, 1742.
- (4) Zheng, J.; Yu, T.; Papajak, E.; Alecu, I. M.; Mielke, S. L.; Truhlar, D. G. *Physical Chemistry Chemical Physics* **2011**, *13*.