Oxidation of Alpha-Pinene initiated by O(³P) and analyzed via Synchrotron Photoionization

Ryan Rodriguez and Giovanni Meloni*

*Department of Chemistry, University of San Francisco, CA, 94117

Abstract

Alpha-pinene oxidation is initiated via photolytically generated atomic oxygen O(³P) under 4 torr pressure at two temperatures (550 and 750K). Reaction products are analyzed using multiplexed photoionization mass spectrometry. Vacuum ultraviolet synchrotron radiation is generated at the Advanced Light Source at the Lawrence Berkeley National Laboratory. Kinetic time traces are used to identify primary products, which are then characterized by comparing the experimental photoionization spectra to literature and/or simulated spectra. Calculations using the CBS-QB3 composite method suggest oxygen addition is the favorable pathway vs hydrogen abstraction, agreeing with experimental data. Three products have been identified with branching fractions labeled (550 K, 750 K): 42 ketene (0.27%, 3.36%), 56 methyl ketene (1.21%, 2.84%), and 70 methyl vinyl ketone (7.71%, 11.3%). Increased fractions indicate access to higher energy pathways, Potential energy scans of the singlet and triplet energy surfaces are underway to verify these pathways.
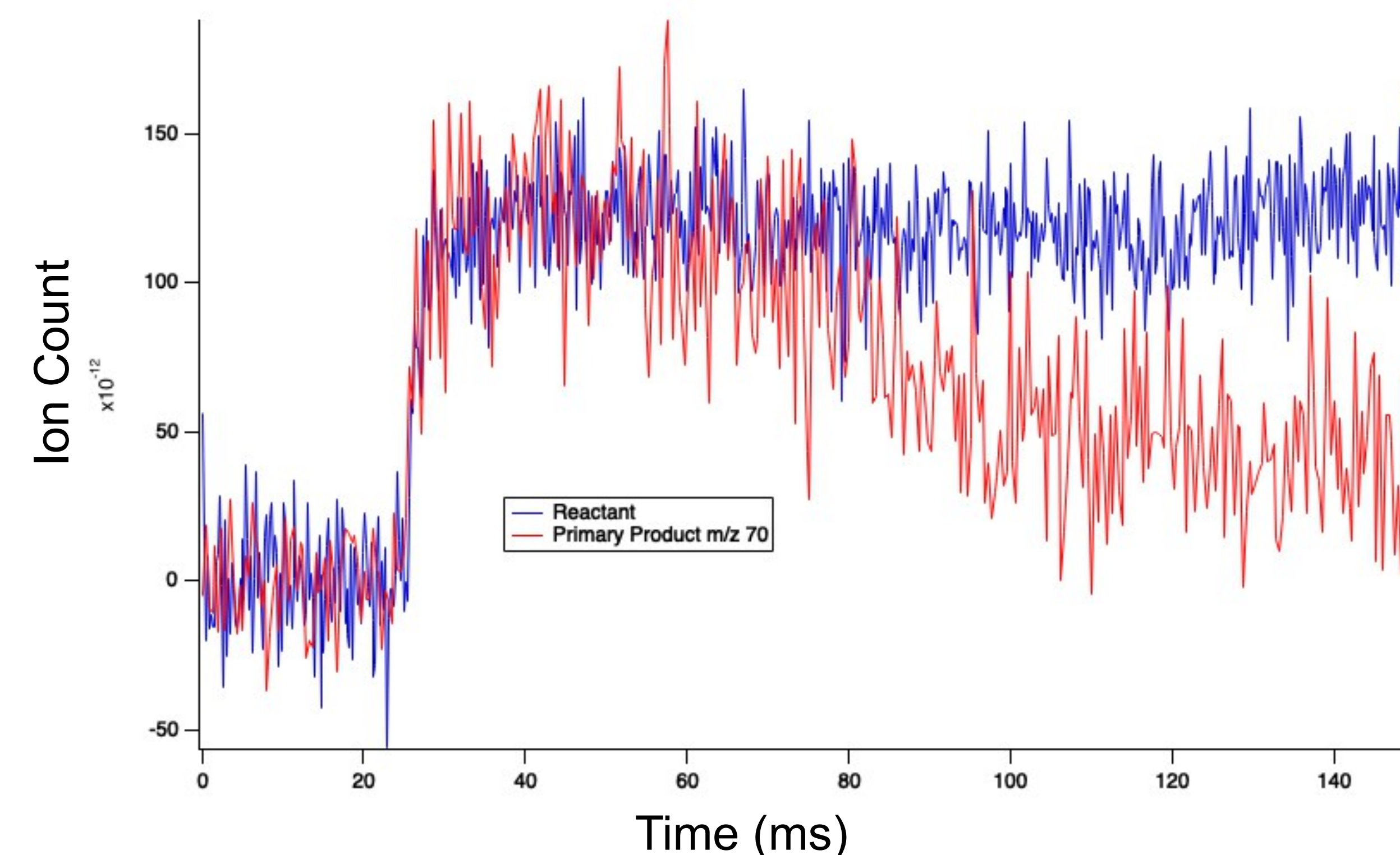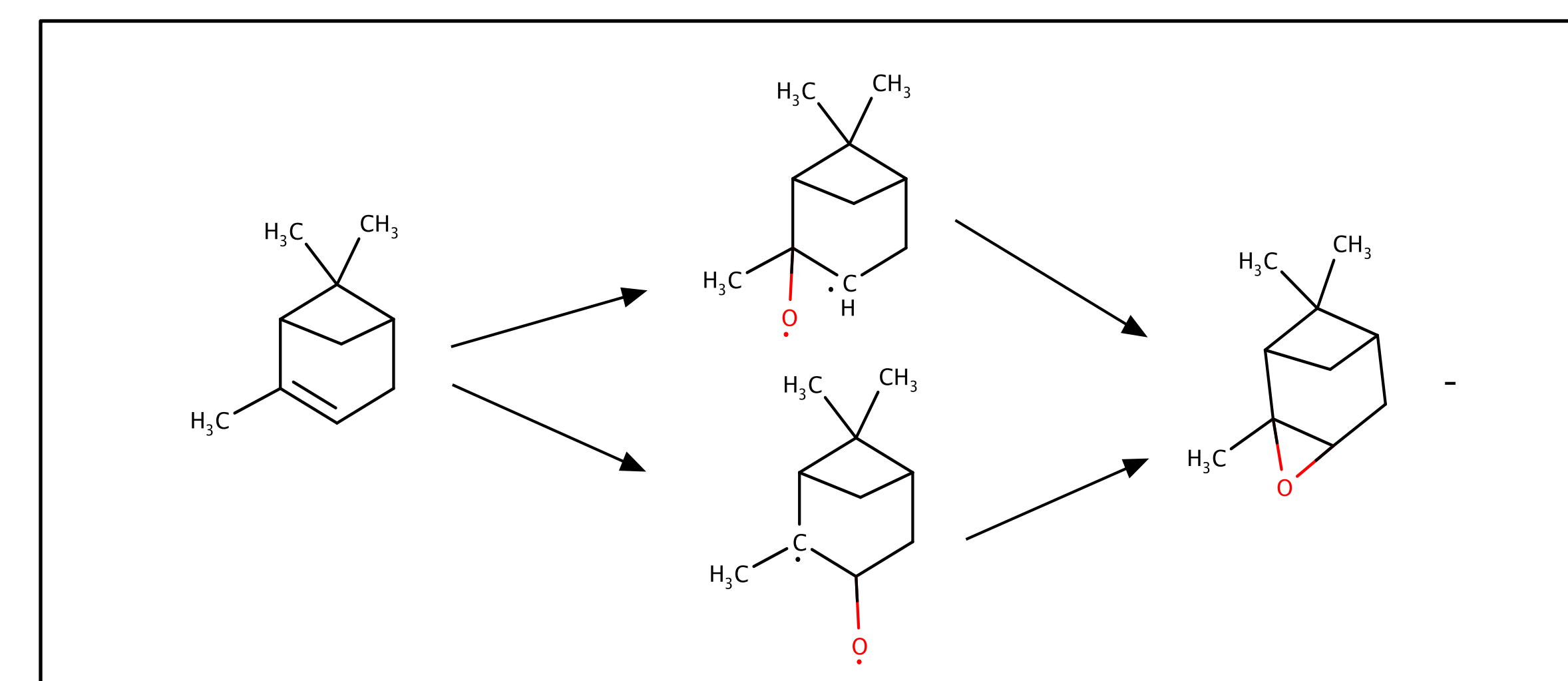
Introduction

Energy consumption is the driving force of the economy and permeates all aspects of human life. In the United States alone, fossil fuels account for 80% of total energy consumption, releasing massive amounts of carbon dioxide into the environment each year. Global energy demand is expected to increase by 47% from 2018 to 2050, straining nonrenewable stores of fossil fuels[1]. Fossil fuel burning is associated with anthropogenic global warning that has implications ranging from rising sea levels, worsening natural disasters, and ecosystem collapse [2-4]. Advances in biofuel research is proving to be a viable source of renewable fuel that could help curb greenhouse gas emissions and provide a secure source of energy for the future.

Alpha-pinene, a terpene derived from pine trees, meets many of the physical properties needed for engines; such as Ignition intensity, gravimetric density, ignition time, and high-octane sensitivity[7]. The specific aims of this research are to determine the immediate products formed from α-pinene oxidation as well as calculate transition state energies between the reactant and primary products.
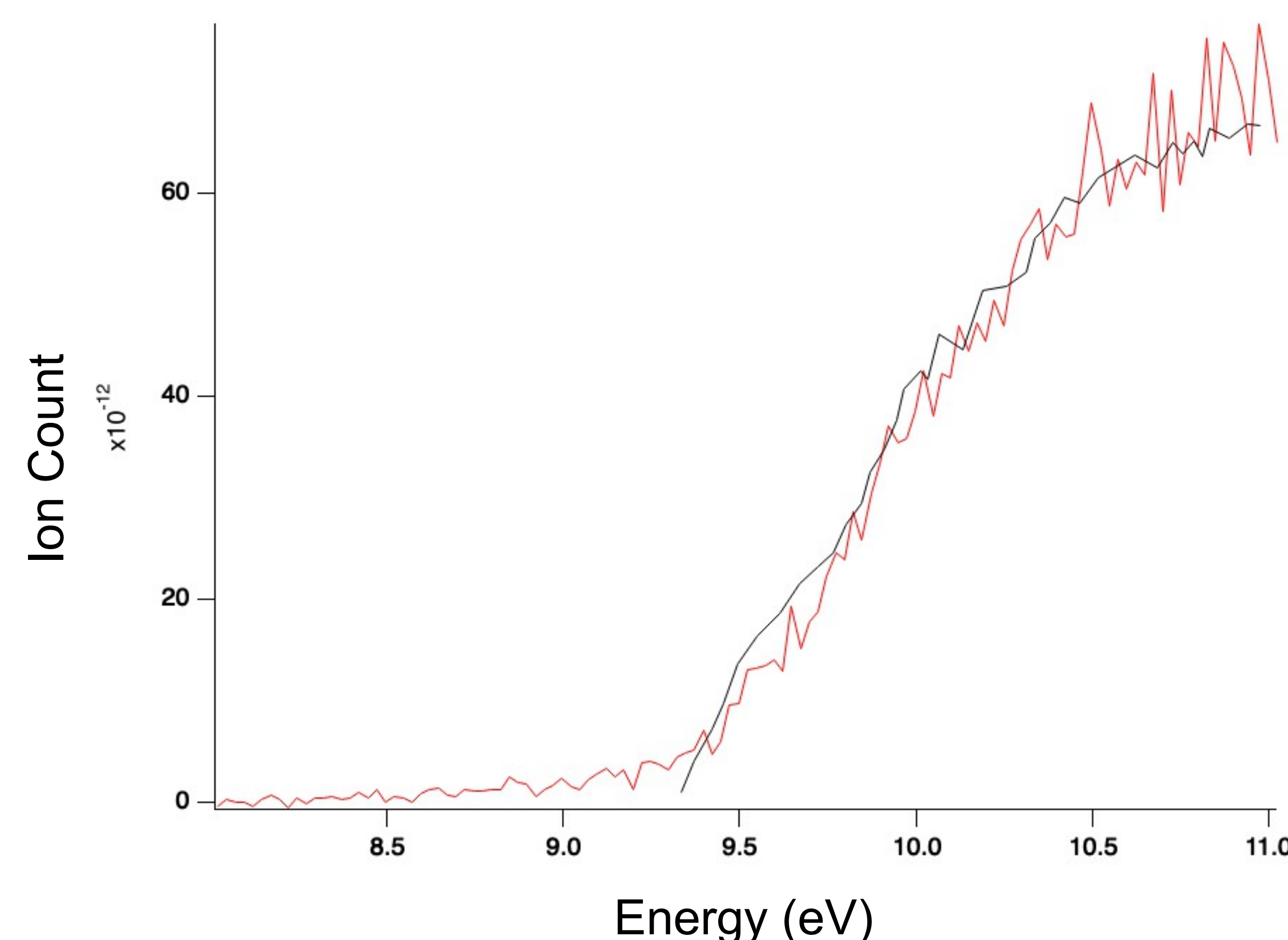

Figure 1: Inverse signal of parent mass (blue trace) appended to a primary product (m/z 70). Parent mass and product mass have identical onset and depletion. Indicating primary products.

Figure 2: Example of a photoionization spectra matching a literature spectra. Structure above is 3-penten-2-one (m/z) 84.

Scheme 1: Using the composite CBSQB3 composite method indicates that oxygen addition is lower than energy than hydrogen abstraction. All products are seen form the oxygen addition pathway.
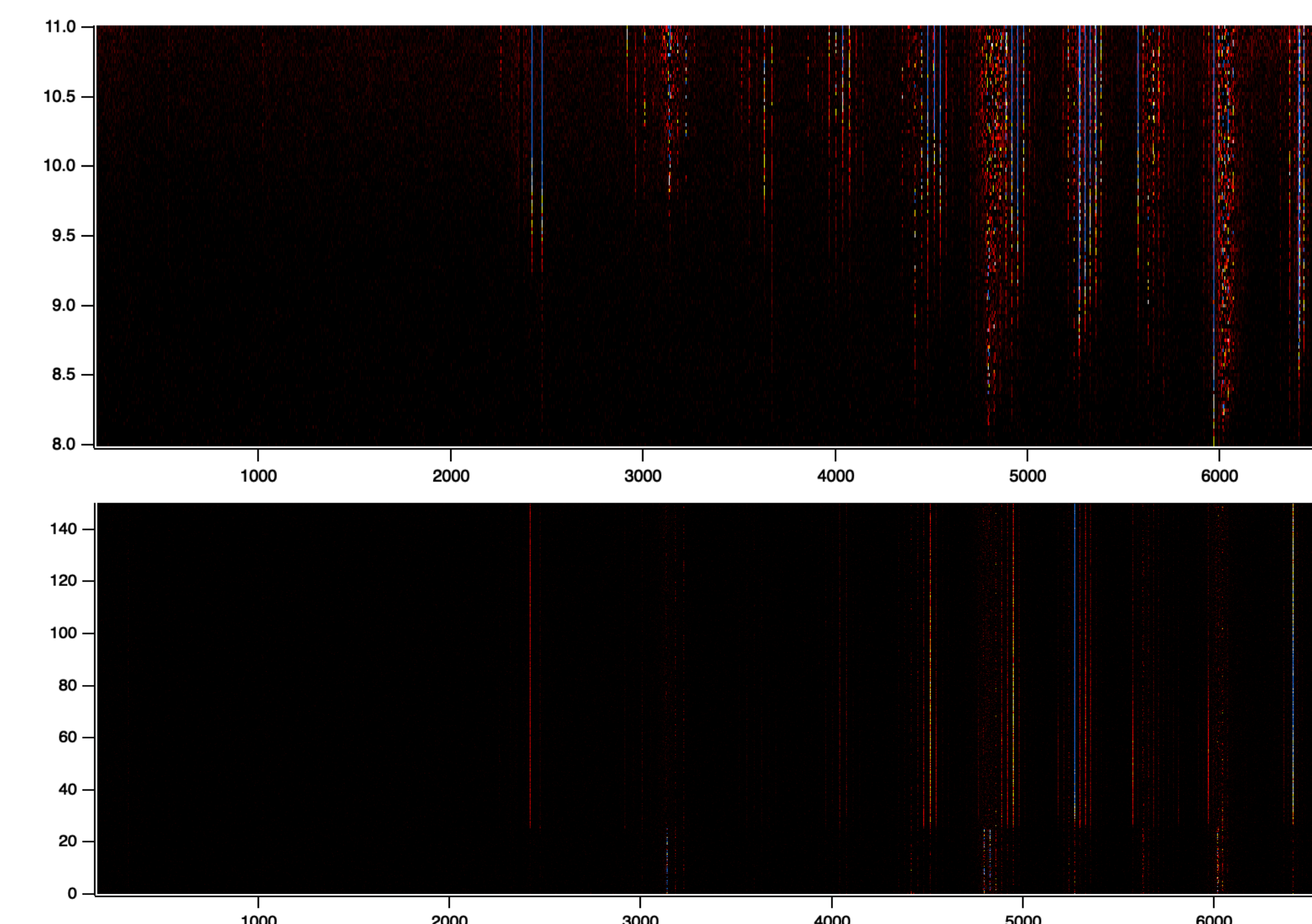

Figure 3: Top Graph: Mass spectrum as a function of photon energy shows what energy products appear. Bottom chart: Shows Kinetic traces as a function of mass. Strong signals at the beginning of the reaction indicate primary products

Methodology

All experimental work was conducted at the Advanced Light Source at the Lawrence Berkeley National Laboratory. The reaction was analyzed via Multiplexed time and energy resolved mass spectrometry. Resultant data comes in a three-dimensional block with the mass to charge ratio (m/z), time (ms), and energy (eV) along each axis. By fixing one variable, the data is able to be analyzed two dimensionally. A 2-D slice of Time vs mass axis gives kinetic traces of product formation and reagent depletion. Primary products are identified by matching the product formation time trace to the inverse of the reactant depletion trace. The energy vs mass axis gives a photoionization spectrum that can be compared to literature or simulated spectra to identify products.

Branching rations were determined using the following equation:

$$Cp/Cr = (\delta p(e)(\varsigma r(e)/(\delta r(e)\varsigma p(e)) * MDF$$

Where $\delta p, r(e)$ are signal intensities of the product and reactant at a given energy, respectively. $\varsigma p, r(e)$ are the photoionization cross sections at that given energy. he mass- dependent response is a signal correction factor and is approximately equal to the mass (m) of the identified species to the power of 0.67.

Energy calculations are conducted using the CBSQB3 composite model to determine absolute energies of reacting spaces and later for transition state calculations.

Conclusions

Photoionization mass spectrometry has proven to be a powerful tool in identifying intermediates in gas phase oxidation reactions. Kinetic time traces allow for analysis of priory products while photoionization spectra serve characterization purposes.

Acknowledgements

References

1. U.S. Energy Information Administration - EIA - Independent Statistics and Analysis. https://www.eia.gov/outlooks/ieo/ (accessed Apr 2, 2020)
2. Philip L. Munday, Mark I. McCormick, Göran E. Nilsson Journal of Experimental Biology **2012** 215: 3865-3873
3. Mousavi, M.E., Irish, J.L., Frey, A.E. et al. Global warming and hurricanes: the potential impact of hurricane intensification and sea level rise on coastal flooding. Climatic Change 104, 575–597 (**2011**).
4. Cerri, C. E. P.; Sparovek, G.; Bernoux, M.; Easterling, W. E.; Melillo, J. M.; Cerri, C. C. Tropical Agriculture and Global Warming: Impacts and Mitigation Options. Scientia Agricola **2007**, 64 (1), 83–99.