

## Kinetics and product branching ratio of the ethyl peroxy self-reaction

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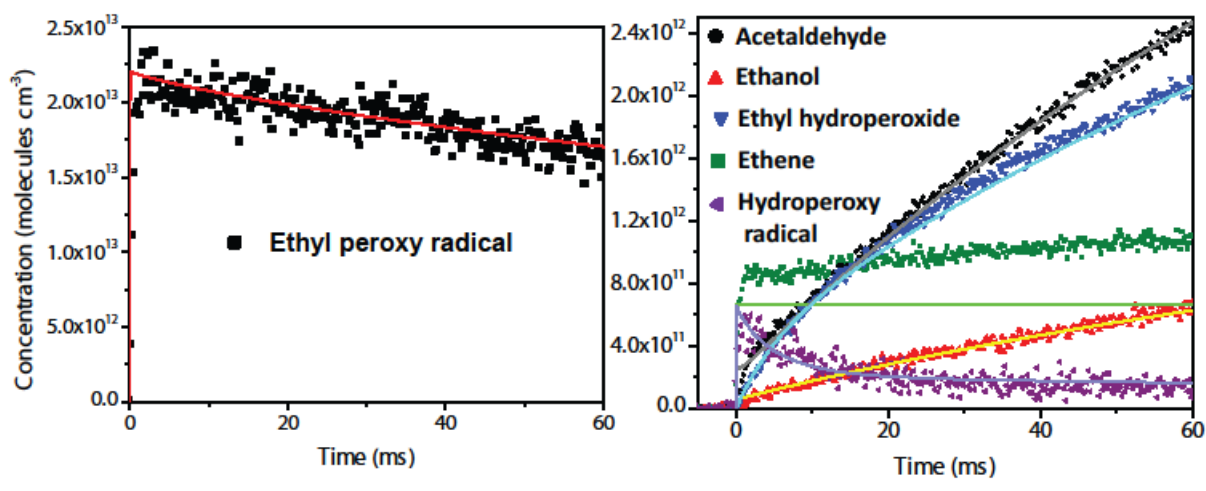
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Peroxy radicals (RO<sub>2</sub>) are key intermediates in the reaction pathways of the oxidation of volatile organic carbon (VOCs) in the troposphere. RO<sub>2</sub> self- and cross-reactions can have two product channels, one forming reactive alkoxy radicals and another forming stable products (aldehydes and ketones), as well as suggestions that peroxides ROOR may be formed. These reactions are thought to proceed through tetroxide intermediates, but the mechanisms remain uncertain. In the atmosphere and in laboratory experiments, the radical channel can lead to secondary production of HO<sub>2</sub>, further complicating kinetics measurements. We recently investigated the product branching ratio of the ethyl peroxy self-reaction using the NASA Jet Propulsion Laboratory Infrared Kinetics Spectroscopy experiment and found substantially lower radical yields than indicated from end product studies. Here we report new results on the kinetics and product yields of the ethyl peroxy radical reaction using the Sandia Combustion Research Facility multiplexed photoionization mass spectrometry apparatus. These experiments use VUV light from synchrotron radiation from the Advanced Light Source (ALS) at the Lawrence Berkeley National Laboratory. This technique has allowed us to observe the concentration of the reactants, reactive intermediates, and end products in real time. In addition to kinetics and product branching ratios, we have determined the photoionization cross sections of HO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> and a lower bound for the rate constant of the reaction of ethyl peroxy and ethoxy radicals.



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Figure 1. Time traces of reactants, radical intermediates and products of the ethyl peroxy self-reaction.