

Abstract Submitted  
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**Direct Measurement of the Unimolecular Decay Rate of Criegee Intermediates to OH Products.**<sup>1</sup> FANG LIU, YI FANG, University of Pennsylvania, STEPHEN KLIPPENSTEIN, Argonne National Laboratory, ANNE MCCOY, University of Washington Seattle, MARSHA LESTER, University of Pennsylvania — Ozonolysis of alkenes is an important non-photolytic source of OH radicals in the troposphere. The production of OH radicals proceeds through formation and unimolecular decay of Criegee intermediates such as syn-CH<sub>3</sub>CHOO and (CH<sub>3</sub>)<sub>2</sub>COO. These alkyl-substituted Criegee intermediates can undergo a 1,4-H transfer reaction to form an energized vinyl hydroperoxide species, which breaks apart to OH and vinyloxy products. Recently, this laboratory used IR excitation in the C-H stretch overtone region to initiate the unimolecular decay of syn-CH<sub>3</sub>CHOO and (CH<sub>3</sub>)<sub>2</sub>COO Criegee intermediates, leading to OH formation. Here, direct time-domain measurements are performed to observe the rate of appearance of OH products under collision-free conditions utilizing UV laser-induced fluorescence for detection. The experimental rates are in excellent agreement with statistical RRKM calculations using barrier heights predicted from high-level electronic structure calculations. Accurate determination of the rates and barrier heights for unimolecular decay of Criegee intermediates is essential for modeling the kinetics of alkene ozonolysis reactions, a significant OH radical source in atmospheric chemistry, as well as the steady-state concentration of Criegee intermediates in the atmosphere.

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