Simultaneous Kinetics and Ringdown Study of Peroxy Radical Reactions

<u>Matthew D. Smarte</u>, Leah G. Dodson, Mitchio Okumura Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California

Peroxy radicals are key intermediates formed in the low temperature combustion and atmospheric oxidation of volatile organic compounds. Over the past decade, spectroscopic and kinetic investigations have increasingly employed near-infrared cavity ringdown spectroscopy to detect these radicals through their forbidden A-X electronic transition. Absorption features associated with distinct organic peroxy radicals exhibit greater spectral isolation in the near-infrared than their more traditional detection in the ultraviolet, thereby aiding the interpretation of time-resolved absorption signals for kinetic studies. In this work, we use near-infrared pulsed cavity ringdown spectroscopy and the Simultaneous Kinetics and Ringdown (SKaR) technique to study the production and decay of organic peroxy radicals. The SKaR technique (S.S. Brown, A.R. Ravishankara, and H. Stark, J. Phys. Chem. A, 2000, 104, 7044-7052) was developed as a way to measure a reaction rate that occurs on the same timescale as a ringdown event. We employ this method and report rate constants for the formation $(R + O_2 \rightarrow RO_2)$ of organic peroxy radicals and their principle loss reaction in polluted environments ($RO_2 + NO \rightarrow products$). We present progress toward measuring these rate constants for the peroxy radicals formed in the OH and Cl initiated oxidation of ethene, propene, 1-butene, 2-butene, 1,3-butadiene, and isoprene.