NEAR-IR CWCRD SPECTROSCOPIC AND KINETIC STUDIES OF SIMPLE ALKYL PEROXY RADICALS

DEAN B. ATKINSON, and JENNIFER L. SPILLMAN, *Department of Chemistry, Portland State University, Portland, OR 97207-0751*.

The near-infrared spectra of the simple alkyl peroxy radicals: methyl peroxy, ethyl peroxy, and isopropyl peroxy have been examined as a function of temperature (300 - 400 K) and pressure (20 to 200 torr). These measurements were carried out in a kinetic reactor system which uses pulsed laser photolysis and continuous laser excitation cavity ring-down spectroscopy (CWCRD) to produce and follow the peroxy radicals in time. Significant spectral broadening is observed at elevated temperatures for all three radicals, which has negative implications for simple kinetic study. Careful investigation of the room temperature kinetics of the self-reactions of the radicals revealed an unexpected first-order component to the radical decay. Possible explanations for and the possible atmospheric implications of this last finding will be presented.