CAVITY RINGDOWN SPECTROSCOPY AND KINETICS OF BUTOXY ISOMERIZATION: DETECTION OF THE Ã-X̃ BAND OF HOC_4H_8OO

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Alkoxy radicals are atmospherically important species, playing a direct role in the HO_x and NO_x cycles that affect tropospheric air pollution. Alkoxy radicals that can form a six membered transition state can isomerize into a hydroxyalkyl radical. In the presence of O_2, a rapid association reaction occurs, forming a hydroxyalkylperoxy radical. The *n*-butoxy radical is the smallest alkoxy to undergo isomerization, forming the γ-hydroxybutylperoxy radical (HOC_4H_8OO). Direct detection of HOC_4H_8OO opens the door to measuring alkoxy reaction kinetics with higher precision than previous end product studies.[b]

In this talk, we report the first detection of the Ã-X̃ electronic spectrum of the HOC_4H_8OO radical. The spectrum is similar in shape to the Ã-X̃ spectrum of *n*-butyl peroxy:[c] a broad spectroscopic band due to the multiple molecular conformers that are present. We also use the Ã-X̃ band to measure the alkoxy isomerization kinetics relative to the alkoxy radical's reaction with O_2, similar to the previous kinetics studies.

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[b]R. Atkinson, D. L. Baulch, R. A. Cox, J. N. Crowley, R. F. Hampson, R. G. Hynes, M. E. Jenkin, M. J. Rossi, and J. Troe *J. Atmos. Chem. and Phys.* **2006**, *6*, 3625.

[c]B. G. Glover and T. A. Miller. *J. Phys. Chem. A* **2005**, *109*, 11191.