SPECTROSCOPIC CHARACTERIZATION OF AN ALKYL-SUBSTITUTED CRIEGEE INTERMEDIATE CH_3CHOO AND ITS OH RADICAL PRODUCTS

JOSEPH M. BEAMES, FANG LIU, LU LU and MARSHA I. LESTER, *Department of Chemsitry, University of Pennsylvania, Philadelphia, PA 19104-6323.*

In the atmosphere, cycloaddition of ozone to the double bond of alkenes produces energized Criegee intermediates, which undergo subsequent decay processes to yield OH radicals. In this laboratory, a simple alkyl-substituted Criegee intermediate CH_3CHOO is produced by 248 nm photolysis of CH_3CHI_2 and subsequent reaction of CH_3CHI with O_2 in a quartz capillary tube reactor, following the same approach utilized for CH_2OO.[a] The CH_3CHOO intermediate (m/z=60) and other products are detected following supersonic expansion using 118 nm VUV ionization in a time-of-flight mass spectrometer. The OH radical products from decomposition of the CH_3CHOO intermediate are also directly detected at m/z=17 using a new UV+VUV ionization scheme, combining UV excitation on the OH A $^2\Sigma^+$-X $^2\Pi$ (1,0) transition with fixed-frequency VUV at 118 nm,[b] or alternatively by UV laser-induced fluorescence on the OH A-X transition; OH products are also observed from CH_2OO. The CH_3CHOO intermediate is characterized by a strong B $^1A'$-X $^1A'$ electronic transition, in which UV excitation near the peak of a broad absorption profile centered at 320 nm results in significant depletion of the CH_3CHOO photoionization signal. The mechanism proposed for OH generation from energized CH_3CHOO and many larger Criegee intermediates is a 1,4 H-atom shift to form vinylhydroperoxide species that decay to produce OH. This reaction scheme provides a non-photolytic source of OH radicals in the atmosphere during night and winter times.

[a] J. M. Beames, F. Liu, L. Lu, and M. I. Lester, J. Am. Chem. Soc. **134**, 20045 (2012).
[b] J. M. Beames, F. Liu, M. I. Lester and C. Murray, J. Chem. Phys. **134**, 241102 (2011).