UV SPECTRUM AND PHOTOCHEMISTRY OF THE SIMPLEST CRIEGEE INTERMEDIATE CH_2OO

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In the troposphere, ozonolysis of ethene as well as other terminal alkenes, such as isoprene, results in formation of the simplest Criegee intermediate, CH_2OO, which gives rise to many products of atmospheric significance. In the laboratory, CH_2OO is prepared in a quartz capillary tube reactor using a new synthetic route[a] based on 248 nm photolysis of CH_2I_2 and subsequent reaction with O_2. The CH_2OO and other products undergo supersonic expansion, and are detected using fixed frequency VUV ionization (118 nm) with mass (m/z=46) and isomer selectivity. Spectroscopic studies of CH_2OO are carried out by UV laser excitation on the B $^1A'$-X $^1A'$ transition prior to photoionization, which results in significant depletion of the ion signal (approaching 100%) near the peak of a broad absorption profile centered at 335 nm.[b] The large depletion and broad absorption are indicative of rapid dissociation, consistent with the repulsive B $^1A'$ state potential in the O-O coordinate that has been computed theoretically. The experimental spectrum is in very good agreement with the absorption spectrum calculated using the one-dimensional reflection principle. The atmospheric lifetime of CH_2OO due to solar photolysis at midday is estimated to be $\sim$ 1 s. These findings provide a UV spectral signature of the strong π^*-π transition associated with the four π electrons on the carbonyl oxide group in CH_2OO. Extensions of this work to methyl substituted Criegee intermediates reveal similar absorption features arising from the COO π -system .

[a] O. Welz, J. D. Savee, D. L. Osborn, S. S. Vasu, C. J. Percival, D. E. Shallcross, and C. A. Taatjes, Science **335**, 204 (2012).
[b] J. M. Beames, F. Liu, L. Lu, and M. I. Lester, J. Am. Chem. Soc. **134**, 20045 (2012).