Infrared Absorption Spectrum of Hydroperoxymethyl Formate [$HC(O)OCH_2OOH$] Produced in the Reaction of the Criegee Intermediate CH_2OO with HCOOH

(Department of Applied Chemistry and Institute of Molecular Science, National Chiao Tung University, 1001, Ta-Hsueh Road, Hsinchu 30010, Taiwan [a]
Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan [b])
Jou-Wei Su[a], Chen-An Chung[a], and Yuan-Pern Lee[a,b]

The Criegee intermediates, which are carbonyl oxides produced in ozonolysis of unsaturated hydrocarbons,[1] play important roles in the production of OH, aerosols and organic acids in the atmosphere. Criegee intermediates react readily with other atmospheric species such as NO_2, SO_2, $(H_2O)_2$ and HCOOH. The reaction of CH_2OO with HCOOH was reported to be extremely rapid, with a rate coefficient of 1.1×10^{-10} cm^3 $molecule^{-1}$ s^{-1}.[2] Quantum-chemical calculations indicate that the reaction of CH_2OO + HCOOH proceeds through a barrierless association path to form hydroperoxymethyl formate (HPMF, $HC(O)OCH_2OOH$),[3] in agreement with experimental results by Neeb et al, who observed HPMF and formic acid anhydride (FAN, $(CHO)_2O$) in ozonolysis experiments; FAN and water was proposed to be produced from dissociation of HPMF.[4]

In this work, a step-scan Fourier-transform spectrometer coupled with a multipass absorption cell was employed to record temporally resolved infrared (IR) absorption spectra of the reactants and products during the reaction of CH_2OO with HCOOH in a flow system. CH_2OO were produced from the reaction of CH_2I with O_2, CH_2I was produced from photolysis of CH_2I_2.[5] Observed bands with origins at 887, 925, 1052, 1115, 1169.5, 1341.5, 1391 and 1760 cm^{-1} can be assigned to ν_{16}, ν_{15}, ν_{13}, ν_{12}, ν_{11}, ν_9, ν_7, and ν_5 modes of HPMF, respectively. The observed wavenumbers and relative intensities agree with the anharmonic vibrational wavenumbers and IR intensities predicted with the B3LYP/aug-cc-pVTZ method. Our results also show that the rate coefficient of the reaction CH_2OO + HCOOH is $(7\pm0.3)\times10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, smaller than the previously reported value.[2]

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