MECHANISM AND KINETICS OF THE REACTION OF CRIEGEE INTERMEDIATE CH_2OO WITH ACETIC ACID STUDIED WITH A STEP-SCAN FOURIER-TRANSFORM IR SPECTROMETER

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Acetic acid $CH_3C(O)OH$ plays an important role in the acidity in the troposphere. The reaction of Criegee intermediate with $CH_3C(O)OH$ was proposed to be a potential source of secondary organic aerosol in the atmosphere. We investigated the detailed mechanism and kinetics of the reaction of Criegee intermediate CH_2OO with $CH_3C(O)OH$. The time-resolved infrared absorption spectra of transient species produced upon irradiation at 308 nm of a flowing mixture of $CH_2I_2/O_2/CH_3C(O)OH$ at 298 K were recorded with a step-scan Fourier-transform infrared spectrometer. Bands of CH_2OO were observed initially upon irradiation; their decrease in intensity was accompanied with the appearance of bands near 886, 971, 1021, 1078, 1160, 1225, 1377, 1402, 1434, and 1777 cm^{-1}, assigned to the absorption of hydroperoxymethyl acetate [$CH_3C(O)OCH_2OOH$, HPMA], the hydrogen-transferred adduct of CH_2OO and $CH_3C(O)OH$. Two conformers of HPMA, an open form and an intramolecularly hydrogen-bonded form, were identified. At a later reaction period, bands of the open-form HPMA became diminished and new bands appeared at 930, 1045, 1200, 1378, 1792, and 1810 cm^{-1}, assigned to the formic acetic anhydride [$CH_3C(O)OC(O)H$, FAA], a dehydrolysis product of HPMA. The intramolecularly hydrogen-bonded HPMA is stable. From the temporal profiles of HPMA and FAA, we derived a rate coefficient k = $(1.3 \pm 0.3) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} for the reaction CH_2OO + $CH_3C(O)OH$ to form HPMA and a rate coefficient k = 980 ± 40 s^{-1} for the dehydration of the open-form HPMA to form FAA. Theoretical calculations were performed to elucidate the CH_2OO + $CH_3C(O)OH$ reaction pathway and to understand the different reactivity of the two forms of HPMA.