

SPECTRAL STUDIES OF THE REACTION OF THE CRIEGEE INTERMEDIATE CH₃CHOO WITH HCL USING A STEP-SCAN FOURIER-TRANSFORM INFRARED ABSORPTION SPECTROMETER

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Reactions between Criegee intermediates and hydrogen halides are important in atmospheric chemistry, because of their large rate coefficients. Employing a Fourier-transform absorption spectrometer in a step-scan mode or a continuous-scan mode, we recorded infrared spectra of transient species and end products in a flowing mixture of CH₃CHI₂/HCl/N₂/O₂ irradiated at 308 nm. Eight bands near 1383.7, 1357.9, 1323.8, 1271.8, 1146.2, 1098.2, 1017.5 and 931.5 cm⁻¹ were experimentally observed and assigned to bands ν_8 to ν_{15} of the *anti*-conformer of chloroethyl hydroperoxide (CEHP, CH₃CHClOOH), according to comparison of vibrational wavenumbers and IR intensities predicted with the B3LYP/aug-cc-pVTZ method. We derived a rate coefficient of *anti*-CH₃CHOO + HCl to be $k_{HCl} = (3.1 \pm 0.2) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹ from the formation of *anti*-CEHP. At a later reaction period, absorption bands of H₂O and acetyl chloride, CH₃C(O)Cl, at 1819.1 cm⁻¹ were observed; these species were produced from the decomposition of *anti*-CEHP or the secondary reactions of CH₃CHClO + O₂ → CH₃C(O)Cl + HO₂ and OH + HCl → H₂O + Cl according to temporal profiles of CEHP, H₂O, and CH₃C(O)Cl; both O₂ and HCl are major species in the system to participate in the secondary reactions. By adding methanol to deplete *anti*-CH₃CHOO, we observed only *anti*-CEHP, indicating that the interconversion from *syn*-CEHP to *anti*-CEHP is rapid. The branching ratio of the formation of CH₃C(O)Cl + H₂O to that of CH₃CHClO + OH was estimated to be 0.5 : 0.5. This observation serves as an excellent example that secondary reactions might interfere with the observation of the original products.