THE REACTION OF CH_2OO WITH HNO_3 INVESTIGATED WITH A STEP-SCAN FTIR SPECTROMETER

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Carbonyl oxides, which are known as Criegee intermediates, are important intermediates produced in ozonolysis of unsaturated hydrocarbons.[a] Criegee intermediates react readily with other atmospheric species such as HNO_3, SO_2, $(H_2O)_2$ and HCOOH, leading to production of OH, aerosols and organic acids in the atmosphere. The reaction coefficient between CH_2OO and HNO_3 was reported to be 5.4×10^{-10} cm^3 molecule^{-1} s^{-1} at 298 K. [b] Theoretical calculations also predict a similar rate coefficient for CH_2OO + HNO_3, the reaction goes through a barrierless path to form nitrooxymethyl hydroperoxide (NMHP, NO_3CH_2OOH). Besides, due to large exothermicity(-184.9 kJ mol^{-1}), internally excited NMHP might decompose further to CH_2ONO_3 and OH.[c]

In this work, we utilized a step-scan FTIR coupled with a multipass White cell to record time-resolved IR absorption spectra of the reactants and products during the reaction of CH_2OO with HNO_3 in a flow system with total pressure about 10 Torr. CH_2OO was produced from the reaction of CH_2I + O_2; CH_2I was produced from photolysis of CH_2I_2 at 308 nm.[d] The IR absorption spectra were recorded at instrumental resolution 0.3 cm^{-1}. Newly observed bands at 825, 967, 1053, 1294, 1348, 1424, 1686 and 3587 cm^{-1}can be assigned to NMHP. The observed wavenumbers and relative intensities agree with the anharmonic vibrational wavenumbers and IR intensities predicted with the B3LYP/aug-cc-pVTZ method. In addition, we also observed several bands with clear rotational structure, which can be assigned to the absorption of NO_2, H_2CO and HO_2. Observation of these species indicates that another decomposition route for excited NMHP might exist. Furthermore, absorption bands of unternally excited HNO_3 was also observed at low pressure, indicating that decomposition of pre-reaction complex can excite HNO_3. By probing the formation of NMHP and NO_2, the rate coefficient of this reaction was determined to be $(5.3\pm0.8)\times10^{-10}$ cm^3 molecule^{-1} s^{-1}.

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