Kinetics of the unimolecular reaction of CH_2OO and its reaction with the water monomer, acetaldehyde and acetone at atmospheric conditions

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Stabilized Criegee Intermediates (sCI) have been identified as oxidants of atmospheric trace gases such as SO_2, NO_2, carboxylic acids or carbonyls. The atmospheric sCI concentrations, and accordingly their importance for trace gas oxidation, are controlled by the rate of the most important loss processes, very likely the unimolecular reaction and the reaction with water vapour ubiquitously present in high concentrations.

In this study, the rate coefficients of the unimolecular reaction of the simplest sCI, formaldehyde oxide CH_2OO, and the bimolecular reaction with the water monomer have been measured at 295 ± 2 K and atmospheric pressure using a free jet flow system. CH_2OO was produced from the reaction of ozone with C_2H_4 and CH_2OO concentrations were probed indirectly detecting H_2SO_4 after titration with SO_2. The rate coefficient of the unimolecular reaction $k_{(uni)}$ was determined from time resolved experiments supported by additional measurements performed under CH_2OO steady-state conditions. Experimental results for $k_{(uni)}$ are analyzed in terms of statistical rate theory on the basis of molecular data from quantum chemical calculations. Furthermore, the rate coefficient $k_{(CH_2OO+H_2O)}$ has been determined for sufficient low H_2O concentrations (< 10^{15} molecule cm^{-3}) allowing separation from the CH_2OO reaction with the water dimer. In order to evaluate the accuracy of the experimental approach, the rate coefficient of the reaction of CH_2OO with acetaldehyde and acetone were reinvestigated.