A Kinetic Study of Aqueous-Phase Reactions of the Nitrate (NO_3) Radical with Aldehydes

A contribution to subproject CMD / APP

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Aldehydes play an important role in the chemistry of the polluted troposphere. They are emitted as primary pollutants from partial oxidation of hydrocarbon fuel, and they arise as secondary pollutants from the oxidation of several volatile organic compounds (VOC). In the present study the reaction of NO_3· with butanal in aqueous solution was studied, because butanal represents an important component in animal waste and automobile emission. Methacrolein represents a compound which is emmitted from automobiles and also in biomass combustion. Chloral is investigated as a specie which is of anthropogenic origin. Glyoxal and glyoxic acid may be formed following the degradation of aromatics. The aldehydes may either photolyse or react further with OH· radicals at day-time or with NO_3· radicals during the night-time. These reactions may represent important sinks for NO_3· radicals within tropospheric droplet at night-time. The degradation of aldehydes with NO_3· is probably not the predominant loss process of aldehydes but kinetic data are necessary for a better understanding of radical loss processes in atmospheric multiphase chemistry systems.

By using the laser-photolysis laser-longpath absorption (LP-LLPA) technique the radical reactions were investigated in aqueous solution. For the reactions of NO_3 with Glyoxal, Butanal and (-)-Myrtenal temperature dependent measurements were carried out. The influence of ionic strength was studied for reaction of NO_3 with Butanal and Chloral. It is important to note that all aldehydes are in equlilibrium to their hydrated species so that the solubility of them is very high. Because of this the aqueous phase reactions of aldehydes with NO_3 may represent a sink for aldehydes in the tropospheric gas phase which may lead to

lowered aldehyde concentration in polluted airmasses with a high aerosol load or within clouds.