



Infrared spectroscopic studies of the heterogeneous reaction of ozone with maleic and fumaric acid aerosols

J Najera (1), C Percival (1), and A B Horn (2)

(1) School of Earth, Atmospheric and Environmental Sciences, Faculty of Engineering and Physical Sciences, The University of Manchester, M13 9PL, Manchester, UK, (2) School of Chemistry, Faculty of Engineering and Physical Sciences, The University of Manchester, M13 9PL, Manchester, UK

Dicarboxylic acids, either directly emitted or formed in chemical processes are found to be a significant component of tropospheric aerosols. To assess any potential role of short unsaturated dicarboxylic acids in tropospheric heterogeneous chemistry, maleic acid (MaH) and fumaric acid (FuH) were selected as surrogates in this study. A new aerosol flow tube apparatus is employed to perform kinetic studies of the oxidation of organic compounds containing aerosols by gas phase ozone. The system consists of a lab-made particle generation system, a vertically oriented glass flow tube with moveable injector and a multi-pass cross beam White cell for measurement of aerosol and gas phase composition via Fourier transform infrared (FTIR) spectroscopy. A flow of single component organic aerosols with mean diameters ranging between 0.8-2.1 μm are introduced in a flow tube, in which the particles are subsequently exposed to a known concentration of ozone for a controlled period of time. These studies are complemented with offline analysis on the reaction products. Data from these studies were used to determine the kinetics of the reaction under a range of conditions. The reaction exhibited pseudo first order kinetics for gas product formation, and the pseudo first order rate coefficients displayed a Langmuir-Hinshelwood dependence on gas phase ozone concentration for both materials. By assuming Langmuir-Hinshelwood behaviour, the following parameters were found: for the reaction of MaH aerosols, $K_{O_3}=(1.9+0.4)\times 10^{-16}\text{cm}^{-3}$ and $k_{max}^I=0.015+0.002$; for the reaction of FuH aerosols, $K_{O_3}=(3.4+0.4)\times 10^{-16}\text{cm}^{-3}$ and $k_{max}^I=0.0128+0.0005$, where K_{O_3} is a parameter that describes the partitioning of ozone to the particle surface and k_{max}^I is the maximum pseudo-first order coefficient at high ozone concentrations. Apparent reactive uptake coefficients were extracted from the pseudo first order rate coefficient and a slight trend of decreasing uptake coefficients with increasing ozone concentrations was observed. In general, we find that the values obtained for maleic and fumaric acid fall within the range of literature values reported by other published studies for other organic or organic-coated particles, although there are some unusual dependencies on RH%.