



A laboratory study of iodine chemistry in the atmosphere

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Iodine chemistry can affect the oxidising capacity of the atmosphere through the role of OIO and INO_3 in the photochemical depletion of ozone. OIO also appears to be an intermediate in ultra-fine particle production in the coastal zone, and the uptake of INO_3 on sea-salt aerosol removes NO_x and provides a route for bromine and chlorine activation. In this paper we will describe a series of kinetic and photochemical studies of OIO and INO_3 .

OIO was produced via the reaction $\text{IO} + \text{IO}$, and observed by cavity ring down spectroscopy (CRDS). The photo-bleaching cross-section of OIO was determined by measuring the fraction of OIO removed by a laser pulse of known fluence, as the laser was scanned across the visible bands between 558 and 578 nm. This cross-section is in good agreement with an absorption cross-section determined at the University of Bremen (J. Carlos, P. Spietz and J. Burrows). Does OIO photolyse between 500 and 640 nm to yield $\text{I} + \text{O}_2$ (the channel to $\text{IO} + \text{O}$ requires photons at wavelengths below 470 nm)? We will show that most of the OIO promoted to the first excited electronic state interconverts into highly vibrationally excited ground state OIO, which is then quenched (within about $1.2 \mu\text{s}$ at 40 torr N_2) and reappears in the lowest vibrational level. The photolysis channel producing atomic I is less than 10%, in agreement with the measured yield of atomic I (T. Dillon and J. Crowley, MPI Mainz). This reduces the effectiveness of OIO in depleting O_3 , but photolysis is still fast enough to explain why OIO is not observed above 1 ppt during daytime.

INO_3 was formed from the recombination of IO and NO_2 , and its absorption cross section measured by time-resolved Fourier transform UV-visible spectroscopy. The

cross-section is significantly smaller than a recent measurement at the University of Cambridge (Mössinger *et al.*), and has a wavelength dependence similar to that of BrNO_3 , shifted to the red by ca. 40 nm. The yield of IO from the photolysis of INO_3 is less than 1% at 248 nm. Production of NO_3 from photolysis of INO_3 at 248 nm was observed by CRDS, but with a yield smaller than indicated from the absorption cross section. This is explained by the production of vibrationally hot NO_3 , a significant fraction of which (ca. 50%) appears to dissociate promptly. The effectiveness of INO_3 in an O_3 -depleting cycle is reduced because the NO_3 formed when INO_3 photolyses mostly photodissociates to $\text{NO}_2 + \text{O}$, producing a null cycle. However, the longer photolytic lifetime of INO_3 in the atmosphere means that reactions of this species on aerosol assume more importance.