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1 Low-temperature surface chemistry of nitrogen oxides relevant to the atmosphere

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Reflection Absorption Infrared Spectroscopy (RAIRS) and Thermally Programmed Desorption (TPD) spectrometry have been employed to study the low-temperature surface chemistry and photolysis of nitrogen oxides, ammonia and water.

The heterogeneous chemistry of nitrogen dioxide has come under considerable experimental scrutiny in recent years as it is believed to be a major source of nitrous acid (HONO) in the atmosphere. Subsequent photolysis of nitrous acid represents a significant source of the hydroxyl radical, which drives gas-phase chemistry in the troposphere.

Nitrogen dioxide in the condensed phase is known to exist almost exclusively in dimeric form, dinitrogen tetraoxide, N_2O_4. The latter can also exist in ionic form as nitrosonium nitrate, $NO^+NO_3^-$. Previous RAIR studies of dinitrogen tetraoxide from this group have shown that an ordered D_{2h}-N_2O_4 film is produced upon deposition of NO_2 at 80K. Thermal treatment of this film to 120K produced no evidence for the asymmetric nitrate conformer ($ONONO_2$) or the ionic nitrosonium nitrate. Further studies concluded that the dinitrogen tetraoxide/water-ice system was non-reactive between 85K and 150K, except for physical interactions. However, photolysis of both the D_{2h}-N_2O_4 and the N_2O_4/H_2O films did yield $NO^+NO_3^-$ via the asymmetric D'-$ONONO_2$ and asymmetric N_2O_3 (λg 300nm).

Nitrogen dioxide is known to undergo heterogeneous hydrolysis in thin water films forming nitrous acid as well as nitric acid. RAIR and TPD studies of dinitrogen

tetraoxide and water at low-temperatures have reported that the gas-phase products HONO and HNO_3 evolve from the ice surface below 150K.With reference to some atmospheric surfaces it has been proposed that it is an $NO^+NO_3^-$ intermediate (formed by autoionisation of asymmetric $ONONO_2$) that reacts with water to generate HONO and HNO_3.

This study explores heterogeneous chemistry of nitrogen oxides on ice, the possibility of production of gas-phase HONO on cirrus cloud ice crystals and also an explanation for recent observations connected to the polar snowpack.