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ABSTRACT

CHEMISTRY OF CHLORINATED SPECIES IN THE ANTARCTIC STRATOSPHERE

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The chemistry of Cl_2O_2, the chlorine monoxide dimer, has been further investigated in order to better assess its potential role in catalytic ozone destruction cycles. The dimer has been generated in a flow system, in the 200-250K temperature range, by using ozone and chlorine atoms as ClO precursors. The Cl-atoms are produced by a microwave discharge of either Cl_2, or of F_2 with subsequent addition of HCl. With this later scheme the dimer can be generated in the absence of Cl_2.

The FTIR spectra of the products clearly indicates the presence of two isomers, in agreement with our earlier results (J. Phys. Chem., 91, 433, 1987). None of the observed IR bands can be attributed to a ClO-OClO adduct, since they all appear in the absence of any detectable amount of OClO.

The dimer decomposes readily on surfaces yielding Cl_2 and O_2 as final products, even at temperatures low enough to rule out significant dissociation back to the monomer. In our flow system these product

species are monitored by absorption spectroscopy in the vacuum ultraviolet. We are currently carrying out these experiments in the presence of water-ice surfaces, in an attempt to predict the behavior of the dimer under Antarctic stratospheric conditions.

We have also continued our studies of the physical chemistry of the HCl-HNO_3-water/ice system. We developed a high sensitivity technique to monitor HCl vapor in the presence of water, by optical absorption in the vacuum ultraviolet, in order to directly determine the vapor pressures and the phase diagram of the system under conditions appropriate to the Antarctic stratosphere. One of the major experimental difficulties is the preparation and characterization of a suitable homogeneous solid phase. The monohydrate of nitric acid has a relatively low affinity for HCl, but this affinity increases rapidly as the water content in the solid crystals increases.

It is likely that the particles in the polar stratospheric clouds will have a relatively dilute nitric acid outer layer, even if the core is the nitric acid monohydrate, since the particles are in equilibrium with the ambient water vapor, which is present initially at levels of a few parts per million.