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PHOTOCHEMICAL MODELING OF THE ANTARCTIC STRATOSPHERE: OBSERVATIONAL CONSTRAINTS FROM THE AIRBORNE ANTARCTIC OZONE EXPERIMENT AND IMPLICATIONS FOR OZONE BEHAVIOR

Jose M. Rodriguez
Nien Dak Sze
Malcolm K. W. Ko

Atmospheric and Environmental Research, Inc.
840 Memorial Dr.
Cambridge, MA 02139 USA
617-547-6207

The rapid decrease in O_3 column densities observed during antarctic spring has been attributed to several chemical mechanisms involving nitrogen, bromine, or chlorine species, to dynamical mechanisms, or to a combination of the above. Chlorine-related theories, in particular, predict greatly elevated concentrations of $C\ell O$ and $OC\ell O$ and suppressed abundances of NO_2 below 22 km. The heterogeneous reactions and phase transitions proposed by these theories could also impact the concentrations of $HC\ell$, $C\ell NO_3$ and HNO_3 in this region. Observations of the above species have been carried out from the ground by the National Ozone Expedition (NOZE-I, 1986, and NOZE-II, 1987), and from aircrafts by the Airborne Antarctic Ozone Experiment (AAOE) during the austral spring of 1987. Observations of aerosol concentrations, size distribution and backscattering ratio from AAOE, and of aerosol extinction coefficients from the SAM-II satellite can also be used to deduce the altitude and temporal behavior of surfaces which catalyze heterogenous mechanisms. All these observations provide important constraints on the photochemical processes suggested for the spring antarctic stratosphere.

Results are presented for the concentrations and time development of key trace gases in the antarctic stratosphere, utilizing the AER photochemical model. This model includes complete gas-phase photochemistry, as well as the heterogeneous reactions:

$$C\ell NO_3 + HC\ell\ (ice) \longrightarrow C\ell_2 + HNO_3\ (ice) \quad (1)$$

$$C\ell NO_3 + H_2O\ (ice) \longrightarrow HOC\ell + HNO_3\ (ice) \quad (2)$$

$$N_2O_5 + HC\ell\ (ice) \longrightarrow C\ell NO_2 + HNO_3\ (ice) \quad (3)$$

$$N_2O_5 + H_2O\ (ice) \longrightarrow 2HNO_3\ (ice) \quad (4).$$

Heterogeneous chemistry is parameterized in terms of surface concentrations of aerosols, collision frequencies between gas molecules and aerosol surfaces, concentrations of $HC\ell/H_2O$ in the frozen particles, and probability of reaction

per collision (γ). Values of γ are taken from the latest laboratory measurements. The heterogeneous chemistry and phase transitions are assumed to occur between 12 and 22 km. The behavior of trace species at higher altitudes is calculated by the AER 2-D model without heterogeneous chemistry. Calculations are performed for solar illumination conditions typical of 60°, 70°, and 80° S, from July 15 to October 31.

The final products of heterogeneous processing by reactions (1)-(4) are very sensitive to the adopted initial concentrations of NO_x ($NO + NO_2 + C\ell NO_3 + 2xN_2O_5$), to the adopted rates of (1) - (4), and to the degree of illumination during the processing. We consider four cases representing different initial conditions for NO_x, and different rates for the heterogeneous processing. These cases illustrate different possibilities for the behavior of antarctic trace species, given the existing uncertainties and the constraints placed by available observations. We have concentrated on the following measurements from AAOE: 1) column densities of $HC\ell$, NO_2, HNO_3 and $C\ell NO_3$ by the infra-red spectrometers aboard the DC-8 aircraft; 2) local densities of NOY ($NO_x + HNO_3$) measured aboard the ER-2 aircraft; 3) local densities of $C\ell O$ measured aboard the ER-2; 4) local densities of ozone measured aboard the ER-2; 5) column densities of ozone from the TOMS instrument.

Comparison of calculations and observations indicate the following:

- The observed column densities of HNO_3 are consistent with mixing ratios of about 2.5 ppbv below 18 km near 70°, and of 1.5 ppbv deeper into the vortex. These values are also consistent with the ER-2 NOY measurement.
- Calculated column abundances of NO_2 are about 50% larger than observations. Since calculations indicate that most of this NO_2 is located above 22 km for the denitrified conditions of antarctic spring, resolution of this discrepancy requires more careful consideration of modeling and measurements in this region.
- The calculated column densities of $HC\ell$ are generally consistent with the low values observed, particularly if heterogeneous processing occurs throughout the month of September.
- Processing by (1) - (4) can yield substantial amounts of chlorine nitrate during August if initial NO_x concentrations during winter were of order 2 ppbv at 18 km. Negligible amounts of $C\ell NO_3$ would be produced if initial

NO_x abundances were a factor of two smaller. The high column densities of $C\ell NO_3$ observed during September could be an indication of $C\ell NO_3$ formation through reaction with NO_2 from photolysis of nitric acid during this month, or that large amounts of $C\ell NO_3$ present in August are not converted to active chlorine.

- Processing by (1) - (4) yields mixing ratios of $C\ell O$ between 0.4 and 1.1 ppbv at 18 km during the early half of September.
- The decrease in local ozone densities observed by the AAOE instruments can be explained by chlorine-mediated catalytic cycles above 15 km. The $C\ell_2O_2$ cycle contributes about 80% of the calculated reduction, if we adopt currently accepted values for the formation and photolysis rates of $C\ell_2O_2$, and assume that the photolysis produces molecular oxygen. Since there are still uncertainties in the above, these conclusions are dependent on future resolution of these issues.
- The calculated behavior of $C\ell O$ after the end of the AAOE mission depends crucially on the amount of HNO_3, its photolysis rate, and the assumed duration of heterogeneous chemistry.
- The calculated reduction in column ozone between August and October ranges from 40 to 110 Dobson units in the four cases considered, depending on the assumed concentrations of NO_x, HNO_3, and the temporal extent of heterogeneous chemistry. Observations of $C\ell O$ during late September and October would further constrain the above estimates.
- Calculated reductions in column ozone at different levels of chlorine exhibit a non-linear behavior. The calculated reduction accelerates for chlorine levels comparable to the adopted initial NO_x abundances during winter. Since these abundances also control the amount of processed $HC\ell$, the deepening of the ozone hole slows down for higher levels of chlorine in the future. Details of this behavior, however, are sensitive to the adopted HNO_3 concentrations and rates of heterogeneous reactions, particularly of (2).