N92-14541

A. Title of Research Task:

Homogeneous and Heterogeneous Chemistry along Air Parcel Trajectories

B. Investigators:

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C. Research Objectives:

The goal of the present research was to study the coupled heterogeneous and homogeneous chemistry due to polar stratospheric clouds (PSC's) using Lagrangian parcel trajectories for interpretation of the Airborne Arctic Stratosphere Experiment (AASE). This approach represents an attempt to quantitatively model the physical and chemical perturbations to stratospheric composition due to formation of PSC's using the fullest possible representation of the relevant processes. Further, the meteorological fields from the UK Met. office global model were used to deduce potential vorticity and inferred regions of PSC's as an input to flight planning during AASE.

D. Summary of Progress and Results

Potential vorticity and inferred PSC maps were made available daily during the AASE mission. In most cases, the inferred PSC's coincided well with those observed and were therefore useful in flight planning.

A detailed cloud microphysics model was coupled to the Lagrangian photochemistry model prior to the AASE mission. The coupled model was implemented on a microvax computer and was run in real time during the field experiment.

The model was used to interpret a great deal of the AASE data. Particular success was achieved for the flight of January 24, 1989. During this period, synoptic scale forcing in the troposphere led to rapid stratospheric cooling above Scandanavia with subsequent PSC cloud formation. The ER-2 sampled air within the cloud during its formation stages. Model calculations of the evolution of cloud particle growth (Poole et al., 1989) and chemical composition (Jones et al., 1989) were in remarkable agreement with observations. The calculated particle volume agreed well with measurements of particles from the ER-2, and the associated production of ClO appeared to be in very good agreement with the model estimates. This cloud event therefore represented an excellent test of current understanding of cloud microphysics and heterogeneous chemistry for a case of relatively rapid cooling.

Heterogeneous chemistry plays a critical role in determining the abundance of reactive nitrogen, which can in turn affect ClO through formation and destruction of the $ClONO_2$ reservoir long after exposure to PSC's. Thus, observations of ClO place important constraints on the abundances of stratospheric NO and NO_2. During some flights, ClO abundances of only a few parts per trillion by volume were observed at ER-2 flight levels, in contrast to levels above a part per billion in heavily processed air. The range of ClO abundance depends on many factors including cloud processing, solar zenith angles, and availability of reactive nitrogen. Trajectory studies can be used to evaluate the first two factors and hence to deduce information about the reactive nitrogen abundances (Solomon et al., 1989).

Many of the AASE flights revealed a general 'dog-dish' structure in ClO, with relatively low values at lower latitudes followed by a maximum near 65-70N, followed by lower values at higher latitudes. Modeling studies showed that this structure is due to the combined effects of processing of air parcels within PSC's coupled with solar zenith angle effects. In particular, heavily processed air at high latitudes displays relatively little ClO due to the large solar zenith angles present there, favoring the ClO dimer as the dominant reservoir for the liberated chlorine. At lower latitudes, solar zenith angles are smaller, favoring ClO over the dimer, but PSC processing is limited. Thus, a maximum in ClO abundance is found at an intermediate latitude region where solar illumination and cloud processing overlap most effectively.

Detailed studies were carried out to evaluate the ozone destruction before, during and post-mission (McKenna et al., 1989). These studies were based largely on ensembles of representative trajectories at various latitudes. For the period of the mission, careful attention was paid to the AASE data, which place important constraints on the available reactive chlorine and nitrogen and hence on ozone depletion.

E. Journal Publications

Jones, R. L., D. L. McKenna, L. R. Poole, and S. Solomon, in preparation for submission to Geophys. Res. Lett., 1989.

McKenna, D. L., R. L. Jones, L. R. Poole, and S. Solomon, in preparation for submission to Geophys. Res. Lett., 1989.

Poole, L. R., S. Solomon, D. L. McKenna, and R. L. Jones, in preparation for submission to Geophys. Res. Lett., 1989.

Solomon, S., R. L. Jones, D. L. McKenna, and L. R. Poole, in preparation for submission to Geophys. Res. Lett., 1989.

UATDAP Research Summary 1988

A. Title of Research Task

Study of Ozone Observations

B. Investigators and Institutions

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C. Abstract of Research Objectives

For the purpose of testing the adequacy of current models of atmospheric chemistry, one dimensional (1D) model calculations have been compared with vertical ozone profiles derived from ground-based diurnal radio measurements.

D. Summary of Progress and Results

One dimensional model calculations accurately reproduce the relative diurnal variation of mesospheric ozone at equinox, suggesting that the model value of the ozone photolysis rate coefficient is accurate to better than 10%. Various changes in model parameters, previously suggested to better reproduce the ozone abundance vertical profile, result in only small differences in the relative diurnal variation, indicating that these observations do not provide a sensitive test of the mesospheric chemistry controlling the abundance of odd oxygen.

E. Journal Publications

W. C. Zommerfelds, K. F. Kunzi, M. E. Summers, R. M. Bevilacqua, D. F. Strobel, M. Allen, and W. J. Sawchuck. Diurnal Variations of Mesospheric Ozone Obtained by Ground-based Microwave Radiometry. *J. Geophys. Res.*, in press (1989).

Theoretical Stduies of Stratospheric Chemistry

NAGW–1230

Principal investigators: M. B. McElroy and S. C. Wofsy

Abstract

The research focussed on elucidating important aspects of stratospheric chemistry, with emphasis on the stratosphere at high latitude and on interpretation of recent satellite observations from ATMOS and SAGE II. The role of heterogeneous processes was examined using data from the laboratory and from recent aircraft experiments in the Antarctic and the Arctic.

Summary of progress and results

Observations of O_3 declines over Antarctica, in combination with measurements of ClO and BrO free radicals, provide the information required to test models of the processes responsible for O_3 loss. Analysis of observations in the Antarctic stratosphere indicated that 60–70% of the observed loss of O_3 was accomplished by reactions of ClO and BrO radicals. Formation of $(ClO)_2$ accounted for about three times the loss associated with reactions involving ClO and BrO. We examined possible additional pathways for ozone recombination, to try to explain the "missing" losses. We found that almost all candidate processes could be rejected after careful analysis of laboratory experiments. Two processes were identified that should be followed up by laboratory studies.

We took part in the Arctic Airborne Ozone Experiment in Stavanger, Norway. In association with the experimenters in this mission, we examined the processes responsible for denitrifying the atmosphere, analyzed the global conversion of N_2O to NO_y, and developed a method for reconstructing 3–dimensional tracer fields (e.g. NO_y, inorganic chlorine) using meteorological data in combination with limited *in situ* data.

The results show that the signature of formation of polar stratospheric clouds is consistent with thermodynamic data for $HNO_3 \cdot 3H_2O$. Denitrification appears to proceed rapidly once the the atmosphere is cooled to the frost point temperature, and we argue that the process is enhance by prior formation of a bi–modal distribution for $HNO_3 \cdot 3H_2O$ particles, as observed by the ER–2 and balloon sondes. The microphysical processes that give rise to the formation of a bimodal distribution remain unclear, an issue we are actively pursuing.

PUBLICATIONS

Chemistry of OClO in the Antarctic Stratosphere: Implications for Bromine, by R. J. Salawitch, S. C. Wofsy and M. B. McElroy, Planet. Space Sci., *36*, 213-224 (1988).

Interactions between HCl, NO_x, and H_2O ice in the Antarctic Stratosphere: Implications for ozone, by S. C. Wofsy, M. J. Molina, R. J. Salawitch, L. E. Fox, and M. B. McElroy, J. Geophysical Research, *93*, 2442 - 2450 (1988).

Chemistry of the Antarctic Stratosphere, by M. B. McElroy, R. J. Salawitch, and S. C. Wofsy, Planet. Space Sci., *36*, 73-87 (1988).

Influence of Polar Stratospheric Clouds on the Depletion of Antarctic Ozone, by R. J. Salawitch, S. C. Wofsy and M. B. McElroy, Geophysical Research Letters, *15*, 871-874 (1988).

Denitrification in the Antarctic Stratosphere, R. J. Salawitch, G.P. Gobbi, S. C. Wofsy, and M. B. McElroy, Nature *339*,525–527 (1989).

Changing composition of the global atmosphere, M. B. McElroy and R. J. Salawitch, *Science* 243, 763–770 (1989).

The challenge of global change, M. B. McElroy, *New Scientist*, 28 July 1988.

Studies of Polar Ice: Insights for atmospheric chemistry, M. B. McElroy, in *The environmental record in glaciers and ice sheets,* eds H. Oeschger and C. C. Langway, pp 363–377 (1989.)