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EFFECTS OF STRATOSPHERIC AEROSOL SURFACE PROCESSES ON THE LLNL TWO-DIMENSIONAL ZONALLY AVERAGED MODEL

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ABSTRACT

We have investigated the effects of incorporating representations of heterogeneous chemical processes associated with stratospheric sulfuric acid aerosol into the LLNL two-dimensional, zonally averaged, model of the troposphere and stratosphere. Using distributions of aerosol surface area and volume density derived from SAGE II satellite observations, we were primarily interested in changes in partitioning within the Cl- and N- families in the lower stratosphere, compared to a model including only gas phase photochemical reactions. We have considered the heterogeneous hydrolysis reactions

$$N_2O_5 + H_2O(\text{aerosol}) \rightarrow 2\ HNO_3(\uparrow)$$

and

$$ClONO_2 + H_2O(\text{aerosol}) \rightarrow HOCl(\uparrow) + HNO_3(\uparrow)$$

alone and in combination with the proposed formation of nitrosyl sulfuric acid (NSA) in the aerosol and its reaction with HCl

$$HCl + NOHSO_4(\text{aerosol}) \rightarrow ClNO(\uparrow) + H_2SO_4.$$

Inclusion of these processes produces significant changes in partitioning in the NO_y and ClO_y families in the middle stratosphere.

INTRODUCTION

Numerical models of the troposphere and stratosphere including only gas-phase homogeneous photochemical processes can reproduce many of the observed features of trace constituent distributions. However, homogeneous models can not represent the chemical processes (Solomon, 1988) responsible for the observed lower stratosphere winter polar behavior of ozone and partitioning among the nitrogen and chlorine species. These processes require local temperatures low enough to condense water or a mixture of nitric acid and water into particles providing a surface for heterogeneous reactions which transform more stable chlorine reservoir species into more labile species.

Homogeneous models also fail to produce the bias toward nitric acid observed in the partitioning of the nitrogen oxide family at mid and high latitudes in the winter hemisphere. Two reactions of importance that would take place on the surface of stratospheric sulfuric acid aerosol have been identified through laboratory investigation (Hofmann and Solomon, 1989, and WMO/UNEP, 1992)

$$N_2O_5 + H_2O(\text{aerosol}) \rightarrow 2\ HNO_3(\uparrow) \qquad (1)$$

and

$$ClONO_2 + H_2O(\text{aerosol}) \rightarrow HOCl(\uparrow) + HNO_3(\uparrow). \qquad (2)$$

Both reactions convert NO_x to HNO_3, supplementing the homogeneous termolecular reaction of OH with NO_2.

In consideration of the upcoming availability of a vastly increased data base of stratospheric trace species from the Upper Atmospheric Research Satellite (UARS), we have investigated the effects, in a numerical atmospheric model, that the sulfuric acid aerosol reactions above would have on species distributions, compared to inclusion of only gas phase processes. In this model study we have used an aerosol burden representing a climatological average of several years of SAGE II satellite data (WMO/UNEP, 1992), but, in order to distinguish the effects of the sulfuric acid aerosol reactions, have not included processes related to polar stratospheric clouds (PSC). Future direct comparison to UARS observations will be done with inclusion of the observed aerosol burden as perturbed by the Mt. Pinatubo eruption, as well as with PSC processes.

We have also taken a preliminary look at the effects of an additional process proposed to occur in sulfuric acid aerosol of appropriate composition. Nitrosyl sulfuric acid ($NOHSO_4$) has been tentatively identified as a common constituent of stratospheric sulfuric acid aerosol (Farlow et al., 1977) and is known from bulk phase laboratory work to be capable of existence as an ionic solute or solid within a range of sulfuric acid concentration and temperature characteristic of stratospheric aerosol. Burley and Johnston (1992) have shown that, based on current thermodynamic knowledge of the system, it is

possible that gaseous HCl in the stratosphere could react with NSA present in aerosol to produce nitrosyl chloride

$$HCl + NOHSO_4(aerosol) \rightarrow ClNO(\uparrow) + H_2SO_4. \quad (3)$$

ClNO absorbs in the near ultraviolet with breaking of the Cl-N bond. Reaction (3), if it occurs, would then act to shift the partitioning of ClO_y toward Cl-containing radical species and temporary Cl reservoirs, such as $ClONO_2$, and away from HCl. Its importance depends on its magnitude compared to the reaction of OH with HCl, which also releases Cl.

MODEL DESCRIPTION

The model used in this study is a version of the Lawrence Livermore National Laboratory (LLNL) two dimensional model of the troposphere and stratosphere, with about 10° latitude resolution and 3 km vertical resolution in the stratosphere extending from pole to pole and the surface to 60 km. The gas phase homogeneous photochemistry in the model encompasses about 50 species and 120 thermal and photolytic reactions, for which kinetic and spectral parameters are taken from current recommendations (NASA, 1990). The circulation in the model is calculated interactively from the net heating rates resulting from the modeled species distributions and a climatological temperature field. In order to isolate the local photochemical effects of, for example, additional reactions, the circulation can be fixed to a previously calculated result.

Reactions (1) and (2) are treated as kinetically controlled, where the rate of the reaction is proportional to the rate of collision through the dimensionless reaction probability γ. The first order rate constant for reaction is given by

$$k = \frac{\bar{v}}{4}\gamma S$$

where $\bar{v}$ is the average molecular velocity and S is the aerosol surface area density. In this study, v is taken to be 5200 cm s^{-1} for both N_2O_5 and $ClONO_2$ throughout the model domain. Based on laboratory results, the reaction probability for N_2O_5 is assigned 0.1. For $ClONO_2$ the reaction probability is given by

$$\gamma(2) = 0.006\exp(-0.15(T-200)),$$

where the temperature dependence arises from the dependence of the reaction probability on aerosol composition, which is in turn dependent on temperature.

Surface area density for this study is based on an analysis of SAGE II data by Poole et al. (WMO/UNEP, 1992) and is representative of an average atmosphere unperturbed by any major recent volcanic eruption. The prescribed values are functions of altitude, latitude, and, coarsely, season, extending from 12 to 32 km and pole to pole. Minimum and maximum values are about 0.025 and 1.75×10^{-8} cm^2cm^{-3}, respectively.

The rate constant for the proposed reaction of HCl with NSA dissolved or incorporated in the aerosol should depend on the NSA concentration in the aerosol, and may be controlled either by the collisional rate constant for HCl with the particle and an associated reaction probability, or by the Henry's Law solubility for HCl and a solution phase rate constant. The presence of NSA in the aerosol depends on the concentration of H_2SO_4. According to Burley and Johnston (1992), NSA can be present at lower stratospheric temperatures when the H_2SO_4 weight per cent exceeds about 60%. The aerosol composition in the model was determined by interpolating from the tabulated results of Jaecker-Voirol (Jaecker-Voirol et al., 1990) for binary H_2O/H_2SO_4 mixtures, using the model temperature and water partial pressure. Fig. 1 below shows the calculated values for July. The modeled concentration is generally below 60% in the lowest portion of the aerosol distribution, but above 60% in the 15-30 km region of greatest importance to ozone controlling processes.

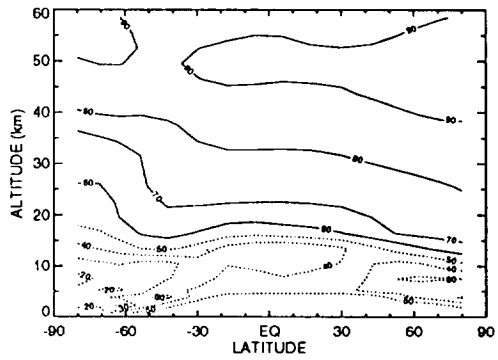

Figure 1. Derived composition of July stratospheric sulfuric acid aerosol in H_2SO_4 weight per cent. Solid contours are greater than 60 per cent. Dashed contours are smaller than 60 per cent.

Burley and Johnston (1992) propose several possible formation reactions for NSA, involving various NO_y species, including

$$NO + HNO_3 + H_2SO_4 \rightarrow NOHSO_4 + NO_2 + H_2O \quad (4)$$

and

$$NO + NO_2 + 2\,H_2SO_4 \rightarrow 2\,NOHSO_4 + H_2O. \quad (5)$$

Farlow et al (1977) tentatively observed solid NSA crystals in the collected aerosol, which would be formed when the NSA concentration in the aerosol exceeded its solubility in H_2SO_4. A proper calculation of the NSA abundance would require representing the processes of aerosol formation, growth, and loss, as well as the heterogeneous NSA-forming reactions. In this preliminary study we have assumed that the processes forming and destroying NSA are rapid compared to its abundance, allowing

the use of a steady state expression for NSA abundance. The formation rate is taken as equal to the NO/aerosol collision rate times a reaction probability of 0.01, following Burley and Johnston (1992). The NSA loss rate is assumed to be the HCl/aerosol collision rate times a reaction probability representing the relative abundance of NSA to H_2SO_4 at the particle surface, so that the atmospheric concentration of NSA is

$$[\mathrm{NSA}(ss)] \cong \left(2*0.01*[\mathrm{NO}]*\frac{V\{\mathrm{H_2SO_4}\}^{2/3}}{[\mathrm{HCl}]} \right)^{1/2}.$$

V is the aerosol volume density and $\{H_2SO_4\}$ is the concentration of sulfuric acid in the aerosol. V is simply scaled from the surface area density assuming that the surface area in 1 cm^3 of atmosphere is on one spherical particle. Fig. 2 shows the resulting atmospheric concentration of NSA when these assumptions are made. The values are typically a few per cent or less of the H_2SO_4 concentration.

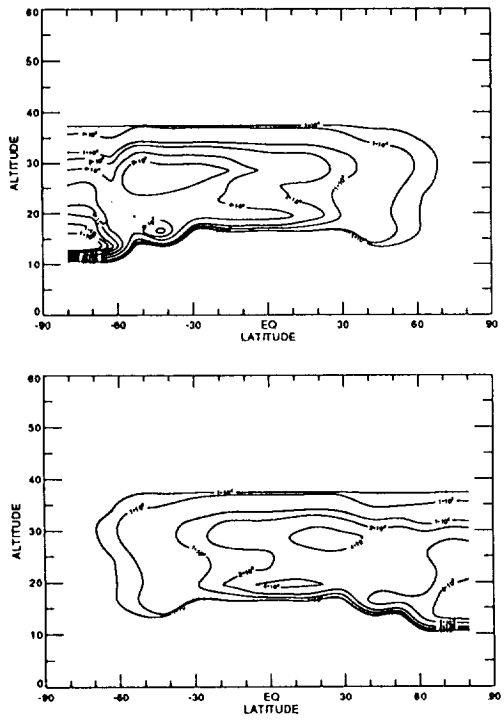

Figure 2. Calculated steady state concentration of NSA in mol cm^{-3}. (a) December, (b) July.

Given these assumptions, the rate of HCl loss and ClNO production in reaction (3) is expressed as

$$\frac{d[\mathrm{ClNO}]}{dt} = \frac{\bar{\nu}}{4} \frac{S}{\left(V\{\mathrm{H_2SO_4}\}\right)^{2/3}} [\mathrm{HCl}][\mathrm{NSA}(ss)].$$

The calculated rate of HCl + NSA is compared to the rate of OH + HCl in Fig. 3.

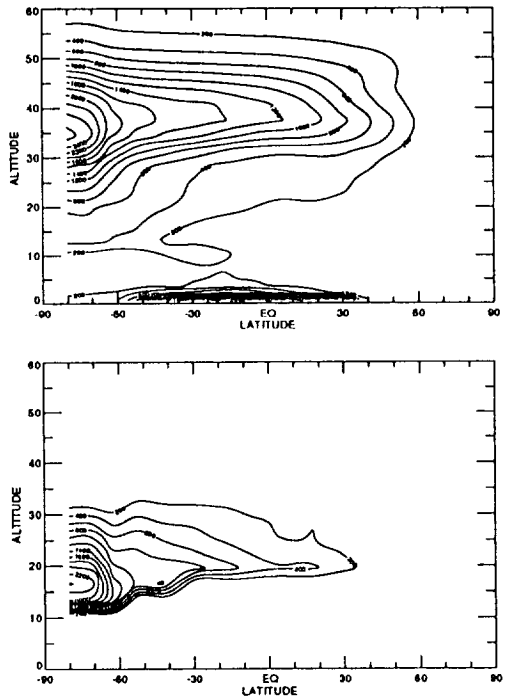

Figure 3. Calculated rates of reaction in December (molecules cm^{-3} s^{-1}) for (a) HCl + OH → Cl + H_2O, and (b) HCl + NSA → ClNO + H_2SO_4.

The model was integrated to steady state using 1990 ambient boundary conditions for the source species, establishing the circulation for the case including reactions (1)-(3). This circulation was then prescribed for integrations to steady state for the case including reactions (1) and (2) and for the case of only gas phase reactions.

RESULTS

An expected major effect of both reactions (1) and (2) is a large increase in HNO_3 (Fig. 4) at middle and upper latitudes particularly in winter and spring, where the rates of (1)+(2) become larger than the rate of OH + NO_2 + M. This is shown in Fig. 5, where in December, the heterogeneous processes dominate northward of about 30°.

As HNO_3 increases, other NO_y family members, particularly NO, NO_2, and N_2O_5, show a corresponding decrease. The abundance of $ClONO_2$ changes little because the γ for reaction (2) is fairly small except in the southern high latitude winter. The effect on ozone of reactions (1) and (2) is to increase the importance of the ClO_x destruction catalytic cycles while somewhat diminishing the dominant position of the NO_x cycle between 20 and 30 km. The net overall effect on ozone is a slight increase of

0.11% relative to the total abundance in the gas phase case.

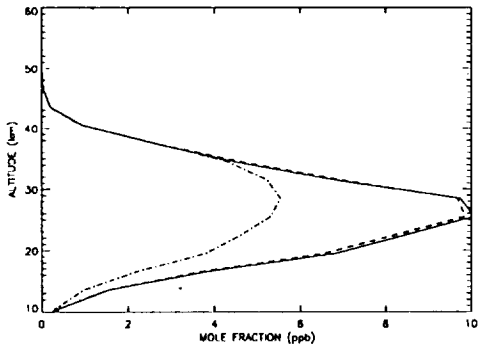

Figure 4. Derived HNO_3 mole fraction at 62° N in December. Solid line includes reactions (1) and (2), dashed line includes (1)-(3), dot-dash line includes only gas phase photochemistry.

The addition of reaction (3) and the associated NSA formation and ClNO photolysis reactions do not produce significant further changes in NO_y partitioning (Fig. 4). However, as expected, ClO and

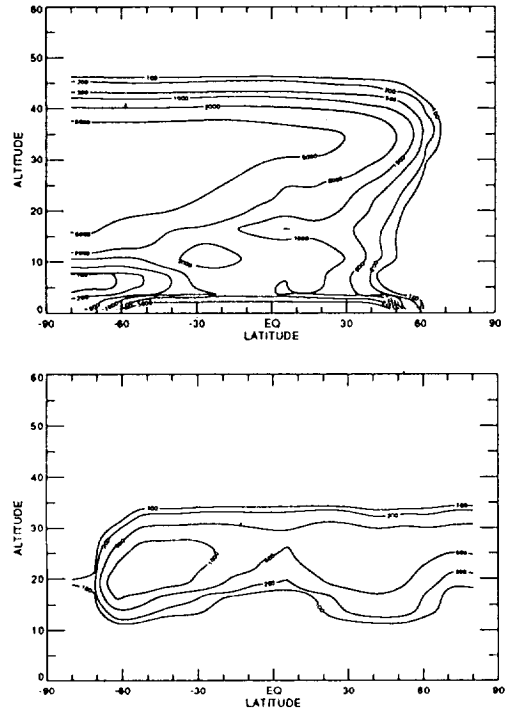

Figure 5. Calculated rates of HNO_3 production in December (mol cm^{-3} s^{-1}). (a) $NO_2 + OH + M \rightarrow HNO_3 + M$, (b) Sum of $N_2O_5 + H_2O$(aerosol) $\rightarrow 2\ HNO_3$ and $ClONO_2 + H_2O$(aerosol) $\rightarrow HOCl + HNO_3$.

$ClONO_2$ are substantially increased between 20 and 30 km globally, while HCl decreases. Fig. 6 shows that in some regions of the stratosphere, with the inclusion of reaction (3), $ClONO_2$ becomes the dominant inorganic Cl-containing species. Total ozone abundance is decreased by about 3% relative to the gas phase case, with the largest effects in regions where the photochemical ozone lifetime is long and the enhancement of ClO produces proportionately a larger reduction in local ozone abundance.

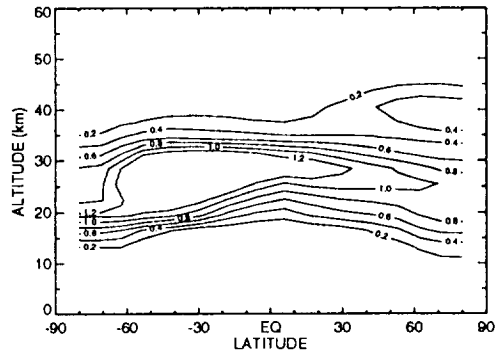

Figure 6. Calculated ratio of $ClONO_2$ to HCl in December with NSA included. Where the value exceeds 1, $ClONO_2$ is the dominant inorganic Cl species.

CONCLUSION

This preliminary study of the effects, on trace species distributions, of heterogeneous processes taking place on stratospheric sulfuric acid aerosol provides some guidance for consideration of observations of NO_y and ClO_y family members. A strong enhancement of HNO_3 in the partitioning in the NO_y family at winter high latitudes is an indicator of aerosol moderated hydrolysis of N_2O_5, while NO, NO_2, and N_2O_5 are substantially decreased. With the proposed NSA-related chemistry, $ClONO_2$ is made the major inorganic Cl-containing species in the 24-31 km region.

Future improvements in our knowledge of the thermodynamic and kinetic properties of the sulfuric acid aerosol/H_2O/NO_y system will allow better model representation of NSA and related chemistry than was attempted here.

Consideration of heterogeneous chemistry on or within sulfuric acid aerosol is important for understanding of natural and anthropogenic influences on the stratosphere. Comparisons to observations of the UARS satellite and other data may provide evidence for the importance of these processes.

ACKNOWLEDGMENTS

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