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Nighttime hydrogen peroxide production on sulfuric-acid-aerosols involving nitrate and sulfate radicals

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Abstract A novel nighttime reaction sequence involving 1) nitrate radicals, 2) sulfate radicals and ultimately 3) hydrogen peroxide is proposed. According to a grossly simplified model calculation this sequence may lead to a twofold increase in the background hydrogen peroxide level during one night. This increase may be accumulated over a long period. Presumably an increased level of hydrogen peroxide will mean increased ozone depletion in the lower stratosphere. Proper modelling and more experimental work is needed to assess the importance of this proposed source of hydrogen peroxide.

Introduction

In two papers [*Brasseur*, 1989] and [*Hofmann et. al.*, 1992] implicate chemistry on the Pinatubo aerosol as a possible cause of enhanced ozone destruction in Antarctica in 1991.

[*Prather*, 1991] and [*Mather and Brune*, 1990] modelled the destruction processes considering oxidation of HCl to Cl_2 by $ClONO_2$ plus the formation of HOCl by hydrolysis of $ClONO_2$. Also denitrification by N_2O_5 reacting with water to form nitric acid was considered.

In the nighttime stratosphere NO is rapidly converted into NO_y by the following gas phase reactions:

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (1)$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \quad (2)$$

$$NO_2 + NO_3 \rightleftharpoons N_2O_5 \quad (3)$$

In the presence of sulfuric acid aerosol heterogeneous processes may also take place, notably between N_2O_5 and the water content of the aerosol, which is believed to consist of 60–80% sulfuric acid in water:

$$N_2O_5 + H_2O \rightarrow 2\ HNO_3 \quad (4)$$

If this process is the predominant process, then loss of NO_y is the consequence. We suggest that with a certain propability the intermediate nitrate radicals in reaction 2 become absorbed in the aerosol droplets.

It has been shown by [*Løgager et. al.*, 1993] that nitrate radicals react with hydrogen sulfate ions to produce hydrogen sulfate radicals in an equilibrium process:

$$NO_3 + HSO_4^- \rightleftharpoons NO_3^- + HSO_4 \quad (5)$$

the equilibrium constant at 22°C is 2.2 10^{-3} and the rate constant $k_5 = 5.6\ 10^3\ \ M^{-1}s^{-1}$, corresponding to a halflife of nitrate radicals of the order of tens of milliseconds in the ($\approx$ 10 M) sulfuric acid aerosol. No values pertaining to stratospheric temperatures are known.

This reaction implies that to the extent that NO_3 enters the aerosol rather than reacting according to reaction (3) then *oxidation capacity is stored in the droplets.*

A possible fate of hydrogen sulfate radicals is to dimerize to produce peroxydisulfuric acid and peroxymonosulfuric acid – Caro's acid:

$$2\ HSO_4 \rightarrow H_2S_2O_8 \quad (6)$$

$$H_2S_2O_8 + H_2O \rightarrow H_2SO_5 + H_2SO_4 \quad (7)$$

Caro's acid on the other hand is in equilibrium with hydrogen peroxide and sulfuric acid:

$$H_2SO_5 + H_2O \rightleftharpoons H_2SO_4 + H_2O_2 \quad (8)$$

We have modelled the kinetics of formation and uptake of NO_3 and N_2O_5 in order to see whether

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the former molecule is actually taken up by the aerosol to a significant degree. The model calculation therefore aims first of all at investigating the relative rate of absorption of N_2O_5 and NO_3 into aerosol droplets. Once absorbed the fates of the reactants are assumed to be as outlined above, and the homogeneous gas phase concentration is obtained by assuming phase (Henry's law) equilibrium.

The reaction scheme assumed is the following:

$$NO_2 + O_3 \rightarrow NO_3 + O_2; \quad k_9 \qquad (9)$$

$$NO_3(g) \rightarrow NO_3(aer); \quad k_{10} \qquad (10)$$

$$NO_2 + NO_3 + (M) \rightarrow N_2O_5 + (M); \quad k_{11} \qquad (11)$$

$$N_2O_5 + (M) \rightarrow NO_2 + NO_3 + (M); \quad k_{12} \qquad (12)$$

$$N_2O_5(g) \rightarrow 2\ HNO_3(aer); \quad k_{13} \qquad (13)$$

The modelling did not aim at giving a realistic picture of the actual stratospheric processes, so the concentrations and assumptions used should only be considered as one possible scenario.

Assumptions and input data

1. Necessary aerosol data are taken from [*Ansmann et. al.*, 1993] who used LIDAR to measure the Pinatubo aerosol over Hamburg in 1992. The liquid aerosol content L, to be defined below, was determined from Ansmanns data.

2. Transfer rate constants k_t are calculated according to [*Schwartz*, 1986] using the aerosol data from Ansmann. The calculational procedure is the same as adopted by [*Lelieveld and Crutzen*, 1991] in their study of cloud photochemistry.

3. Model concentrations of nighttime NO_2 have been taken from [*Brasseur and Solomon*, 1986] namely as the sum of daytime [NO] and [NO_2]. [O_3], pressures, air concentrations [M] and temperatures have been taken from from the same source.

4. Rate constants for gas phase reactions are from [*deMore et. al.*, 1992].

5. The liquid aerosol content is the volume of liquid in a certain volume of air, divided by the latter, i.e. L is a dimensionless quantity. A very much simplified variation of L with heigth is assumed, thus $L = 10^{-12}$ has been assumed at 15 and 25 km heigth, while $L = 3\ 10^{-12}$ has been assumed at 20 km. This crudely mimicks the distribution observed by Ansmann et at. when the Pinatubo aerosol cover was maximal.

6. The absorption of NO_3 and N_2O_5 into the aerosol is assumed to be irreversible. For NO_3 this is due to the assumption of reaction (5) and subsequent reactions. For N_2O_5 reaction (4) is the rationale. O_3 and NO_2 are assumed not to enter the aerosol, i.e. only gas phase oxidation is considered.

7. The gas phase concentration of hydrogen peroxide is obtained using the Henry's law constant for aqueous solutions of hydrogen peroxide, as quoted by [*Lelieveld and Crutzen*, 1991].

Results

In a preliminary report [*Pedersen*, 1993] it was assumed that both $C_g^{NO_3}$ and $C_g^{N_2O_5}$ would come to steady-state fairly rapidly. While this is actually found to be the case for $C_g^{NO_3}$, then it takes several hours for $C_g^{N_2O_5}$ to even approach steady-state, this is evident from figure 1. This implies that *more* NO_3 reaches the aerosol phase than was to be anticipated using the steady-state assumption. The graphs of figure 1 show the time development under the more optimistic assumption about the very critical quantity, the sticking coefficient α and for 3 different heigth. $C_g^{H_2O_2}$ is calculated as half the absorbed NO_3 per cm^3, i.e. assuming that all the NO_3 is converted into hydrogen peroxide as outlined above. The result for $\alpha = 0.01$ is quoted for the hydrogen peroxide production only,

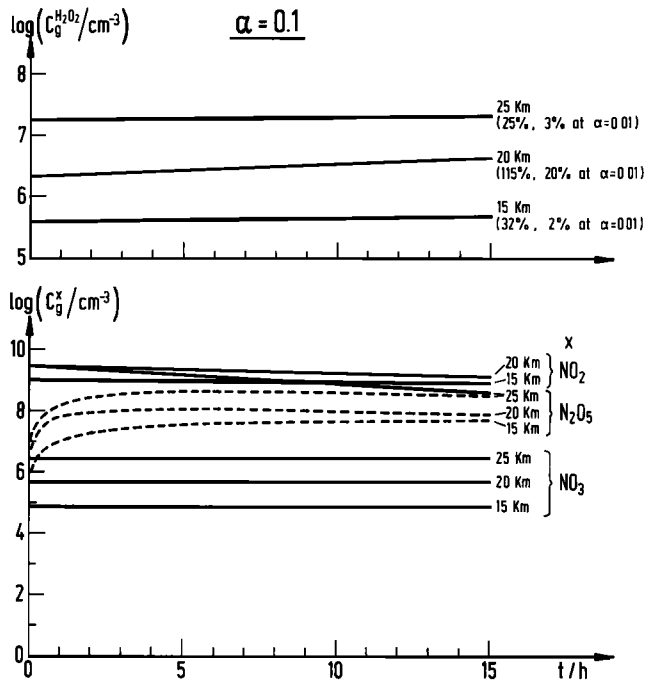

Figure 1. Simulation of the kinetics relating to eqns. 9–13 for $\alpha = 0.1$. Results for $\alpha = 0.01$ are indicated in the parantheses, see text.

the percentages are given as the rise in gasphase concentration over the background level as given in [*Brasseur and Solomon*, 1986].

Discussion

Hydrogen peroxide in the lower stratosphere photolyses to form OH in the daytime OH can in turn enter into 2 ozone destruction cycles producing HO_2, which may form H_2O_2 again in the nighttime see [*Brasseur and Solomon*, 1986]. One of the referees supplied a value of 150 $cm^{-3}s^{-1}$ for the daytime production of H_2O_2. The modelling above gives about half that amount for the nighttime production. There is a possibility that a rise in the level, as that indicated here, may be accumulated over time since a fresh start will take place at sunset every day. It will take proper modelling to sort this out.

There are a number of points that need experimental clarification. First of all the hydrogen peroxide-sulfuric acid system, including the peroxoacids, should be studied at low temperature. We hope to do that using sulfuric acid films and mass spectrometry as detection device for H_2O_2, and Raman spectroscopy for peroxospecies. Secondly data for the nitrate radical sulfate radical interconversion reaction (5) at stratospheric temperatures are needed.

There is also a need to study side reactions to reaction (6), one possible alternative reaction would be oxidation of H_2O to O_2.

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