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Aerosol-mediated partitioning of stratospheric Cl_y and NO_y at temperatures above 200 K

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Abstract. Rates of aerosol-mediated reactions involving inorganic halogen species are small but non-negligible for moderate aerosol abundances at temperatures of 200-210 K. We have used a photochemical model to demonstrate that at these temperatures such reactions provide a significant sink for HCl. Gas-phase production rates are slower for HCl than for $ClNO_3$. The net result is preferential partitioning of Cl_y into [$ClNO_3$] to compensate for the accelerated loss of [HCl]. Under such conditions, [HNO_3] decreases in response to enhanced partitioning of NO_y into [$ClNO_3$]. The results indicate a high sensitivity and synergistic response of HCl, $ClNO_3$, and HNO_3 distributions to aerosol content and temperature.

Introduction

Rates for aerosol-mediated reactions that involve HCl and $ClNO_3$ decrease approximately exponentially with increasing temperature above 200 K in response to the reduced solubility of HCl in aqueous sulfuric acid [e.g., *Hanson et al.*, 1994; *Abbatt*, 1995; *Donaldson et al.*, 1997; *Hanson*, 1998]. Nevertheless, probabilities for these reactions, although small, can be significant at temperatures between 200 and 210 K, temperatures commonly encountered in the midlatitude lower stratosphere. At high (post-volcanic) aerosol levels (>20 $\mu m^2/cm^3$) these reactions have been implicated in significant perturbations to inorganic chlorine (Cl_y) and nitrogen oxide (NO_y) species distributions and enhanced O_3 destruction at temperatures as high as 210 K [e.g., *Hofmann and Solomon*, 1989; *Prather*, 1992; *Solomon et al.*, 1993, 1998; *Rodriguez et al.*, 1994; *Hanson et al.*, 1994].

We demonstrate that even for low to moderate aerosol loading (<10 $\mu m^2/cm^3$), these reactions can play a distinct and important role in partitioning Cl_y and NO_y in the stratosphere by accelerating the photochemical destruction of HCl. Gas-phase production rates for HCl from the resulting reactive products, Cl and ClO, are slow compared to those for $ClNO_3$, and the net result is an enhancement in abundances of $ClNO_3$. Since $ClNO_3$ is readily photolyzed to produce reactive chlorine and nitrogen radicals, partitioning of Cl_y and NO_y into $ClNO_3$ instead of HCl and HNO_3 should accelerate ozone loss through catalytic cycles involving halogen- and nitrogen-oxide radicals.

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Using a model based on measured rates for aerosol reactions [*Abbatt*, 1995; *Donaldson et al.*, 1997; *Hanson*, 1998] and the assumption of photochemical steady state, we have studied the dependence of the partitioning of Cl_y and NO_y on temperature and aerosol abundance. The results of this analysis show that aerosol-mediated reactions can have a more pronounced effect than expected on the partitioning of Cl_y and NO_y at moderate temperatures (200-210 K) and aerosol abundances (3-10 $\mu m^2/cm^3$), implying a pervasive influence of these reactions throughout the lower stratosphere.

Model description

We used an updated version of the Harvard photochemical code [e.g., *Wofsy*, 1978; *Logan et al.*, 1981, *Jaeglé et al.*, 1997] to simulate the stratospheric chemistry. We included ~200 reactions, among which were the heterogeneous reactions described below, and solved for ~35 reactive species concentrations. Photolysis rates were allowed to vary throughout the day. The six-stream radiative transfer code [*Prather et al.*, 1974], used to compute photolysis frequencies, includes absorption by O_3, absorption by O_2 in the Schumann-Runge bands [*Minschwaner et al.*, 1992], Rayleigh scattering, absorption and isotropic scattering by aerosols, and reflectance by tropospheric clouds or the Earth's surface. The model ensures that the net photochemical production over a 24-hour period balances the net photochemical loss. Alternatively, the model can be run in a relaxation mode in which species concentrations evolve with time from the initial conditions.

For this study we calculated the steady-state solution, maintaining closure for the Cl_y, NO_y, and Br_y families of species, i.e., total inorganic chlorine, bromine, and nitrogen were conserved, whereas species concentrations within each family were allowed to interconvert. Kinetic parameters for the gas-phase reactions were based on recommended values [*DeMore et al.*, 1997] with modifications to the rates of $ClO+OH \rightarrow HCl+O_2$ [*Lipson et al.*, 1997], $Cl+CH_4 \rightarrow HCl+CH_3$, and $OH+HCl \rightarrow Cl+H_2O$ [*Michelsen et al.*, 1996]. Calculations included the following heterogeneous reactions:

$$N_2O_5 + H_2O\ (aerosol) \rightarrow 2HNO_3\ (aerosol) \quad (1)$$

$$BrNO_3 + H_2O\ (aerosol) \rightarrow HOBr + HNO_3\ (aerosol) \quad (2)$$

$$ClNO_3 + H_2O\ (aerosol) \rightarrow HOCl + HNO_3\ (aerosol) \quad (3)$$

$$ClNO_3 + HCl\ (aerosol) \rightarrow Cl_2 + HNO_3\ (aerosol) \quad (4)$$

$$HOCl + HCl\ (aerosol) \rightarrow Cl_2 + H_2O\ (aerosol) \quad (5)$$

$$HOBr + HCl\ (aerosol) \rightarrow BrCl + H_2O\ (aerosol) \quad (6)$$

using reactive uptake coefficient (γ) estimates derived from recent laboratory measurements [*Abbatt*, 1995; *Donaldson et al.*, 1997; *Hanson*, 1998] for liquid binary H_2SO_4/H_2O solutions (γ represents the probability that $ClNO_3$, HOCl, or HOBr will react with solvated or adsorbed HCl upon collision with the aerosol surface). We assumed a spherical particle radius of 0.5 µm, the mean value measured in the first few years following the eruption of Mt. Pinatubo [*Russell et al.*, 1996], during which time SA declined from ~30 $\mu m^2/cm^3$ to ~3 $\mu m^2/cm^3$ at 20 km [*Thomason et al.*, 1997]. Statistical corrections to the rates of reactions (4)-(6) were imposed for conditions under which the average number of solvated HCl molecules was estimated to be less than one [*Mozurkewich*, 1997].

Reaction (1) was assumed to have a constant γ of 0.1 [*DeMore et al.*, 1997]. Rates for reaction (2) were calculated from a parameterization given by D. R. Hanson (private communication, 1997). We used formulations from *Hanson* [1998] for reactions (3) and (4). The diffusion constant, effective Henry's constant, and second order rate coefficient for HOCl were taken from *Donaldson et al.* [1997] for reaction (5), and the corresponding values for HOBr, from *Abbatt* [1995] for reaction (6). The effective Henry's constant for HCl for reactions (4)-(6) were taken from *Hanson* [1998]. Sulfate weight percent and activity of water were derived from *Tabazadeh et al.* [1997]. Current values of γ are higher than previous values [*Hanson et al.*, 1994; *Hanson and Ravishankara*, 1994] by ≤26% for reaction (3), ≤100% for reaction (4), and factors of 2-8 for reaction (5) between 200 and 210 K.

Abundances of O_3 (2.1 ppm), H_2O (4.9 ppm), CH_4 (1.2 ppm), N_2O (220 ppb), C_2H_6 (12 ppt), CO (12 ppb), Cl_y (1.6 ppb), NO_y (6.1 ppb), and Br_y (15 ppt) input into the model were held constant. Albedo was assumed to be 0.25, aerosol optical depth was given as 0.13 at 310 nm with a wavelength (λ) dependence of $1/\lambda$. Calculations presented here were performed for a latitude of 45°N and pressure of 55 mbar (~20 km) at equinox unless otherwise noted.

Results

Figure 1a shows the calculated temperature dependence of the steady-state values of [HCl] and [$ClNO_3$] for a (background, i.e., non-volcanic) aerosol surface area density (SA) of 1 $\mu m^2/cm^3$. At temperatures above 198 K [HCl] exceeds [$ClNO_3$], which is generally the case throughout the stratosphere [e.g., *Notholt et al.*, 1995; *Dessler et al.*, 1995; *Michelsen et al.*, 1996]. Below 198 K, however, $ClNO_3$ is the dominant reservoir for Cl_y. Aerosol-mediated reactions are responsible for this redistribution of Cl_y at temperatures below the "transition temperature", T_{trans}, of 198 K. If heterogeneous reactions were neglected, [HCl] would exceed [$ClNO_3$] at all temperatures. Since this mechanism for redistributing Cl_y depends on reactions mediated by aerosol particles, the partitioning of Cl_y is predictably sensitive to SA; an increase in SA leads to an increase in T_{trans}. For a SA of 5 $\mu m^2/cm^3$, T_{trans} is calculated to occur at ~201 K (Fig. 1b), and a (post-volcanic) SA of 20 $\mu m^2/cm^3$ yields a value for T_{trans} of ~204 K (Fig. 1c).

At temperatures lower than the transition temperature, aerosol-mediated reactions repartition Cl_y by reducing the lifetime of HCl. The decomposition rate for HCl attributable to these reactions at temperatures less than T_{trans} exceeds the rate of loss via reaction with OH, which is the dominant gas-phase destruction mechanism for HCl. Rates for reactions (3)-(6) increase approximately exponentially with decreasing temperature. As a result, the chemical lifetime of HCl declines markedly with temperature between 210 and 200 K (from 37 days to 11 days for SA≈5 $\mu m^2/cm^3$). Photolysis is the dominant sink for $ClNO_3$, on the other hand, and enhanced loss through reactions (3) and (4) has little effect on the $ClNO_3$ lifetime when UV radiation is available; the lifetime of $ClNO_3$ is nearly the same at 210 and 200 K (14.3 vs 13.6 hours for SA≈5 $\mu m^2/cm^3$).

Reactions (4) and (5) contribute the most significantly to aerosol-mediated loss of HCl. In the temperature range at which $ClNO_3$ is the major Cl_y reservoir, the rate for reaction (5) is comparable to that of OH+HCl. The rate for reaction (4) is only 35% slower (reaction (6) is 90% slower) than loss via OH+HCl.

At temperatures 2-3 K below the transition temperature, [$ClNO_3$] reaches a maximum from which it declines with decreasing temperature. At these lower temperatures reaction (3) makes a more significant contribution to the Cl_y partitioning. For SA=5 $\mu m^2/cm^3$, for example, reaction (3) destroys $ClNO_3$ at a rate only a factor of six slower than that of photolysis at 196 K (at 200 K the difference is a factor of 20). In addition, at 196 K this reaction proceeds six times faster than $OH+NO_2$, the principal gas-phase source of HNO_3, making $ClNO_3$ hydrolysis the major production mechanism for HNO_3. Thus, reaction (3) leads to a redistribution of NO_y that favors HNO_3 over $ClNO_3$ at temperatures several Kelvin below T_{trans}. Under these conditions, HCl is lost predominantly via reaction (5), which proceeds ~30 times faster than OH+HCl and 3 times faster than reaction (4). Despite the enhancement in reaction (3) under these low-temperature conditions, the major source of HOCl is the gas-phase reaction $ClO+HO_2$, which proceeds ~9 times faster than $ClNO_3$ hydrolysis. The set of reactions that contributes most significantly to enhanced heterogeneous loss of HCl under these conditions can thus be summarized as follows:

$$ClO + HO_2 \rightarrow HOCl + O_2 \qquad (7)$$

$$HOCl + HCl\ (aerosol) \rightarrow Cl_2 + H_2O\ (aerosol) \qquad (5)$$

$$ClO + HO_2 + HCl\ (aerosol) \rightarrow Cl_2 + H_2O + O_2\ (aerosol) \qquad (8)$$

Molecular chlorine is rapidly converted to Cl via photolysis, and Cl generates ClO by reacting with O_3, making the above cycle autocatalytic. Since neither HCl nor $ClNO_3$ is lost predominantly via reaction (4) in either temperature regime below T_{trans}, the aerosol-mediated activation of HCl and $ClNO_3$ is not stoichiometrically linked for the conditions studied here.

Figure 2 shows the dependence of T_{trans} on SA for values ranging from 1-30 $\mu m^2/cm^3$. At SA less than ~5 $\mu m^2/cm^3$, T_{trans} increases rapidly with increasing SA, whereas at SA greater than 20 $\mu m^2/cm^3$, T_{trans} increases slowly and nearly saturates at SA exceeding ~40 $\mu m^2/cm^3$.

Fig. 2 also demonstrates the effect of a change in solar irradiance. A(n) decrease (increase) in the average daily photolysis rate of $ClNO_3$ with a(n) decrease (increase) in the length of day or increase (decrease) in mean solar zenith angle will shift the partitioning of Cl_y in the favor of $ClNO_3$ (HCl), thus increasing (decreasing) the transition temperature. At equinox the length of day is maintained while the mean solar zenith angle is increased with increasing latitude, thereby leading to higher values of T_{trans} at 65 relative to 45°N. Likewise, calculations for summer solstice yield lower values of T_{trans} than those for equinox, whereas those for winter solstice yield higher values. In general, conditions that enhance $ClNO_3$ production or reduce its loss will tend to shift T_{trans} to higher values; those that favor HCl will lower T_{trans}. An increase in $[O_3]$ by 20% increases T_{trans} by 1.5 K, an increase in $[CH_4]$ by 20% decreases T by ~0.5 K, and an increase in $[H_2O]$ by 20% or aerosol radius by a factor of two, both of which lead to faster rates for reactions (3)-(6), increases T_{trans} by ~1 K. Under certain conditions (e.g., high $[O_3]$ or $[H_2O]$, low UV radiative flux), decomposition of HCl via these reactions can be important at temperatures as high as 210 K for moderate aerosol loading, despite small values (10^{-1}-10^{-5}) of γ for reactions (3)-(6).

As shown in Fig. 1, the temperature response of the Cl_y partitioning is highly non-linear over a 2-5 K range near the transition temperature. When temperatures fall below this value, the atmosphere is driven rapidly toward equilibrium conditions for which $[ClNO_3]>[HCl]$. When temperatures increase, however, relaxation to steady state is limited by the slow rate of the gas-phase reaction $Cl+CH_4$. The asymmetry between these rates leads to hysteresis in the temperature response of the Cl_y partitioning [*Hanson et al.*, 1994; *Müller et al.*, 1994; *Murphy and Ravishankara*, 1994; *Borrmann et al.*, 1997]. Temperature oscillations about a mean temperature above T_{trans} will lead to calculated values of $[HCl]/[ClNO_3]$ that are lower than values calculated for the mean temperature if these oscillations allow the instantaneous temperature to periodically drop below T_{trans}. Thus, calculations based on temporal or spatial averages of temperatures will systematically underestimate ozone loss rates when the atmosphere is near the transition temperature.

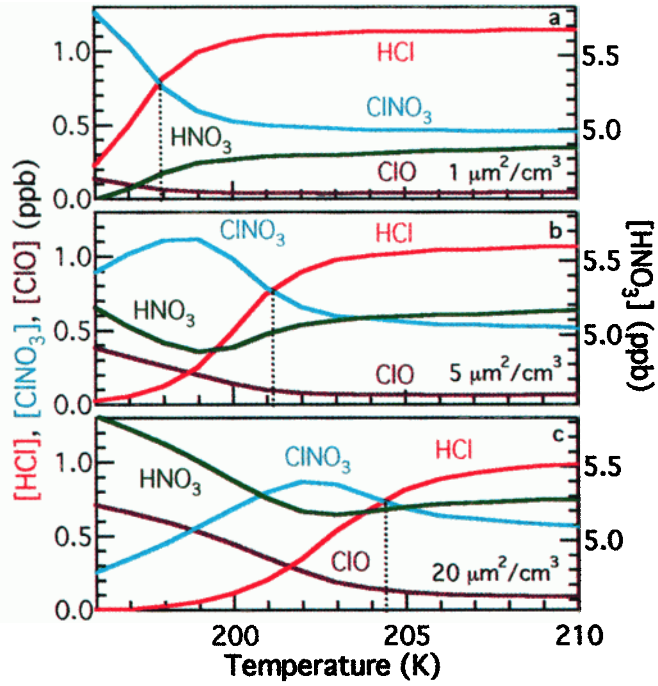

Figure 1. Calculated steady-state mixing ratios are shown for HCl (magenta), $ClNO_3$ (cyan), ClO (purple), and HNO_3 (green) relative to temperature. Calculations were performed for values of SA of (a) 1, (b) 5, and (c) 20 $\mu m^2/cm^3$, latitude of 45°N, altitude of ~20 km, and solar declination of 0.0 (equinox).

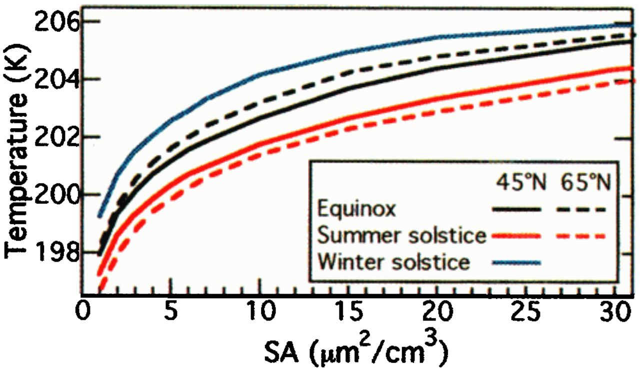

Figure 2. The SA dependence of T_{trans} is demonstrated for latitudes of 45°N (solid) and 65°N (dashed) for an altitude of ~20 km at equinox (black) and summer (red) and winter (blue) solstice.

Reactions (2)-(6) also influence the distribution of reactive nitrogen species. Despite the enhanced heterogeneous production of HNO_3 via reactions (2)-(4), the net effect of reactions (2)-(6) just below T_{trans} is a reduction in $[HNO_3]$. Since reaction (5), which does not produce HNO_3, contributes the most significantly to the heterogeneous redistribution of Cl_y and hence NO_y, the result is a preferential partitioning of NO_y into $ClNO_3$.

At temperatures below T_{trans}, ~50% of the enhancement in $[ClNO_3]$ is balanced by a reduction in $[HNO_3]$ (Fig. 1), ~35% by a decrease in $[NO_x]$ (=$[NO]+[NO_2]$), and the remainder by loss of other NO_y species. Although $ClNO_3$ photolyzes more readily than HNO_3 (The HNO_3 lifetime is 20 days compared to that of $ClNO_3$ of 14 hrs.), depletion of $[HNO_3]$ in favor of $[ClNO_3]$ does not enhance production of reactive nitrogen radicals [NO] and $[NO_2]$. Reactions (2)-(6) suppress $[NO_x]$ by accelerating the rate of $ClO+NO_2$, which leads to a 50-60% reduction in $[NO_x]/[HNO_3]$. With regard to ozone destruction, the aerosol-initiated enhancement in [ClO] (shown in Fig. 1 for noontime values) is not balanced by this suppression of $[NO_x]$, and the net effect of including these reactions is a promotion in the calculated ozone loss rates.

Implications

Evidence for the effects of these reactions is provided by measurements of low $[HCl]/[Cl_y]$ [*Webster et al.*, 1998], high $[BrO]/[Br_y]$ [*Eisinger et al.*, 1997], and low $[NO_x]/[NO_y]$ [*De Mazière et al.*, 1998] for moderate (3-8 $\mu m^2/cm^3$) SA at northern midlatitudes in spring 1993 (almost 2 years after the Mt. Pinatubo eruption). If reactions (2)-(6) had been responsible for values of 0.4 for $[HCl]/[Cl_y]$ [*Webster et al.*, 1998], these reactions would have led to an enhancement in ozone loss rates by factors of 3-5 over conditions for which $[HCl]/[Cl_y]\approx0.8$, as is characteristic of high temperatures (>210 K) and low SA (~1 $\mu m^2/cm^3$) [*Webster et al.*, 1998].

Reactions (2)-(6) may also have been responsible for the increased $[ClNO_3]$ and decreased [HCl] observed in the Arctic vortex early in the 1992/93 winter [*Blom et al.*, 1995; *Notholt et al.*, 1995]. Similarly, these reactions may have led to values of $[ClNO_3]$ in excess of [HCl] early in the Arctic winter of 1991/92, as inferred by *Webster et al.* [1993] from measurements of [HCl] and [ClO] in pre-PSC-processed air.

Fig. 2 shows that, even under background aerosol loading, these reactions could be important in repartitioning Cl_y and NO_y early in the winter as temperatures approach 200 K.

Conditions conducive to repartitioning of halogen and nitrogen reservoirs will become more common at midlatitudes as the stratosphere cools [*WMO/UNEP*, 1995] in response to decreasing ozone abundance, providing positive feedback and leading to increased ozone depletion in the lower stratosphere. This trend, coupled with other possible trends that enhance the rates of reactions (2)-(6), such as an increase in stratospheric humidity [*Oltmans and Hofmann*, 1995], aerosol loading [*Hofmann*, 1990], and bromine content [*Wamsley et al.*, 1998], places the stratosphere in a state susceptible to significant loss of midlatitude ozone, particularly under moderate to high aerosol loading following future volcanic eruptions.

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