Uncertainties in reactive uptake coefficients for solid stratospheric particles—2. Effect on ozone depletion

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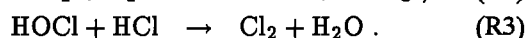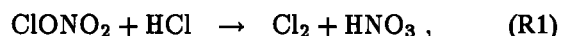Max Planck Institute for Chemistry, Mainz, Germany

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Abstract. Uncertainties in reactive uptake coefficients for reactions involving HCl, $ClONO_2$ and HOCl on nitric acid trihydrate (NAT) and sulfuric acid tetrahydrate (SAT) are shown to affect modeled Arctic stratospheric ozone depletion in a photochemical box model. The main contribution to the difference arises from the reaction $ClONO_2 + HCl \rightarrow Cl_2 + HNO_3$ in early to mid-winter. During this period, differences in predicted HCl and $ClONO_2$ are more than 1 ppbv for several weeks when an upper limit for solid PSC existence is assumed. Ozone depletion is greater when liquid aerosols persist through the winter compared with cases where solid particles are assumed to form.

Introduction

The most important heterogeneous reactions leading to activation of chlorine reservoir gases in the polar stratosphere are

$$ClONO_2 + HCl \rightarrow Cl_2 + HNO_3, \quad (R1)$$
$$ClONO_2 + H_2O \rightarrow HOCl + HNO_3, \quad (R2)$$
$$HOCl + HCl \rightarrow Cl_2 + H_2O. \quad (R3)$$

In companion paper I it was shown that various laboratory measurements for these key reactions on frozen stratospheric aerosol materials (NAT and SAT) could differ considerably when extrapolated to typical stratospheric conditions. Here, we investigate the potential effect of these uncertainties on modeled chlorine activation and ozone destruction in a photochemical box model for typical Arctic conditions.

Uptake Rates Under Stratospheric Conditions

Two different schemes for reactions R1-3 on solid particles are considered, see Table 1. Scheme 1 is considered to be an upper limit of the reactive uptake coefficients, and is based on the measurements of *Hanson and Ravishankara* [1993]. Scheme 2, a lower limit, is derived from the measurements of *Abbatt and Molina* [1992a,b] on NAT and *Zhang et al.* [1994] on SAT, as described in paper I.

Figure 1 shows calculated uptake coefficients under stratospheric conditions, as well as the approximate reaction lifetime of $ClONO_2$ or HOCl (τ) for a particle surface area of 10

μm^2 cm^{-3}. For reaction R1 on NAT, the two schemes are in reasonable agreement at the ice frost point (2 hrs $< \tau <7$ hrs), but differ substantially just below the NAT formation temperature (1 day $< \tau < 3$ months). It is therefore under marginal PSC conditions close to the NAT equilibrium temperature that uncertainties in reaction rates will be most important for calculations of chlorine activation.

The rate of reaction $ClONO_2 + H_2O$ on NAT and SAT is also uncertain. *Henson et al.* [1996] have shown that the variation of γ_{ClONO_2} with water partial pressure and temperature can be well described in terms of the humidity. They restricted their analysis to the data of *Abbatt and Molina* [1992a] for NAT and *Zhang et al.* [1994] for SAT. However, as shown in Fig. 1, the measured uptake coefficients of *Hanson and Ravishankara* [1993] for NAT are systematically higher, by as much as a factor of 6-7 at the NAT equilibrium temperature. We take the *Hanson and Ravishankara* [1993] measurements as an upper limit of γ_{ClONO_2} (scheme 1), and those of *Abbatt and Molina* [1992a] as a lower limit (scheme 2). The measurements of *Zhang et al.* [1994] and *Hanson and Ravishankara* [1993] for this reaction are in reasonable agreement for SAT.

The Photochemical Box-Model

The Mainz photochemical box model is described by *Müller et al.* [1994]. A comprehensive set of chemical reactions is integrated using the Gear-code method FACSIMILE [*Curtis and Sweetenham*, 1987], and photolysis rates are calculated by the method of *Lary and Pyle* [1991]. Here, we describe only the updated aspects of the model that are important to the present work.

The model includes ternary HNO_3-H_2SO_4-H_2O liquid aerosols with an equilibrium composition calculated according to *Carslaw et al.* [1995]. The solubility of HOCl is calculated according to *Huthwelker et al.* [1995] and that of HCl from *Luo et al.* [1995]. Reactions R1-3 are included for the liquid aerosols, with rates calculated using expressions given by *Hanson and Ravishankara* [1994] and *Hanson et al.* [1994]. The reaction $N_2O_5 + H_2O$ is included with $\gamma = 0.1$.

Particle phase transitions. Transitions between liquid, NAT, SAT and ice particles are complex, and still not fully understood [*Peter*, 1997]. Most important to this work, it remains uncertain what proportion of stratospheric aerosols are solid or liquid at any one time. To examine the effect of different solid phase reaction schemes, we adopt the scenario for solid particle formation shown in Fig. 2, assuming that HNO_3-H_2SO_4-H_2O droplets freeze completely (to form NAT and SAT) at the NAT equilibrium temperature. We note

Table 1. Heterogeneous parameters used in photochemical box model simulations.

Reaction	scheme 1	scheme 2

$CIONO_2 + HCl^{(a)}$	on NAT:
	 $\gamma_0 = 0.7022\exp[-0.518(T - T_{ice})]$
	 $1/\gamma = 1/0.23 + 1/[\gamma_0 \times (p_{HCl}/7.5 \times 10^{-8}\text{torr})^{0.6}]$
	 on SAT:
	 $1/\gamma = 1/0.23 + 1/\exp[-0.636 - 0.4802(T - T_{ice})]$ [note b]
	 T_{ice} = ice frost point
	 Hanson and Ravishankara [1993]
		$1/\gamma = 1/\alpha + 1/A\theta_{HCl}$
		 $\theta_{HCl} = K_{HCl}p_{HCl}$
		 on NAT: $K_{HCl} = \exp(-1.8 + 8.7s_{ice})$ Pa^{-1}
		     $A = 8.2$, $\alpha = 0.3$
		 on SAT: $K_{HCl} = \exp(0.59 + 7.3s_{ice}^{1/2})$ Pa^{-1}
		     $A = 1.1$, $\alpha = 0.1$
		 Eqns. from companion paper I

$HOCl + HCl^{(c)}$	as in scheme 2	$1/\gamma = 1/\alpha + 1/A\theta_{HCl}$ on NAT: $A = 5.1$, $\alpha = 0.15$
$CIONO_2 + H_2O$	on NAT: $\gamma = \exp(-9.03 + 2.81s_{ice})$ *Hanson and Ravishankara* [1993] on SAT: γ as in scheme 2	on NAT: $\gamma = \exp(-11.47 + 4.97s_{ice})$ on SAT: $\gamma = \exp(-7.41 + 2.94s_{ice})$ see note d

Other uptake coefficients in the box model were taken from *DeMore et al.* [1994].

[a] In scheme 2, R1 is assumed to depend linearly on the HCl partial pressure, as described in paper I. In scheme 1 we use *Hanson and Ravishankara*'s parameterized uptake coefficient expression appropriate for 1-2 ppbv at 50 torr (their Eqs. 1 and 3) and assume a weak variation with HCl partial pressure of $\gamma \propto p_{HCl}^{0.6}$, as suggested by their additional measurements for a range of p_{HCl}.

[b] To prevent $\gamma > 1$ a limit of 0.23 was used for γ_{CIONO_2} on SAT, as recommended by *Hanson and Ravishankara* [1993] for NAT.

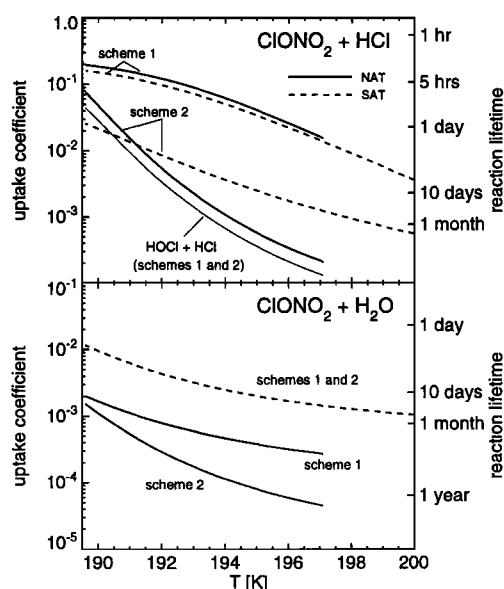[c] The fitted data of *Abbatt and Molina* [1992b] were used in both schemes (see companion paper I).

[d] Functions were fitted to data of *Abbatt and Molina* [1992a] for NAT and *Zhang et al.* [1994] for SAT.

that the scenario in Fig. 2 likely produces close to an upper limit for the frequency with which solid particles occur. Using this upper limit for solid particle existence, combined with upper and lower limits for reaction rates on the solid particles, allows the maximum likely uncertainties (for example, in ozone depletion) due to solid phase kinetics to be examined. A further uncertainty in trying to calculate chlorine activation and ozone loss is, of course, how often solid particles actually exist. This may be important since, as shown

Figure 1. Reactive uptake coefficients under stratospheric conditions (60 mb pressure, 5 ppmv H_2O, 2 ppbv HCl). Solid lines – reactions on NAT; dashed lines – reactions on SAT. Uptake coefficient expressions are given in Table 1. Reaction lifetime $\tau = 4/\bar{v}A$, where $\bar{v}$ is the mean molecular speed of $CIONO_2$ and A is the particle surface area density (10 μm^2 cm^{-3}). Uptake coefficients for NAT are given only below the NAT equilibrium temperature with 10 ppbv HNO_3. The lower temperature in the figure is the ice frost point.
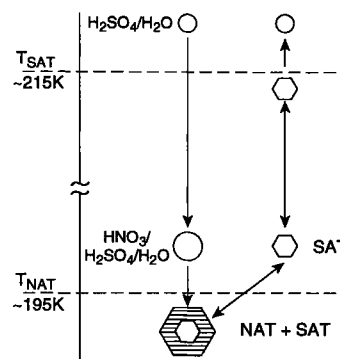
by *Ravishankara and Hanson* [1996], reaction rates on solid and liquid particles can be different. The effect of liquid versus solid heterogeneous processing is explored below.

Trajectory and Initialisation. The long-term trajectory (1 December - 15 April) of a typical air parcel confined within the Arctic vortex was simulated for the winter 1994/95 by imposing a latitude oscillation from 58 to 78°N as well as a temperature oscillation of ±10 K amplitude, with maximum and minimum temperatures adjusted to agree with ECMWF polar vortex analyses. Further, the air parcel was assumed to descend from a potential temperature of 625 K in late November to 425 K in late March, as derived from HALOE methane measurements for the 1994/95 winter. Such simulated trajectories [*Müller et al.*, 1994; *Brühl et al.*, 1996] serve as a useful test-bed for comparison between different chemical schemes within the well-defined conditions of the vortex, although do not allow the motion of a real air parcel to be followed.

Mixing ratios of O_3 (3.6 ppmv), H_2O (5.4 ppmv), HCl (1.77 ppbv), NO, NO_2 and CH_4 were initialised using observations from HALOE inside the vortex on 1 December 1994. Total inorganic chlorine ClX (3.14 ppbv) was initialised from HALOE HF and a ClX – HF correlation with

Figure 2. Particle phase transitions used in the box model simulations.

latitude and season-dependent coefficients obtained from results of the Mainz two-dimensional chemistry model (Grooß, 1996). Initial partitioning between HCl, $ClONO_2$ (1.19 ppbv), HOCl and ClO was also determined from the Mainz 2-D model, as well as NOy (14.1 ppbv) from the model NOy – HF correlation. The amount of sulfuric acid aerosol at the beginning of the trajectory was adjusted to agree with aerosol surface areas derived from HALOE extinction measurements and amounted to 0.4 ppbv H_2SO_4 in the air parcel.

Results

Figure 3 shows the air parcel temperature (a), NAT, SAT and liquid surface areas (b), mixing ratios of $ClONO_2$ and HCl (c), $ClO + 2 \times Cl_2O_2$ (d), ozone loss rate (e), and ozone mixing ratio (f).

The differences between reactive uptake coefficients in the two schemes lead to significant differences in the amount of activated chlorine (d) and hence in the rate of ozone loss

Figure 3. Box model results for the Arctic winter 1994/95 assuming particle phase transitions in Fig. 2. Thin lines – using scheme 2 in Table 1; thick lines – scheme 1. In (d) $2 \times Cl_2O_2 + ClO$ are noontime values. Ozone depletion rates are 5 day means. Particle surface areas are approximately the same in both cases.

(e), particularly in December and early January. The greatest contribution to the difference is due to the reaction $ClONO_2$ + HCl; complete HCl depletion is predicted to occur by mid-December using scheme 1, but only by late January using scheme 2. The ozone destruction rate during this period is up to a factor 4 higher with scheme 1. The calculated ozone loss by the end of the winter is 2.3 ppmv (corresponding to 64%) with scheme 1, compared with only 1.8 ppmv (50%) with scheme 2. *Henson et al.* [1996] present an alternative formulation for reaction R1, yielding uptake coefficients of up to a factor 40 lower than *Hanson and Ravishankara* [1993]. Replacing these in our scheme 2 yields ozone loss of 2.1 ppmv, midway between our schemes 1 and 2.
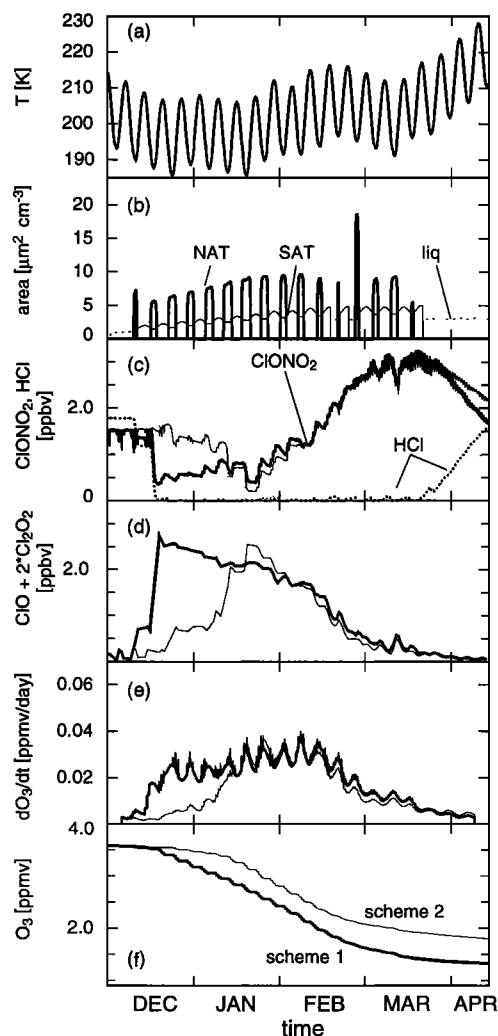
The reaction $ClONO_2$ + H_2O (R2) on solid particles is much less important as a source of active chlorine than the reaction with HCl; even with a NAT surface area of 10 μm^2 cm^{-3} the reaction lifetime of $ClONO_2$ is on the order of 10 days close to the ice frost point (Fig. 1). Furthermore, the greatest difference in γ_{ClONO_2} between schemes 1 and 2 occurs close to the NAT equilibrium temperature, where the reaction lifetime is longer than a month. Differences between the two schemes regarding reaction R3 are therefore unimportant.

We have made similar comparisons for the winters 1992/3, 1993/4 and 1995/6, and find, as in Fig. 3, that the ozone destruction rates differ significantly only while HCl concentrations remain high, which is typically until mid- to late January. The greatest difference is predicted to occur during the winter 1993/4, which was comparably warm [*Naujokat et al.*, 1994], leading to sporadic and infrequent NAT formation and O_3 destruction rates in January up to 5 times higher using scheme 1 compared with scheme 2. This large effect can be explained by the large differences in reactivity when temperatures are close to the NAT formation temperature (Fig. 1).

Role of Liquid Aerosols

Sensitivity calculations were also performed assuming that only liquid aerosols existed throughout the winter (results not shown). All the reactions R1-3 are faster on liquids than on NAT and SAT [*Ravishankara and Hanson*, 1996]. For the winter 1994/95 shown in Fig. 3, ozone loss was calculated to be almost identical to the results using scheme 1 (thick lines) until mid-March. This is because the higher uptake coefficient for reaction R1 on liquids [*Ravishankara and Hanson*, 1996] is compensated by the shorter duration of large liquid surface areas when compared with NAT in equilibrium. In mid-March, the brief cold period led to rapid conversion of $ClONO_2$ to HOCl with liquid aerosols, due to the approximate factor 10 higher uptake coefficient for reaction R2 compared with NAT [*Ravishankara and Hanson*, 1996]. This led to a further 0.3 ppmv ozone loss beyond that calculated using scheme 1 in Fig. 3.

Further sensitivity model runs were made assuming that NAT forms only 3 K below the NAT equilibrium temperature. This substantially reduces the frequency with which NAT occurs, but leaves the frequency of SAT occurrence almost unchanged. This led to 2.1 ppmv O_3 loss with scheme 1 and 1.7 ppmv with scheme 2, which is less than the depletion in Fig. 3 mainly because of the lower particle surface areas that result from suppressing NAT formation. A fourth case in which NAT formed at the NAT equilibrium tempera-

ture, but upon evaporation released liquid aerosols instead of SAT, led to 2.5 ppmv loss with scheme 1 (very close to that predicted assuming liquid aerosols only) and 2.3 ppmv using scheme 2. These preliminary comparisons indicate that the presence of liquid aerosols can enhance ozone depletion rates beyond those calculated assuming that solid particles predominate (using either scheme 1 or 2). More thorough investigations are required to fully understand these differences.

Discussion

It is commonly assumed that the occurrence of NAT PSCs leads to the rapid heterogeneous conversion of $ClONO_2$ and HCl to Cl_2 within a period that is short compared to the overall process of ozone destruction. We have shown here that existing laboratory measurements for this reaction are consistent with a lifetime of these species of between about 3 months and a few hours for temperatures between the NAT equilibrium temperature and the ice frost point. Because the predicted uptake coefficients cannot always be considered fast on the timescale of ozone destruction, the large uncertainties that exist in their measurement do strongly affect the extent of ozone depletion on the timescale of an Arctic winter.

Model simulations using the minimum likely uptake coefficients on solid particles (scheme 2 in Table 1) predict ozone destruction that is less than estimated from HALOE observations in the winter 1994/95 Arctic vortex (1.8 ppmv compared with 2.5 ppmv [Brühl et al., 1996]). A reliable comparison with observations is difficult due to the idealised nature of the trajectory that was used, and the significance of this difference should be interpreted with caution. However, it is worth noting from this preliminary study that the significantly lower reactive uptake coefficients used in scheme 2 cannot be excluded.

These simulations probably represent an upper limit to the difference in model-calculated ozone loss due to uncertainties in solid particle heterogeneous reaction rates. The results suggest that care should be taken when comparing with observations, either with long-term simulations, but particularly with individual case studies. These uncertainties in O_3 depletion must be compared with those arising from uncertainties in the phase of PSCs [Ravishankara and Hanson, 1996], which could be of the same order. Heterogeneous processing rates on liquids are generally faster than on solids, and the long-term simulations shown here suggest that one consequence of solid PSC formation may be to reduce chlorine activation and ozone depletion.

A key indicator of which scheme is operating in the stratosphere is the amount of HCl in early winter. Simultaneous observations of HCl and measurements of aerosol phase along air-parcel trajectories would help to better define the role of PSC phase in ozone depletion.

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