Modeling Studies of the Effects of the Heterogeneous Reaction ClOOCl + HCl → Cl2 + HOOCl on Stratospheric Chlorine Activation and Ozone Depletion

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Modeling studies of the effects of the heterogeneous reaction ClOOCl + HCl → Cl₂ + HOOCl on stratospheric chlorine activation and ozone depletion

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Abstract. The heterogeneous reaction ClOOCl + HCl → Cl₂ + HOOCl was introduced into a chemical trajectory model of the stratosphere. Ten-day trajectories ending at ozonesonde stations at various northern latitudes were run to simulate the period January–March 1994. The reaction on sulfuric acid aerosol surfaces has a negligible effect on ozone chemistry if a sticking coefficient similar to that of ClONO₂ + HCl is assumed. On polar stratospheric cloud (PSC) surfaces the chemical effects of the addition of this reaction depend on the fate of proposed product HOOCl: if this species photolyzes to produce either ClO + OH or Cl + HO₂, then HCl is activated by the reaction with chlorine peroxide. This heterogeneous activation of chlorine by active chlorine can have a significant effect on Arctic ozone depletion rates in the days following an air parcel's encounter with PSC surfaces. The ozone depletion rate usually increased but in some cases decreased, depending on the extent of PSC processing and on the initial [HCl]/[ClONO₂] ratio. Averaged over 3 months, the column ozone loss rates between 350 and 675 K were accelerated by as much as 35% for a set of 10-day trajectories ending at an Arctic station. If, on the other hand, HOOCl decomposes at the surface into HCl and O₂, the net effect of these reactions is to convert ClOOCl into Cl₂. These species are functionally equivalent, and such a conversion does not perturb the model chemistry.

Introduction

The behavior of halogenated gases in the atmosphere has been a subject of great interest since the 1970s, when it was realized that industrially produced, long-lived chlorofluorocarbons (CFCs) were accumulating in the global atmosphere [Lovelock et al., 1973]. Assumed at first to be benign atmospheric tracers, CFCs were soon recognized as potentially damaging to the stratospheric ozone layer [Molina and Rowland, 1974]. The addition of CFCs has now increased the total amount of stratospheric chlorine to more than 5 times natural levels [Russell et al., 1996], resulting in the formation of the "ozone hole" over Antarctica [Farman et al., 1985; Solomon et al., 1986]. Current models of the global stratosphere predict that total chlorine will remain at unacceptably high levels, even with a tight ban on CFC production, until the year 2050 [Dowdell et al., 1994].
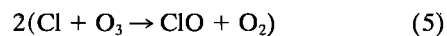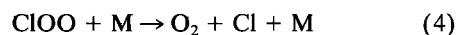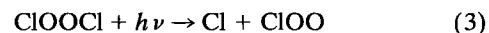
Inorganic, halogen-containing molecules in the atmosphere are divided into two categories, active and inactive, referring to their ability to catalyze ozone depletion. Chlorine and bromine have a more variable atmospheric chemistry than the other two halogens. Fluorine has no known activation pathways [Hanson and Ravishankara, 1992a], and iodine is typically 90% activated [Solomon et al., 1994]. BrO, on the other hand, has a large diurnal variation [Avallone et al., 1995], and chlorine exhibits huge spatial and temporal variations in the concentrations of inactive (e.g., HCl and ClONO₂) and active forms (e.g., ClO

and ClOOCl) [Crewell et al., 1995]. Chlorine is also unique in that its activation depends mainly on several "heterogeneous" chemical reactions that occur at polar stratospheric cloud (PSC) surfaces and on sulfuric acid aerosol (SAA) [Webster et al., 1993]. Significant chlorine activation therefore occurs only where there are large numbers of these particles present, such as in the cold polar stratosphere during winter and spring.

A heterogeneous reaction between active and inactive forms of chlorine has been recently identified [De Haan, 1994; D. O. De Haan and J. W. Birks, Kinetics of the heterogeneous reactions of chlorine peroxide with halide ions, submitted to Journal of Physical Chemistry, 1996, hereinafter referred to as DB96]:

$$\text{ClOOCl} + \text{HCl} \rightarrow \text{Cl}_2 + \text{HOOCl} \qquad (1)$$
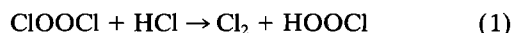
Chlorine peroxide (ClOOCl) is a nighttime reservoir of active chlorine and an intermediate in the most important "ozone hole" catalytic cycle:

$$\text{ClO} + \text{ClO} + \text{M} \leftrightarrow \text{ClOOCl} + \text{M} \qquad (2)$$

$$\text{ClOOCl} + h\nu \rightarrow \text{Cl} + \text{ClOO} \qquad (3)$$

$$\text{ClOO} + \text{M} \rightarrow \text{O}_2 + \text{Cl} + \text{M} \qquad (4)$$

$$2(\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2) \qquad (5)$$

$$\text{Net} \qquad 2\text{O}_3 \rightarrow 3\text{O}_2$$

Hydrochloric acid (HCl), the second reactant in (1), is the most common form of inactive chlorine in the atmosphere, although it is occasionally surpassed by chlorine nitrate (ClONO₂), especially at high latitudes [Webster et al., 1994]. The discovery of the heterogeneous reaction between chlorine peroxide and

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Table 1. Heterogeneous Reactions Included in "Normal Case" Model

	Surface Reaction Probability γ	
Reaction	NAT	SAA
$ClONO_2 + H_2O \rightarrow HOCl + HNO_3$	0.006	$10^{(1.86-0.0747(W))}*$
$ClONO_2 + HCl \rightarrow Cl_2 + HNO_3$	0.3	$0.1\ (10^{(1.86-0.0747(W))})\dagger$
$HOCl + HCl \rightarrow Cl_2 + H_2O$	0.1	$0.1\ (10^{(1.86-0.0747(W))})\ddagger$
$N_2O_5 + H_2O \rightarrow 2\ HNO_3$	0.0006	0.1
$N_2O_5 + HCl \rightarrow ClNO + HNO_3$	0.003	0

Reaction probabilities are not corrected for small particle size in the model. All heterogeneous reaction probabilities are based on the Jet Propulsion Laboratory summary [DeMore et al., 1992] except as noted. W is weight percent H_2SO_4.

*Hanson and Ravishankara [1991a].

†Upper limit [Hanson and Ravishankara, 1991a].

‡Approximation based on work by Hanson et al. [1994, Figure 4].

hydrochloric acid has raised several questions. First, could such a reaction ever occur to a significant extent in the stratosphere? If so, could it affect chlorine peroxide concentrations? Could ozone loss rates and chlorine partitioning be affected by this reaction? Because of the large variations in concentrations of ClOOCl, HCl, and the necessary reaction surfaces in the atmosphere, we used a chemical trajectory model to answer these questions and to estimate the potential contribution of this reaction to chlorine activation and ozone depletion throughout the northern stratosphere.

Methods

The Norwegian Institute for Air Research (NILU) chemical trajectory model follows discrete air parcels as they move over surfaces of constant potential temperature, driven by wind fields obtained from the European Centre for Medium-Range Weather Forecasts (ECMWF). Ten-day back trajectories of air parcels arriving daily (at local noon) at particular measurement stations or grid points in the northern hemisphere were calculated based on ECMWF analyses [Knudsen and Carver, 1994]. The model uses a 150+ reaction chemistry code adapted from the Oslo two-dimensional (2-D) model [Isaksen et al., 1990; Stordal et al., 1985]; the heterogeneous reactions included in the model are listed in Table 1. A two-stream radiative scheme is used to generate photolysis rates [Isaksen et al., 1977]. Rate constants were taken from the NASA summary [DeMore et al., 1992], while sulfuric acid aerosol surface areas were adopted from Stratospheric Aerosol and Gas Experiment (SAGE) field measurements [Trepte et al., 1993; L. Thomason, personal communication, 1994].

PSC formation was simulated by a detailed microphysical module [Larsen, 1991], which used temperature and pressure histories and local mixing ratios of HNO_3 and H_2O to predict condensation events. In this three-stage model, frozen sulfate aerosol particles act as nucleation centers for type I PSCs (assumed to be nitric acid trihydrate (NAT)) when temperatures are low enough for nitric acid vapor to become supersaturated with respect to NAT. NAT particles will in turn serve as nucleation centers for type II PSCs (assumed to be ice crystal particles) when temperatures drop below the ice frost point. The microphysical module computes particle composition, size distribution, and surface area, which are greatly affected by the

cooling rates encountered by the air parcel. The calculations of Luo et al. [1994] indicate, however, that frozen sulfuric aerosol cores are not likely to form, thus eliminating solid nucleation sites on which NAT can directly condense. This has led to a new model of particle condensation into a liquid ternary solution ($HNO_3/H_2SO_4/H_2O$) [Carslaw et al., 1994], which is currently being introduced into our microphysical module. The old three-stage model may generate PSC surface areas which are too large between 191 and 196 K, but too small as temperatures approach the frost point at 188 K [Carslaw et al., 1994]. These errors add a fundamental uncertainty to our estimates of the extent of any type of heterogeneous processing. Since the purpose of our study is to define limits for the potential significance of the reaction ClOOCl + HCl in the stratosphere, such differences should not be crucial.

The chemistry is initialized at the starting latitude by monthly output from the Oslo 2-D model. As there is often a difference in time of day between the initialization conditions (noon) and the trajectory starting time, all chemical changes are computed as compounded growth or loss rates using only the last 9 days of the trajectory, after the diurnal equilibria have been reestablished in the model.

Since a 10-day trajectory contains a realistic history of solar zenith angle and temperature changes, if the radiative structure and condensation behavior in the atmosphere can be accurately modeled, then the trajectory can be used as the basis of simulations of photochemical and heterogeneous processing. We report here tests of the effects of a heterogeneous reaction of a photolabile species (ClOOCl) on the concentrations of chemicals in an air parcel. By running the model through a set of trajectories a "time series" of daily chemical concentrations can be calculated for any endpoint position which takes into account stratospheric dynamics and can ideally be compared to field measurements.

There are some significant uncertainties involving the ClOOCl + HCl reaction. First, a reaction probability for ClOOCl on chloride-doped ice surfaces has been measured ($\gamma = 0.0035$) using discharge-flow methods but is considered a lower limit because surface saturation processes caused ClOOCl uptake rates to decrease quite rapidly with time (DB96). Higher sticking coefficients in the atmosphere are possible, especially considering the similarity between the reaction of ClOOCl and those of $ClONO_2$ and HOCl; the latter two molecules are known to react very efficiently with HCl at both type I and II PSC surfaces [Abbatt and Molina, 1992; Hanson and Ravishankara, 1991b, 1992b]. Second, while ab initio calculations have suggested the thermal gas phase stability of the HOOCl molecule is much greater than that of ClOOCl [Lee and Rendell, 1993], HOOCl has not yet been directly identified as a product. Furthermore, several pathways for further reaction, including photolysis, reaction, and decomposition, may conceivably exist. In order to include the heterogeneous reaction of ClOOCl in the model, several assumptions must be made in the face of these uncertainties. Two rate parameterizations, three different sets of products, and a range of surface reaction probabilities tested the sensitivity of the model to the addition of the reaction ClOOCl + HCl and to each assumption made.

Results and Discussion

We began with a study of reaction (1) followed by a proposed decomposition of HOOCl into HCl [Connick, 1947]:

Case I

$$ClOOCl + HCl \rightarrow Cl_2 + HOOCl$$

$$HOOCl \rightarrow HCl + O_2 \tag{6}$$
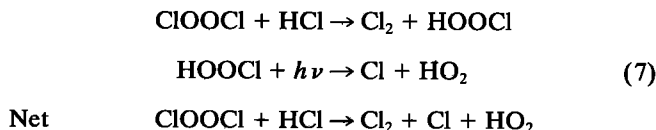
Net
$$ClOOCl \rightarrow Cl_2 + O_2$$
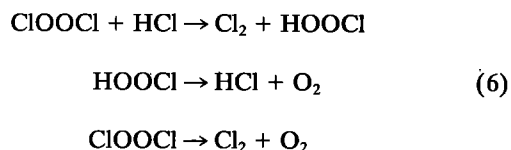
This decomposition regenerates the chloride ion at the ice surface and thus does not activate chlorine. These reactions were parameterized in the model as the net reaction without accounting for the dissociation of HCl at the ice surface or the temporary formation of HOOCl. The decomposition rate of chlorine peroxide was set equal to its collision rate with atmospheric surfaces multiplied by a surface reaction probability between 0.3 and 0.0035 and by an "HCl availability factor," which estimated the monolayer coverage of HCl at the surface. The collision rate is equal to $\gamma \omega A/4$, where γ is the surface reaction probability, ω is the average molecular velocity, and A is the total particle surface area. HCl monolayer coverage was obtained by multiplying the total condensed HCl by the surface site area, estimated at 20 Å^2, and dividing by the combined SAA and PSC surface area. Coverages greater than 1 were set equal to 1, so that the HCl availability factor was always within the range 0–1. In this approximation the model does not explicitly take into account whether reaction surfaces are rich in water, which is known to increase HCl dissociation and reactivity on real-world solid particles [Hanson and Ravishankara, 1993].

As a first test of this chemical scheme, simplified artificial trajectories were constructed. These trajectories remained geosynchronous with various positions between 30° and 80°N, and had constant low temperatures so that type I PSCs would be present during the entire 10-day model run. The diurnal cycles were therefore regular, and surface chemistry occurred at maximum possible rates. Under these extreme conditions the heterogeneous channel became an important sink for ClOOCl in the Arctic due to the scarcity of sunlight, accounting for a maximum of 2–20% of ClOOCl loss in the model depending on the reaction probability used ($\gamma = 0.0035$–0.3, respectively).

At the same time, the artificial trajectories demonstrated that the ozone loss rate was hardly affected by this process. Even if chlorine peroxide was entirely converted to molecular chlorine and oxygen during periods of darkness, ozone loss rates changed by less than 3%. The reason for this is that ClOOCl and Cl$_2$ are functionally equivalent in the lower stratosphere in our model. Both molecules have comparable absorption cross sections in the relevant wavelength range of 300–400 nm, and both produce two chlorine atoms upon photolysis [Molina et al., 1990]. As soon as an air parcel encounters sunlight, the reservoirs of both ClOOCl and Cl$_2$ that have built up overnight begin to photolyze at the same time, yielding chlorine atoms at similar rates. We conclude that if HOOCl (or another conceivable product such as ClOO$^-$) quickly decomposes into HCl and O$_2$, as is assumed in case I, the reaction ClOOCl + HCl will have a negligible effect on the degree of stratospheric chlorine activation and therefore ozone loss rates.

The second reaction scenario tested consisted of reaction (1) followed by photolysis of HOOCl, which has been proposed to occur [Lee and Rendell, 1993] by analogy with both HOOH and ClOOCl:

Case II

$$ClOOCl + HCl \rightarrow Cl_2 + HOOCl$$

$$HOOCl + h\nu \rightarrow Cl + HO_2 \tag{7}$$

Net
$$ClOOCl + HCl \rightarrow Cl_2 + Cl + HO_2$$

Unlike case I, case II results in a net activation of chlorine. We selected Cl + HO$_2$ as the most probable HOOCl photolysis products by analogy with the photolytic behavior of both ClOOCl and ClONO$_2$. Other potential products are ClO + OH (case III); however, because of the fast interconversion within the ClO$_x$ and HO$_x$ chemical families, model results are not sensitive to this choice, as was demonstrated in testing at $\theta = 550$ K.

As a first approximation, the net reaction was inserted into the model without accounting for HOOCl formation. No requirement for sunlight was included; instead, the reaction rate was set equal to the collision rate with particle surfaces. Since HCl is consumed in this reaction scheme, a different parameterization of HCl availability was used [Isaksen and Stordal, 1986], where the lifetimes for chlorine peroxide and hydrochloric acid removal via this reaction (τ_{ClOOCl} and τ_{HCl}) are modified by relative availability factors:

$$\tau_{ClOOCl} = \tau_F\left(1 + \frac{ClOOCl_{(g)}}{HCl_{(s)}}\right) \tag{8}$$

$$\tau_{HCl} = \tau_F\left(1 + \frac{HCl_{(s)}}{ClOOCl_{(g)}}\right) \tag{9}$$

where subscripts (g) and (s) refer to gas phase and condensed phase concentrations, respectively. With the appearance of PSCs in the model, nearly all HCl is adsorbed onto particle surfaces. This parameterization therefore compares the amounts of ClOOCl and HCl available for heterogeneous reaction, and if one is in large excess over the other, the removal rate for the more abundant compound will be greatly slowed.

Initial model runs with constant PSCs showed that the net conversion of HCl to ClO by this reaction significantly affected the chlorine activation level, and therefore the ozone loss rate, of the air parcel. The ClO/HCl ratio calculated for the lower polar stratosphere could be increased by such a process. There is a discrepancy at midlatitudes between modeling and in situ measurements of this ratio [Webster et al., 1993]. Could the reaction ClOOCl + HCl, occurring on sulfuric acid aerosol surfaces, be effective outside of the polar regions, perhaps explaining this discrepancy in ClO/HCl ratios? To answer this question, artificial geosynchronous 30-day trajectories ($\theta = 550$ K) were constructed at seven latitudes between 30° and 80°N. The air parcels were held at a temperature of 198 K so that the only available reaction surfaces were the sulfuric acid aerosol. To simulate the effects of a volcanically enhanced SAA layer, runs were performed with surface areas taken from 1992, 1993, and 1994 field measurements [Trepte et al., 1993; L. Thomason, personal communication, 1994]. Reaction probabilities were set equal to an upper limit determined for the reaction ClONO$_2$ + HCl on liquid SAA particle surfaces (about 2 × 10^{-4} on 60 wt % H$_2$SO$_4$/H$_2$O, varying with H$_2$SO$_4$ concentrations) [Hanson and Ravishankara, 1991a].

Because PSCs were excluded from these artificial trajectories, active chlorine levels north of 60°N declined during runs. The reason for this decline is that the trajectory initialization comes from the 2-D model, which takes PSC formation into
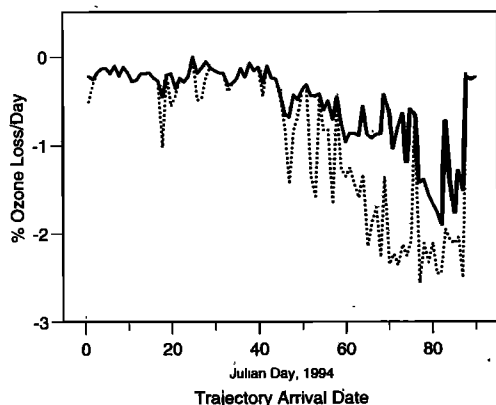
Figure 1. Average daily ozone loss rates calculated for 10-day trajectories (435 K) arriving in Ny Ålesund, Spitsbergen, every day at noon. Solid line denotes normal model chemistry; dotted line denotes case II model (ClOOCl + HCl added with $\gamma = 0.3$).

account through zonal averaging. Heterogeneous chemistry involving HCl on sulfate aerosol alone cannot effectively maintain equally high concentrations of ClO and ClOOCl at 198 K with our model chemistry. Below 60°N, significant amounts of active chlorine were not present at the start of the trajectory runs, making a reaction between active and inactive forms of chlorine impossible. Even at Arctic latitudes, the ClOOCl + HCl reaction did not occur to an appreciable extent on sulfuric acid aerosol surfaces; changes in ozone and active chlorine mixing ratios compared to the model with "normal" chemistry were always less than 1%. We conclude that if the reaction speed of ClOOCl on sulfuric acid aerosol surfaces is comparable to that of ClONO$_2$ + HCl, then the reaction can be neglected at all latitudes.

To examine case II chemistry on PSCs more realistically in the model, the species HOOCl was included so that its formation and photolysis could be simulated as two distinct steps. The absorption cross sections of HOCl [*DeMore et al.*, 1992] were adopted as an analog for HOOCl. Three-month time series of 10-day trajectories were run for five Arctic and two midlatitude stations. In other words, the 10-day histories of air parcels arriving at each of the stations at noon were calculated for every day in the period January–March 1994. The stations were Athens, Greece; Hohenpeissenberg, Germany; Gardemoen, Norway; Yakutsk, Russia; Sodankylä, Finland; Thule, Greenland; and Ny Ålesund, Spitsbergen, Norway.

Compared with those of previous winters, 1993–1994 winter stratospheric temperatures in the northern hemisphere were generally quite high during January and most of February, with temperatures hovering around the threshold for NAT condensation ($\approx$195 K at the 475 K potential temperature (θ) surface). This suggests that PSC formation during this period was limited. By the end of February, however, temperatures dropped well below the PSC threshold for about 2 weeks before the onset of the final stratospheric warming in mid-March [*Naujokat et al.*, 1994]. The temperatures in this period were low enough for the formation of type I PSCs between the 350 K and 550 K θ surfaces, with maximum PSC areal coverage in our model near 435 K. An enhancement of ClO was observed during this period [*Waters et al.*, 1995], and this chlorine activation coupled with abundant solar radiation could have resulted in appreciable amounts of ozone depletion.

Of the 180 air parcels arriving at the midlatitude stations (Hohenpeissenberg and Athens) during this time period, only 7 had encountered PSCs in the previous 10 days and therefore showed any effects of heterogeneous ClOOCl chemistry. Air parcels ending at the Arctic stations, however, commonly encountered PSC processing, with especially heavy exposure in early March. The daily percentage ozone loss experienced by each air parcel ($\theta = 435$ K) arriving at Ny Ålesund is plotted in Figure 1. Over half of the trajectories have undergone processing by type I PSCs at some point within 10 days before their arrival at Ny Ålesund. As PSCs appear in the trajectories, the model results with and without ClOOCl + HCl ("normal" and case II models, respectively) start to diverge. By the spring equinox, ozone loss in the normal model accelerated to reach 1.75%/d for the first time. The case II model (where we have set the ClOOCl sticking coefficient to its maximum possible value of $\gamma = 0.3$), however, had already seen ozone loss at rates greater than this for 2 weeks. At this potential temperature level, the case II model calculates 72% more ozone loss than the model with "normal" heterogeneous chemistry averaged over the 3-month time series of trajectories shown here.

During the same time period, trajectories ending at the other four stations above 60°N showed similar enhancements of between 43 and 71% in averaged ozone losses at 435 K, with divergence increasing throughout the winter until the end of PSC encounters in late March. Model data for these stations are summarized in Figure 2, along with data at the same potential temperature level for two midlatitude stations and Ny Ålesund. When considering the average properties of 90 trajectories, the main differences between the endpoint stations are sunlight and PSC exposure levels, which are, of course, both correlated with latitude. The ozone loss rates in both the normal model and the case II model depend on these factors and thus correlate with each other. Upward divergence from the 1:1 line in Figure 2 indicates a contribution to ozone depletion by the extra chlorine activation caused by the addition of case II ClOOCl + HCl to the model. In the normal
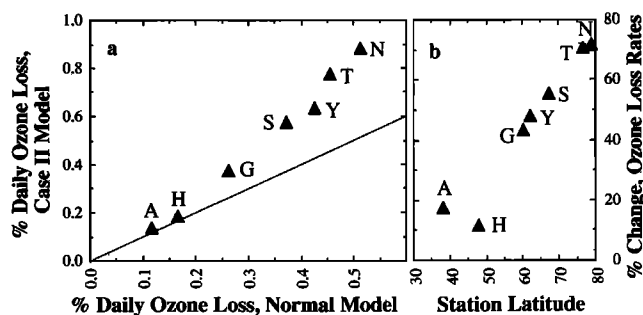

Figure 2. (a) Average daily ozone loss rates at $\theta = 435$ K, computed over 90 ten-day trajectories ending at the following midlatitude and Arctic stations: A, Athens (37.9°N, 23.7°E); H, Hohenpeissenberg (47.8°N, 11.0°E); G, Gardemoen (60.1°N, 11.0°E); S, Sodankyla (67.2°N, 26.4°E); Y, Yakutsk (62.1°N, 129.8°E); T, Thule (76.3°N, 291.6°E); and N, Ny Ålesund (78.9°N, 11.9°E). Line is 1:1 ratio, where the model with (case II, $\gamma = 0.3$) and without ("normal") the ClOOCl + HCl reaction would calculate identical O$_3$ loss rates. (b) Percent difference in ozone loss rates between the two models, plotted against trajectory endpoint station latitude. The enhancement in ozone loss rates caused by ClOOCl + HCl depends on station latitude, an indicator of average PSC exposure.

model the chlorine activation (and O_3 loss) is maximized at stations whose trajectories commonly encounter PSCs. The extra chlorine activation by ClOOCl + HCl increases O_3 loss rates under the same conditions. Thus the higher the average O_3 loss rate calculated by the normal model, the greater the deviation from the line in the graph.

What if ClOOCl surface reaction probabilities are less than $\gamma = 0.3$? The surface reaction probabilities were varied for the Ny Ålesund 435 K trajectory set to study the effectiveness of the case II ClOOCl reaction at modulating ozone loss rates at lower surface reaction efficiencies. The dependency on this crucial variable is shown in Figure 3. There is an approximate dependence in the enhancement of ozone loss rates on the log of the sticking coefficient used in the model. At the lower limit suggested for ClOOCl reaction probabilities in the stratosphere ($\gamma = 0.0035$), ozone depletion is accelerated by an average of 3.6% over the normal model for the 3-month time series of 10-day trajectories at $\theta = 435$ K. Only a slightly larger reaction probability is necessary to reach a 10% enhancement in ozone loss rates at this station and altitude.

Since it is clear from Figure 3 that the differences between the case II and normal models are altitude dependent, time series calculations were performed for Ny Ålesund trajectories at seven potential temperature levels. The average ozone loss rates from January 1 until March 31 (when PSCs were no longer present at any altitude) are displayed in Figure 4. Enhancement of ozone loss by ClOOCl + HCl reaches a maximum in our model at the 435 K level, corresponding to about 16 km altitude. At this height, PSC exposure is near maximum (in early spring 1994), HCl input mixing ratios from the 2-D model are at a local maximum, and $ClONO_2$ concentrations, though increasing with altitude, have not yet reached maximum levels. The $[HCl]:[ClONO_2]$ ratio is thus at a maximum for the region of the stratosphere where PSCs commonly form. Integrating across the ozone layer in altitude units, the loss rate for the ozone column (between the 350 and 675 K levels) is accelerated by about 35% for this set of trajectories when $\gamma = 0.3$. This is clearly an upper limit for the importance of the ClOOCl + HCl reaction in the Arctic stratosphere.

The chemistry of many sample trajectories was studied to determine the importance of the $[HCl]:[ClONO_2]$ ratio. Al-

Figure 4. Altitude dependence of averaged ozone loss rates for all trajectories arriving in Ny Ålesund in the time period January–March 1994. Solid squares denote normal model chemistry. Open circles denote case II model, with heterogeneous ClOOCl reaction probabilities spanning the range from 0.0035 to 0.3. Increasing reaction probabilities $\gamma = 0.0035$, 0.03, 0.1, and 0.3 are expressed by increasing circle diameter at the 435 K and 550 K levels. The light gray region, which covers the entire altitude range of PSC formation, approximately describes the effect of heterogeneous chlorine activation on ozone loss rates for this set of trajectories, while the dark gray region indicates the possible enhancement of ozone loss rates caused by the addition of ClOOCl + HCl to the model.
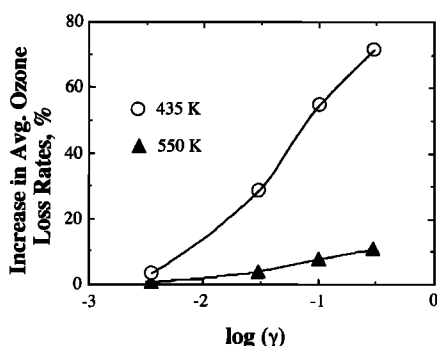

Figure 3. Difference between normal and case II models plotted as a function of ClOOCl + HCl reaction probability used in the case II model, for 10-day trajectories arriving daily at noon in Ny Ålesund during the time period January–March 1994. The reaction probabilities shown cover the range $0.0035 < \gamma < 0.3$. Open circles denote averages of all 88 full-length trajectories at the 435 K potential temperature level. Solid triangles denote averages of 550 K trajectories.
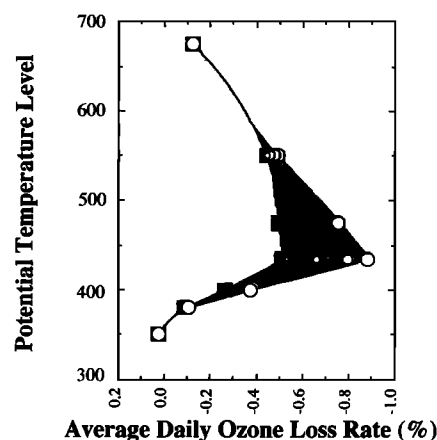
though the ozone loss rates averaged over 90 trajectories always increased by the addition of the reaction ClOOCl + HCl, it is interesting to note that several individual trajectories at higher altitudes show the opposite effect due to competition between ClOOCl and $ClONO_2$ for a limited supply of HCl. Many of the trajectories with the most rapid ozone depletion rates arrive with more ozone and less active chlorine when case II heterogeneous chlorine peroxide chemistry is included. Figures 5 and 6 show chemical concentrations for sample trajectories where the heterogeneous ClOOCl reaction decreases and increases the ozone loss rates, respectively.

The trajectory shown in Figure 5 (at $\theta = 550$ K) has undergone extensive PSC processing over its 10-day history. The initially low $[HCl]:[ClONO_2]$ ratio ($\approx 1.2:1$) allows HCl to be depleted by reacting with $ClONO_2$. The addition of heterogeneous ClOOCl chemistry in this situation depletes HCl more quickly, leaving larger amounts of unreacted $ClONO_2$. This trajectory can be thought of as representing typical late winter conditions, when the increase of sunlight in the Arctic increases HNO_3 photolysis rates, thereby increasing NO_x concentrations and the rate of formation of $ClONO_2$. When PSCs form in March, HCl is more likely to be depleted by the heterogeneous reaction with $ClONO_2$ during those few weeks with both PSCs and sunlight present. Typically, this period is also the period of rapid ozone loss, when sunlight is available to drive the ozone depletion cycles catalyzed by active chlorine. Thus (at least for the 550 K level and above), the addition of the reaction ClOOCl + HCl does not significantly accelerate ozone depletion rates when they are already at a maximum under these conditions.

Figure 6 shows a $\theta = 435$ K trajectory where initially $[HCl] > [ClONO_2]$. When PSCs are encountered, the normal model reaches a limit of chlorine activation by heterogeneous
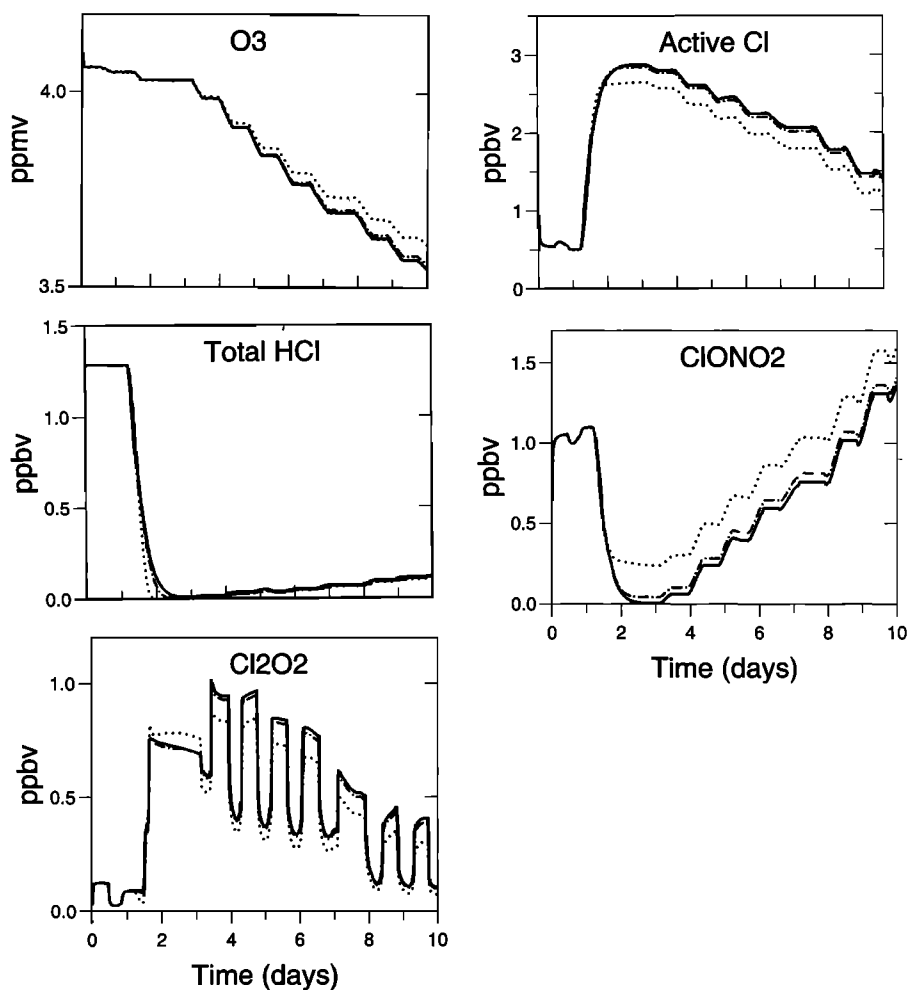
Figure 5. Comparison of model mixing ratios for the March 12, 1994, Ny Ålesund trajectory at θ = 550 K, where the [HCl]/[ClONO$_2$] ratio is near unity when type I PSCs are encountered. Solid line denotes normal model chemistry. Dashed gray line denotes ClOOCl + HCl added with γ = 0.03. Dotted line denotes ClOOCl + HCl added with γ = 0.3. PSCs were encountered twice, on the second day and again on the sixth day. Note that the addition of ClOOCl + HCl actually reduces chlorine activation and ozone loss rates in this air parcel because of "leftover" ClONO$_2$.

chemistry because ClONO$_2$ is depleted. However, the addition of ClOOCl + HCl allows substantially more loss of HCl when ClOOCl reaction probabilities are set to either 0.03 or 0.3.

In our model the maximum in integrated PSC surface area was between the 435 and 475 K surfaces. At 435 K, NO$_x$ concentrations are quite low, and HCl is clearly in excess relative to ClONO$_2$, allowing the ClOOCl + HCl reaction to always make a positive contribution to chlorine activation, resulting in large enhancements of ozone depletion (e.g., Figures 1 and 6). Although 2-D models (like that used to initialize our trajectory chemistry) tend to overestimate HCl in the lower stratosphere, our initializations at 550 K ($\approx$22 km) are consistent with satellite measurements of approximately equal HCl and ClONO$_2$ [Dessler et al., 1995]. The trend of increased abundance of HCl relative to ClONO$_2$ at lower altitudes in our model is also seen in field data [Webster et al., 1994]. A maximum enhancement of ozone loss rates caused by the addition of ClOOCl + HCl to the model would therefore be expected at the lowest level where PSCs are common.

The extent of PSC processing is a second important parameter which, in addition to the [HCl]:[ClONO$_2$] ratio, deter-

mines the response of the model to the addition of heterogeneous ClOOCl chemistry. The largest relative increases in ozone depletion typically are seen in those trajectories that are only lightly processed by PSCs. In these cases, HCl concentrations can be reduced by simultaneous reaction of both ClONO$_2$ and ClOOCl without being severely depleted. The result is that ClOOCl + HCl makes a large short-term contribution to the activation of HCl, while ClONO$_2$ concentrations are not yet affected and ClO$_x$-catalyzed ozone depletion accelerates noticeably. Later, more extensive PSC processing may reverse this effect. In the 1994 winter that we studied, extensive PSCs appeared for only a 2-week period, and so this later effect was observed only in certain runs at potential temperature levels of 550 K and above. In colder years where PSCs appear in the Arctic stratosphere in early winter, initially high [HCl]:[ClONO$_2$] ratios could allow an early enhancement of chlorine activation by ClOOCl + HCl like that seen in Figure 6, at all altitudes where PSCs are formed. Then as PSC processing continues and HCl is depleted (e.g., in late spring), there can be no further enhancement of chlorine activation by the reaction ClOOCl + HCl but only a net decrease in chlorine
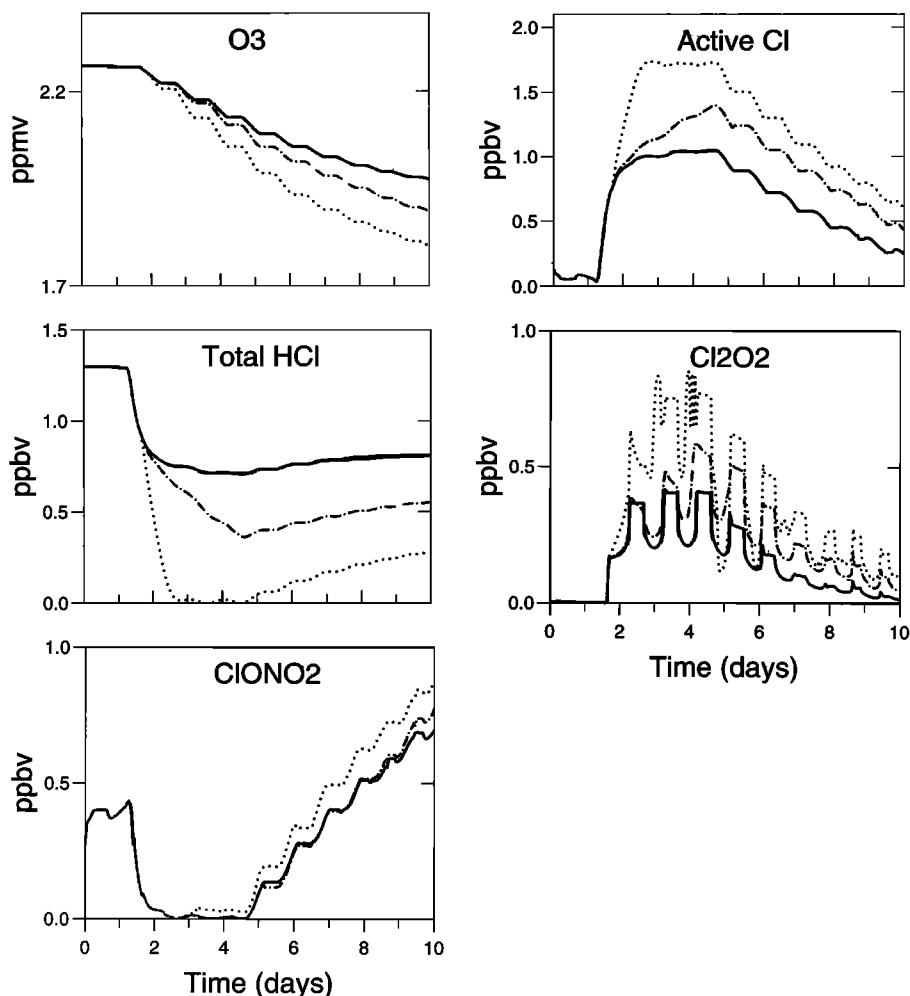
Figure 6. Comparison of model mixing ratios for the March 28, 1994, Ny Ålesund trajectory at θ = 435 K. The [HCl]:[ClONO$_2$] ratio is high when an extensive encounter with type I PSCs begins on the second day. Line designations are identical to those in Figure 5. The addition of ClOOCl + HCl at either γ = 0.3 or 0.03 greatly increases the ozone loss rate.

activation due to (case II) ClOOCl + HCl because of an increased amount of extra ClONO$_2$ present.

These effects are, of course, the maximum possible. The purpose of this study was to identify under what conditions the reaction of ClOOCl + HCl might alter the mechanism of chlorine activation and affect ozone depletion rates. We have used ClOOCl sticking coefficients between 0.0035 and 0.3 in this study. The actual sticking coefficients under stratospheric conditions are not known but lie within this range (DB96). All the effects of the case II model depend on the activation of chlorine via ClOOCl + HCl via the photolysis of the proposed product HOOCl. This pathway must be demonstrated in laboratory studies. Without it, the conversion of ClOOCl to Cl$_2$ in the presence of HCl has no effect on chlorine activation or ozone. Finally, the reaction in the model occurred on solid NAT (type Ia) PSCs. The real Arctic stratosphere contains both freshly condensed ternary solution (type Ib) and subsequently frozen NAT particles, whose combined surface areas may in some cases be smaller than those calculated in our model.

Conclusion

The trajectory model simulates the heterogeneous processing and sunlight encounters of individual parcels of air. Our

model shows that occasional encounters with sunlight throughout the 1994 winter allow ClOOCl and HCl to be present simultaneously in the Arctic stratosphere, making significant reaction between them a possibility. The reaction ClOOCl + HCl on sulfuric acid aerosol (and therefore at midlatitudes) can be neglected, since there is no effect on model chemistry if the reaction efficiency on these surfaces is no larger than that of ClONO$_2$ + HCl.

On PSC surfaces the results of the addition of ClOOCl + HCl $\rightarrow$ Cl$_2$ + HOOCl to the model depend primarily on the decomposition pathway of proposed product HOOCl (DB96). If it decomposes at the reaction surface, forming HCl and O$_2$, chlorine is not activated. The reaction serves merely to convert ClOOCl into Cl$_2$, which does not affect ozone chemistry, since these two gases are functionally equivalent in the lower stratosphere. If chlorine is activated by the reaction between ClOOCl and HCl (for example, through photolysis [*Lee and Rendell*, 1993] of the proposed reaction product HOOCl), the reaction may have a hand in modulating Arctic stratospheric ozone depletion rates, but only if its reaction efficiency is quite large ($\gamma \geq 0.03$). The simulations presented in this paper show that increases in chlorine activation may occur when PSCs are encountered and when [HCl] > [ClONO$_2$] before heteroge-

neous chemistry begins. In our model these conditions existed from January through March 1994 in the lower Arctic stratosphere (below 20 km), though in other years this period may end earlier in the winter. Because of the potential importance of the heterogeneous reaction ClOOCl + HCl in the high-latitude stratosphere it is crucial that uncertainties in heterogeneous ClOOCl reaction rates and ultimate product reaction pathways be addressed.

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