Chlorine chemistry and the potential for ozone depletion in the arctic stratosphere in the winter of 1991/92

R. Müller, Th. Peter, P. J. Crutzen, H. Oelhaf, G. P. Adrian, Th. v. Clarmann, A. Wegner, U. Schmidt, and D. Lary

Abstract. We present an analysis of chlorine chemistry in the Arctic stratosphere during the winter of 1991/92 and assess its potential implications for ozone depletion. In accordance with observations of total organic chlorine, C1ONO2 and HCl, box model results indicate the following: (1) An almost complete activation of chlorine during the cold winter period. (2) A possible contribution from the heterogeneous reaction HOC1 + HC1 and the gas-phase reaction CHaO2 + C10 to the complete conversion of HC1 to active chlorine. (3) A strong buildup of C1ONO2 following PSC disappearance in accordance with the observations, we further investigated the potential consequences of the simulated high levels of active chlorine for ozone loss.

Model description

We use a chemical box model [Crutzen et al., 1992] including a complete set of gas-phase and heterogeneous reactions, the latter both on liquid sulfuric acid and nitric acid trihydrate (NAT) surfaces (Table 1). In the model, NAT particles form at 3 K supercooling, as indicated by observations in the Arctic [Schlager et al., 1990; Dye et al., 1992]. For the computation of the photolysis rates, a scheme was adopted that accurately describes photolysis at large solar zenith angles [Lary and Pyle, 1991] and includes the temperature dependence.

Table 1. Reactions important to this work

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H1 ( \text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3 )</td>
<td>0.0006</td>
</tr>
<tr>
<td>H2 ( \text{ClONO}_2 + \text{H}_2\text{O} \rightarrow \text{HOCI} + \text{HNO}_3 )</td>
<td>0.006</td>
</tr>
<tr>
<td>H3 ( \text{ClONO}_2 + \text{HC}1 \rightarrow \text{Cl}_2 + \text{HNO}_3 )</td>
<td>0.3</td>
</tr>
<tr>
<td>H4 ( \text{HOCI} + \text{HC}1 \rightarrow \text{Cl}_2 + \text{H}_2\text{O} )</td>
<td>0.1</td>
</tr>
<tr>
<td>H5 ( \text{N}_2\text{O}_5 + \text{HC}1 \rightarrow \text{ClNO}_2 + \text{HNO}_3 )</td>
<td>0.003</td>
</tr>
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</table>

One objective of the European Arctic Stratospheric Ozone Experiment (EASOE) was to provide a wide spatial and temporal coverage of measurements of chemical species in the polar stratosphere. Here, we use several of these measurements in an attempt to provide a synoptic view of the chemical evolution of chlorine and nitrogen species in the Arctic lower stratosphere during the winter of 1991/92.

Ground-based observations of total column C1ONO2 over the entire winter [Adrian et al., 1994], along with balloon-borne observations of C1ONO2 inside the vortex on January 13, 1992, and March 14, 1992 [v. Clarmann et al., 1993; Oelhaf et al., 1994], indicate a sizable conversion of this species to active chlorine during the coldest period from the end of December to the end of January, followed by an almost complete transformation of the available chlorine to ClONO2 during the beginning March. Moreover, ground-based observations of very low column densities of HC1 during the winter and spring of 1992 [Adrian et al., 1994; Bell et al., 1994] suggest a substantial conversion of HC1 to active chlorine.

In order to analyze the mechanisms responsible for the exceptional, unprecedented observations of chlorine species we conducted chemical box model calculations for air parcels representative of the conditions in the Arctic vortex in 1991/92. Encouraged by the ability of our model to reproduce the principal features of the disturbed chlorine chemistry in accordance with the observations, we further investigated the potential consequences of the simulated high levels of active chlorine for ozone loss.

For the heterogeneous reactions H1-H5, reaction probabilities $\gamma$ for NAT [DeMore et al., 1992] are listed. On sulfuric acid (with weight percentage W) only H1 ($\gamma = 0.1$) and H2 ($\gamma = 10^{3.86-0.0747\cdot W}$) were included [Hanson and Ravishankara, 1991]. For the gas-phase reactions R1-R14, rate constants (in cm$^3$ s$^{-1}$ molec$^{-1}$) were included [DeMore et al., 1992] for 100 mbar and 200 K and photolysis rates (in s$^{-1}$) for 85$^\circ$ zenith angle are given.
of the UV-cross sections for HNO₃ [Burkholder et al., 1993]. We use one quarter of the recommended upper limit [DeMore et al., 1992] as reaction rate for R10. A rate of this order has recently been substantiated by measurements which further disclosed CH₃OC₁ as a product of R10 [Helleis et al., 1993].

The temperature history (Fig. 1), of the air parcels inside the polar vortex in the lower stratosphere during the winter of 1991/92 was estimated from observations [Naujokat and Labitzke, 1993; Waters et al., 1993]. Further, to simulate the diabatic descent in the vortex indicated by observations of inert tracers [Schmidt et al., 1993], they are assumed to sink from 550K to 450K (22-17km) over the model period. Some simulations have also been performed for different height levels to estimate total column amounts. The air parcels are either constrained to constant latitude (58°N-78°N), or sinusoidal variations in latitude (68°-10°N) were prescribed. In accordance with meteorological observations, the cooling episodes and the southward excursions are assumed to take place over northern Europe.

There are some limitations in using a box model in this, highly idealized way, and, consequently, a detailed, quantitative comparison with measurements is not attempted. Nonetheless, since the model assumptions are representative of the situation inside the polar vortex in the winter 1991/92, some conclusions about the chemical mechanisms at work may be drawn on account of the model results.

Model results and observations

Chlorine and nitrogen species. In the model, NAT particles exist from the end of December to the end of January (Fig. 1) in accordance with estimates based on a thorough meteorological analysis [Newman et al., 1993] and lidar measurements [Stein et al., 1993]. The surfaces of these particles catalyze the heterogeneous reactions H₃-H₅ that activate HCl. While H₅ is unlikely to be very effective due to prior removal of N₂O₅ by reaction on sulfate aerosol particles via H1, reactions H₃ and H₄ proceed rapidly, effectively titrating the available ClONO₂ and HOCl against HCl on a timescale of hours (Fig. 2). The further depletion in HCl is much slower and is controlled by the supply of reaction partners for HCl. The most important partner under sunlight conditions and when PSCs exist is HOCl produced via R3. Further, whenever PSCs evaporate during warm periods (Fig. 1), HNO₃ is released into the gas-phase and ClONO₂ recovers via R2 (Fig. 2), thereby using up the NO₂ produced by R7 and R8. Thus, NO₂ concentrations remain low. Similarly, in PSC-free periods, HOCl builds up via reaction R3 (Fig. 3). With the PSCs reappearing during cold periods, HCl is removed via H₃ and H₄ with ClONO₂ and HOCl being about equally important. Since the buildup of HCl during the warm periods is much slower than that of HOCl and ClONO₂ (see below), the recurrent evaporation of PSCs thus enhances the depletion of HCl. In the model, HCl is severely depleted in the lower stratosphere, a finding supported by the very low column amounts of HCl measured at the end of January. The ClONO₂ concentrations remain extremely low in the model throughout the period when PSCs exist, in good accordance with the balloon-borne observation on January 13.

After the last PSCs disappear in the model simulation, the active chlorine is almost completely converted to ClONO₂.
field et al., 1993] have simulated significant ozone loss for
pletion [McKenna et al., 1990; Brune et al., 1991; Chipper-
period) show an integral ozone destruction of 15%-38% in the
representative of the polar vortex (78°N-68°N, corresponding
rates for the period from mid January to mid February 1992
focus on the entire winter of 1991/92. Our model results rep-
the lower stratosphere for February 1989 and 1990. Here, we
air parcel (Table 2) in accordance with observed ozone loss
via R2; the recovery of HCl via R1 is much slower (Fig. 2). This pattern is clearly borne out by measurements which show (in agreement with the model) extremely high column amounts of ClONO2, yet only a slow recovery of HCl towards the end of winter (Fig. 2). It is further corroborated by the balloon-borne observation on March 14 which shows very high mixing ratios of ClONO2 in the lower stratosphere.

The reason for the preferred production of ClONO2 over HCl can be explained by the relative effectiveness of reactions R1 and R2 for the removal of active chlorine:

$$\alpha = \frac{d[HCl]_i}{d[ClONO_2]_i} = \frac{k_1[CH_4][Cl]}{k_2[NO_2][CIO]} \approx \frac{k_1[CH_4]k_6[NO]}{k_2[NO_2]k_4[O_3]}$$

Assuming NO/NO2 ≈ 1 and mixing ratios of O3 and CH4 in the ppmv range, $\alpha \approx 10^{-2}$, and thus practically all the active chlorine will initially be converted into ClONO2. The rate of increase in ClONO2, and thus the rate of chlorine deactivation, is controlled by the rate of release of NO2 from the HNO3 via R7 and R8 after the evaporation of NAT.

The activation of chlorine is further reflected in the high mixing ratios of ClO indicated by the model results (Fig. 3). The simulated temporal variation of ClO is consistent with aircraft [Crewell et al., 1994] and satellite observations [Waters et al., 1993].

Ozone. Previous modeling studies of Arctic ozone depletion [McKenna et al., 1990; Brune et al., 1991; Chipperfield et al., 1993] have simulated significant ozone loss for the lower stratosphere for February 1989 and 1990. Here, we focus on the entire winter of 1991/92. Our model results representative of the polar vortex (78°N-68°N, corresponding to a total of 300-670 hours of sunlight over the model period) show an integral ozone destruction of 15%-38% in the air parcel (Table 2) in accordance with observed ozone loss rates for the period from mid January to mid February 1992 [Proffitt et al., 1993]. The results of model runs performed for vortex conditions at lower latitudes (58°N and 63°N, Table 2) as a sensitivity study, are consistent with the finding of Brune et al. [1991] that the amount of ozone depletion strongly increases with decreasing latitude. To demonstrate the sensitivity of ozone depletion to the duration of PSC existence, model runs were performed for an unrealistically short (10 days) and long (50 days) PSC periods by shifting temperatures up and down by 3 K (Table 2). However, in 1992, possibly also unprocessed air masses existed in the vortex [Newman et al., 1993], for which the present analysis is not applicable.

Furthermore, the suggestion by Crutzen et al. [1992], that a cycle involving R10 and H4, could be of relevance to Antarctic ozone depletion is extended here to the Arctic (Table 2, Figs. 2 and 3). For the Arctic high latitude ozone loss, this cycle may be of comparable importance as the BrO-C10 cycle (Table 2). Since it is strongly dependent on solar illumination [Crutzen et al., 1992], it is triggered earlier during southward excursions if variations in latitude are considered, so that in this case, the HCl activation, and thus the ozone depletion, is slightly stronger (Table 2, Figs. 2, 3).

In a study for the 1991/92 Arctic vortex [Salawitch et al., 1993], the model was initialized with more ClONO2 than HCl based on in-situ measurements of HCl [Webster et al., 1993]. Under these circumstances, the complete activation of HCl proceeds via H3 and requires no further explanation. Thus, the impact of H4 and R10 would be reduced. Further, if H2 does not occur in the stratosphere, as suggested by Webster et al. [1993], the inorganic chlorine reservoir would not be activated completely since any ClONO2 in excess of HCl would remain unprocessed; consequently, less ozone depletion than for the initialization with excess HCl employed here is simulated [Salawitch et al., 1993]. In contrast to this view, the ClONO2 profile measured on January 13, 1992 [v. Clarman et al., 1993; Oelhaf et al., 1994] indicates that only very little ClONO2 is present in the lower stratosphere during the coldest period of the winter 1992.

**Conclusions**

Measurements and model results discussed here yield a consistent picture. Specifically, the activation of chlorine

![Figure 3. The mixing ratios of HOCI, ClO and ozone in the lower stratosphere (at 68°N) over the model period. Dotted line in lower panel indicates ozone simulated neglecting reactions H4 and R10, dashed line the results allowing excursions in latitude.](image_url)

**Table 2. Ozone depletion in percent**

<table>
<thead>
<tr>
<th>lat.</th>
<th>$T - 3K$</th>
<th>$T$</th>
<th>$T + 3K$</th>
<th>$A$</th>
<th>$B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>58°N</td>
<td>81</td>
<td>60</td>
<td>39</td>
<td>64</td>
<td>45</td>
</tr>
<tr>
<td>63°N</td>
<td>70</td>
<td>56</td>
<td>33</td>
<td>49</td>
<td>42</td>
</tr>
<tr>
<td>68°N</td>
<td>49</td>
<td>38</td>
<td>23</td>
<td>28</td>
<td>27</td>
</tr>
<tr>
<td>73°N</td>
<td>27</td>
<td>23</td>
<td>18</td>
<td>13</td>
<td>15</td>
</tr>
<tr>
<td>78°N</td>
<td>17</td>
<td>15</td>
<td>14</td>
<td>7</td>
<td>9</td>
</tr>
<tr>
<td>68°± 10°N</td>
<td>53</td>
<td>42</td>
<td>24</td>
<td>29</td>
<td>30</td>
</tr>
</tbody>
</table>

Ozone depletion simulated in the model from 15.12.91 to 15.3.92 for temperature $T$ (as in Fig. 1) and with the temperature history shifted upward ($T + 3K$) and downward ($T - 3K$) by three Kelvin. Further, results are shown from model runs neglecting $A$: Reactions H4 and R10 and $B$: neglecting bromine chemistry.
during the cold winter period, reflected in balloon-borne measurements of little ClONO$_2$ [v. Clarmann et al., 1993; Oelhaf et al., 1994], aircraft measurements of high concentrations of ClO, low levels of HCl [Crewell et al., 1994] and large column amounts of OClO [Brandtjen et al., 1994] and ground-based observations of low column amounts of HCl and ClONO$_2$ inside the polar vortex [Adrian et al., 1994; Bell et al., 1994] is matched by the model results. After the final disappearance of the PSCs, the model shows high column amounts of ClONO$_2$ and an almost complete conversion of active chlorine to ClONO$_2$ (Fig. 2), which remains the dominant inorganic chlorine compound for more than a month, all in accordance with the observations.

Our model results show that reactions H4 and R10, hitherto omitted in model studies of Arctic ozone loss, may possess a substantial impact on halogen-catalyzed ozone destruction (Table 2). The simulations performed for conditions representative of the lower stratosphere inside the polar vortex for the Arctic winter of 1991/92 indicate, in accordance with observations [Proffitt et al., 1993], that considerable chemical ozone loss may have taken place.

Acknowledgments. We thank Th. Wawers, H. Gimm and T.-O. Gunström for computer support during the campaign and M. Flender for help performing the model runs. Part of this work was funded by the European Community and the German Ministry for Research and Technology (BMFT).

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P. J. Crutzen, R. Müller, and Th. Peter, Max Planck Institute for Chemistry, Dep. Atmospheric Chemistry, Postf. 3060, 55020 Mainz, Germany (e-mail: muller@nike.mpch-mainz.mpg.de)
Th. v. Clarmann, H. Oelhaf, G. P. Stiller (formerly Adrian), and A. Wegner, Institute for Meteorology and Climate Research, KFK, Postf. 3640, 76021 Karlsruhe, Germany
U. Schmidt, KFA, ICG-3, Postf. 1913, 52425 Jülich, Germany
D. Lary, Dep. Chemistry, University of Cambridge, Lensfield Rd, Cambridge CB2 1EW, UK

(received November 17, 1992; revised January 24, 1994; accepted February 9, 1994.)