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and ozone loss  
processes

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# The potential impact of $\text{ClO}_x$ radical complexes on polar stratospheric ozone loss processes

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## Abstract

The importance of radical-molecule complexes for atmospheric chemistry has been discussed in recent years. In particular, the existence of a  $\text{ClO}\cdot\text{O}_2$  and  $\text{ClO}_x$  water radical complexes like  $\text{ClO}\cdot\text{H}_2\text{O}$ ,  $\text{OCIO}\cdot\text{H}_2\text{O}$ ,  $\text{OCIO}\cdot(\text{H}_2\text{O})_2$ , and  $\text{ClOO}\cdot\text{H}_2\text{O}$  could play a role in enhancing the ClO dimer ( $\text{Cl}_2\text{O}_2$ ) formation and therefore may constitute an important intermediate in polar stratospheric ozone loss cycles. Model simulations performed with the Chemical Lagrangian Model of the Stratosphere (CLaMS) will be presented to study the role of radical complexes on polar stratospheric ozone loss processes. The model simulations are performed for the Arctic winter 2002/2003 at a level of 500 K potential temperature and the results are compared to observed ozone loss rates determined by the Match technique. Moreover, recently reported values for the equilibrium constant of the ClO dimer formation are used to restrict the number of possible model results caused by large uncertainties about radical complex chemistry. Our model simulations show that the potential impact of  $\text{ClO}\cdot\text{O}_2$  on polar ozone loss processes is small ( $d\text{O}_3/dt \ll 0.5 \text{ ppb/sunlight h}$ ) provided that the  $\text{ClO}\cdot\text{O}_2$  complex is only weakly stable. Assuming that the binding energies of the  $\text{ClO}_x$  water complexes are much higher than theoretically predicted an enhancement of the ozone loss rate by up to  $\approx 0.5 \text{ ppb/sunlight h}$  is simulated. Because it is unlikely that the  $\text{ClO}_x$  water complexes are much more stable than predicted we conclude that these complexes have no impact on polar stratospheric ozone loss processes. Although large uncertainties about radical complex chemistry exist, our findings show that the potential impact of  $\text{ClO}_x$  radical molecule complexes on polar stratospheric ozone loss processes is very small considering pure gas-phase chemistry. However the existence of  $\text{ClO}_x$  radical-molecule complexes could possibly explain discrepancies for the equilibrium constant of the ClO dimer formation found between recent laboratory and stratospheric measurements.

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## 1. Introduction

Stratospheric polar ozone loss attracted worldwide attention since the discovery of the ozone hole over Antarctica by [Farman et al. \(1985\)](#). For more than a decade, strong halogen-induced ozone losses have also been observed in cold Arctic winters (e.g., [Solomon, 1999](#); [Müller et al., 1997](#); [Manney et al., 2003](#); [WMO, 2003](#); [Tilmes et al., 2004](#); [von Hobe et al., 2006](#)<sup>1</sup>). However, there are still open questions regarding the quantitative understanding of Arctic polar ozone chemistry. Discrepancies are being found in comparisons of observed and simulated ozone losses (e.g., [Hansen et al., 1997](#); [Becker et al., 1998](#); [Deniel et al., 1998](#); [Goutail et al., 1999](#); [Woyke et al., 1999](#); [Kilbane-Dawe et al., 2001](#); [Rex et al., 2003](#)), whereby these discrepancies mainly appear for early winter conditions (e.g., [Becker et al., 1998](#); [Woyke et al., 1999](#); [Rex et al., 2003](#)).

Beyond that, the role and importance of radical-molecule complexes on atmospheric chemistry and specifically on stratospheric ozone destruction has been a topic of discussion for a number of years (e.g., [Prasad and Lee, 1994](#); [Shindell, 1996](#); [Hansen and Francisco, 2002](#)). [Shindell \(1996\)](#) examined whether a ClO·O<sub>2</sub> complex could have a major role in chlorine catalyzed ozone depletion chemistry. He found that either: (1) the ClO·O<sub>2</sub> is fairly stable, but does not significantly enhance ClO dimer formation and therefore has a negligible effect on ozone loss rates, or (2) the ClO·O<sub>2</sub> complex is only very weakly stable, but does rapidly form the ClO dimer, and therefore can influence stratospheric ozone depletion. [Shindell \(1996\)](#) finds that the ClO·O<sub>2</sub> complex would impact the ClO/Cl<sub>2</sub>O<sub>2</sub> ratio, but at that time no measurements of Cl<sub>2</sub>O<sub>2</sub> were available. Today such measurements are made ([Stimpfle, 2004](#); [von Hobe et al., 2005](#)) so that more constraints exist. Further, [Francisco and Sander \(1995\)](#) proposed that a ClO·H<sub>2</sub>O

<sup>1</sup>von Hobe, M., Ulanovsky, A., Volk, C. M., Grooß, J.-U., Tilmes, S., Konopka, P., Günther, G., Werner, A., Spelten, N., Shur, G., Yushkov, V., Ravegnani, F., Schiller, C., Müller, R., and Strohm, F.: Chlorine activation, denitrification and ozone depletion in the cold Arctic winter 2004–05, *Geophys. Res. Lett.*, to be submitted, 2006.

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complex could possibly enhance the ClODimer ( $\text{Cl}_2\text{O}_2$ ) formation. In addition, theoretical studies predict the existence of  $\text{OCIO}\cdot\text{H}_2\text{O}$ ,  $\text{ClOO}\cdot\text{H}_2\text{O}$ , and  $\text{OCIO}\cdot(\text{H}_2\text{O})_2$  radical-molecule complexes (Aloisio and Francisco, 1999; Hansen and Francisco, 2002).

Here, we analyze if such  $\text{ClO}_x$  radical-molecule complexes can explain the discrepancies between measured and simulated ozone loss processes, in particular the unexplained stratospheric ozone losses during cold Arctic Januaries (e.g., Rex et al., 2003).

We study this question performing model simulations with the Chemical Lagrangian Model of the Stratosphere (CLaMS) (McKenna et al., 2002a,b). The simulation results are compared to chemical induced ozone losses inside the stratospheric polar vortex determined with the Match technique (e.g., von der Gathen et al., 1995; Rex et al., 1997, 1999; Streibel et al., 2005). In the present study, the focus is on the winter 2002/2003 at the 500 K potential temperature level, where the discrepancies between model simulations and observations are large (Feng et al., 2006<sup>2</sup>).

## 2. The model study

For the present study we use the Chemical Lagrangian Model of the Stratosphere (CLaMS) (McKenna et al., 2002a,b). This model simulates both the chemistry of multiple air parcels and their transport and is used here as a photochemical box model. The absorption cross sections for the photolysis reactions and reaction rate constants are taken from standard recommendations (Sander et al., 2002), except the equilibrium constant of the  $\text{Cl}_2\text{O}_2$  formation (see Eq. 1). Here an equilibrium constant recently reported by Plenge et al. (2005) is used which is lower than current reference data (Sander et al., 2002) but agrees well with high altitude aircraft measurements (Stimpfle, 2004; von Hobe et al., 2005); the overall ozone loss rate in the Arctic winter stratosphere is only marginally affected by this choice (Plenge et al., 2005). For

<sup>2</sup>Feng, W., Chipperfield, M., Backmann, L., Godin, S., Lehmann, R., and Müller, R.: Inter-comparison of European stratospheric chemical transport models during the Arctic and Antarctic Match campaigns, in preparation, 2006.

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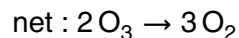
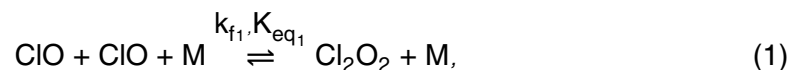
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simulations with the CLaMS model, the family method (IMPACT) (Carver and Scott, 2000) is usually employed as the integration solver (McKenna et al., 2002a). In all model simulations presented in this work, the explicit stiff solver SVODE (Carver et al., 1997) is used which is more precise but numerically more expensive. As input data for the photolysis scheme an ozone climatology (Grooß and Russell, 2005) was used derived from observations of the Halogen Occultation Experiment (HALOE) on board the UARS satellite (Russell et al., 1993). The CLaMS simulations were initialized using output from a simulation with the SLIMCAT 3-D model (Feng et al., 2005). The simulations were performed along trajectories of air masses sampled during the Match campaign 2002/2003 (Streibel et al., 2005).

### 3. Ozone chemistry with radical complexes

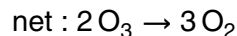
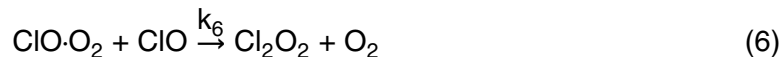
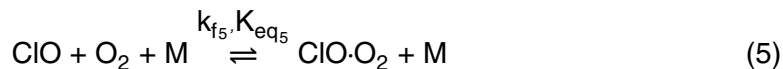
#### 3.1. New catalytic cycles with radical complexes

In currently accepted stratospheric ozone chemistry, halogens destroy polar ozone primarily through the ClO dimer ( $\text{Cl}_2\text{O}_2$ ) cycle (Molina and Molina, 1987) and ClO-BrO cycle (McElroy et al., 1986). The ClO dimer cycle

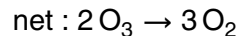
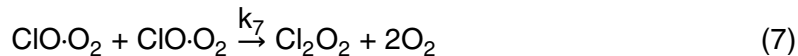
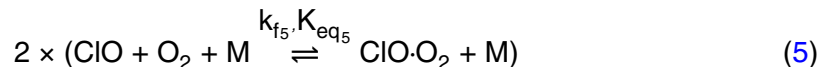


is limited under typical polar stratospheric conditions by the rate of the ClO dimer formation described by the termolecular reaction rate constant ( $k_{f1}$ ) of the ClO dimer

formation and the equilibrium constant ( $K_{eq1}$ ). New catalytic cycles could take place involving a ClO-O<sub>2</sub> complex via (Shindell, 1996) cycle I:



and cycle II:



Further, the following reaction scheme (cycle III) involving the ClO-H<sub>2</sub>O complex for

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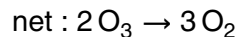
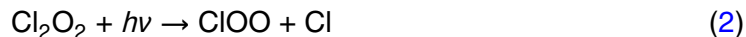
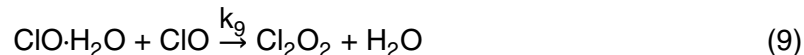
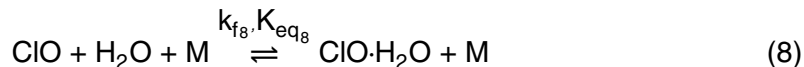
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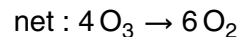
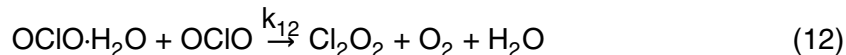
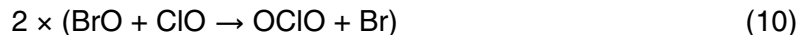
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stratospheric ozone depletion was proposed by [Francisco and Sander \(1995\)](#):



The reaction of ClO with BrO has three reaction channels  $\text{Br} + \text{Cl} + \text{O}_2$ ,  $\text{BrCl} + \text{O}_2$ , and  $\text{OClO} + \text{Br}$ , where the latter one normally results in a null cycle for ozone destruction. However, the following cycles including  $\text{OClO}\cdot\text{H}_2\text{O}$ ,  $\text{OClO}\cdot(\text{H}_2\text{O})_2$ , and  $\text{ClOO}\cdot\text{H}_2\text{O}$  could enhance the ozone depletion due to the reaction  $\text{ClO} + \text{BrO} \rightarrow \text{OClO} + \text{Br}$  via cycle IV:



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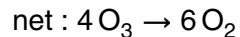
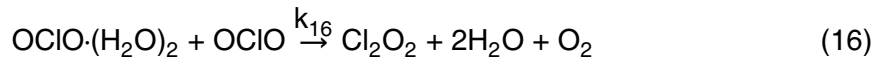
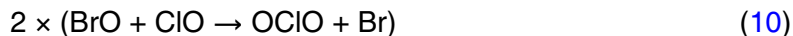
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cycle V:



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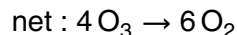
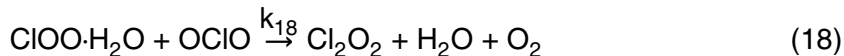
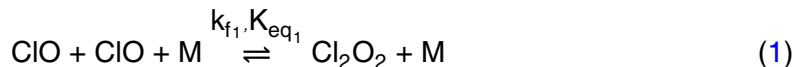
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and cycle VI:



To study the impact of these radical-molecule complexes on stratospheric ozone chemistry considered in pure gas-phase chemistry the reactions (Eqs. 5, 6, 7, 8, 9, 11, 12, 15, 16, 17, and 18) were implemented into the CLaMS model. In general, the complex formation is described by the reaction rate constant ( $k_f=k_{f5}$ ,  $k_{f8}$ ,  $k_{f11}$ ,  $k_{f15}$ , or  $k_{f17}$ ), where the chemical equilibrium between complex formation and its thermal decay is described by the equilibrium constant ( $K_{\text{eq}}=K_{\text{eq}5}$ ,  $K_{\text{eq}8}$ ,  $K_{\text{eq}11}$ ,  $K_{\text{eq}15}$ , or  $K_{\text{eq}17}$ ) for this termolecular reaction. The complex destruction is characterized by the bimolecular reaction rate constant ( $k=k_6$ ,  $k_7$ ,  $k_9$ ,  $k_{12}$ ,  $k_{16}$ , or  $k_{18}$ ) of the ClO dimer formation.

### 3.2. Kinetic parameters of the ClO<sub>x</sub> radical complexes

In stratospheric chemistry models a parameterization of the form  $K_{\text{eq}}(T)$  [ $\text{cm}^3 \text{molecules}^{-1}$ ]= $A \times \exp(\frac{B}{T})$  is usually used to describe the equilibrium constant. The

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parameters A and B are calculated from the reactions entropy ( $\Delta_r S$ ) and enthalpy ( $\Delta_r H$ ) (Sander et al., 2002):

$$A = \frac{R'T}{N_{av}} \exp\left(\frac{\Delta_r S}{R}\right) \quad \text{and} \quad B = -\frac{\Delta_r H}{R},$$

with  $R'=82.1 \text{ cm}^3 \text{ atm molecules}^{-1} \text{ K}^{-1}$ ,  $N_{av}$  the Avogadro constant, and  $R$  the universal gas constant.  $\Delta_r S$  can be calculated from the formation entropies of the species taking part in the reaction.  $\Delta_r H$  can be calculated from the binding energies  $D_0$  of the  $\text{ClO}_x$  radical complex ( $\Delta_r H = -D_0$ ) (see Tables 1 and 2).

For the  $\text{ClO-O}_2$  radical complex we used parameter A and B to calculate  $K_{\text{eq}5}$  recommended by Sander et al. (2002) and both  $k_6$  and  $k_7$  values (Eqs. 6 and 7) proposed by Prasad and Lee (1994) (see Table 1). For the  $\text{ClO}_x$  water radical complex, the equilibrium constant is calculated from the formation entropy and from the binding energies  $D_0$  as described above (see Table 2). As upper limit for the reaction rate constants ( $k_9$ ,  $k_{12}$ ,  $k_{16}$ , and  $k_{18}$ ) of the reactions (Eqs. 9, 12, 16, and 18) where the  $\text{ClO}_x$  water complexes are destroyed, we assume that the reaction is gas-kinetic. Here the  $k$  values are derived for stratospheric temperatures and the collision cross-sections are estimated from geometric parameters (see Table 2). The collision cross-sections are very rough estimated, therefore sensitivity tests varying the  $k$  values are performed (see below).

For the reaction rate constants  $k_f$  ( $=k_{f5}$ ,  $k_{f8}$ ,  $k_{f11}$ ,  $k_{f15}$ , and  $k_{f17}$ ) for all  $\text{ClO}_x$  radical-molecule complex formation reactions (Eqs. 5, 8, 11, 15 and 17), we assume as first approximation values similar to the termolecular reaction rate ( $k_{f1}$ ) of the  $\text{ClO}$  dimer formation (Eq. 1). Because large uncertainties about the radical complex chemistry exist, we perform sensitivity studies varying  $k_f$ ,  $K_{\text{eq}}$ , and  $k$  to analyze the impact of the several kinetic parameters on stratospheric ozone chemistry. In general, the system is not sensitive on  $k_f$  provided that the formation of the complex is not too slow, because then the formation of the complex is suppressed and thus the proposed ozone loss cycle cannot proceed.

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## 4. Results

For the  $\text{ClO}_x$  radical complexes model simulations are performed as first guess with kinetic parameters shown in Tables 1 and 2, respectively, (case 1). Sensitivity studies are performed along one particular Match trajectory from mid-January until the beginning of February 2003, where the discrepancies between simulated and observed ozone loss rates are large. For all these complexes no additional ozone loss compared to the standard case, i.e. without radical complex chemistry, is simulated by the model. Further model simulations show that an additionally calculated ozone loss is very sensitive on the relation between  $K_{\text{eq}}$  and  $k$  (see Figs. 1, 5, 6 and 8). In the following, we will discuss this for each  $\text{ClO}_x$  radical-molecule complex taking into account that the  $k$  values can not be faster than the gas-kinetic limit. Further at the end of this section we will discuss the potential impact of  $\text{ClO}_x$  complexes on stratospheric in situ measurements.

### 4.1. The $\text{ClO}\cdot\text{O}_2$ complex

To study the impact of a  $\text{ClO}\cdot\text{O}_2$  complex on polar ozone chemistry sensitivity studies are performed (see Table 3 and Fig. 1). Here simulations performed as first guess (case 1) with kinetic parameters recommended by Sander et al. (2002) and Prasad and Lee (1994), but without considering the  $\text{ClO}\cdot\text{O}_2$  self-reaction (i.e.  $k_7=0$ ) (cf. Table 1) yield a slightly smaller ozone loss compared to the standard case. In this case 1, the  $\text{ClO}\cdot\text{O}_2$  complex formation is faster than the complex destruction and up to  $\approx 600$  pptv  $\text{ClO}\cdot\text{O}_2$  is produced by the model changing the partitioning within the chlorine family compared to the standard case. In fact, further increasing the reaction rate constant for the complex destruction ( $k_6$ ) would yield more ozone destruction, but simultaneously the simulated  $\text{ClO}$  mixing ratios would likewise decrease compared to case 1 (not shown in Fig. 1), so that the simulated  $\text{ClO}$  mixing ratios would be much lower than what we know from stratospheric measurements which is most unlikely. Therefore the  $K_{\text{eq}5}$  values, that mean the stability of the  $\text{ClO}\cdot\text{O}_2$  complex, have to be decreased (case 2) to simulate an ozone loss similar to the standard case as shown in Fig. 1 (left panel).

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Further decreasing the  $K_{\text{eq}5}$  value (case 3) yield a bit lower ClO·O<sub>2</sub> values as for case 2 (Fig. 1, left panel). But taking the  $K_{\text{eq}5}$  values of case 2 and increasing the  $k_6$  values (case 4–6) (see Fig. 1, right panel) the model produces higher ClO dimer mixing ratios and therefore an additional ozone loss and lower ClO mixing ratios compared to the standard case. However, for case 4–5, the simulated ClO mixing ratios are higher than in case 1, whereas for case 6 the simulated ClO mixing ratios are in a similar range as for case 1 (max. ≈800 pptv).

Further the impact of cycle II (cf. Sect. 3.1), i.e. the impact of the ClO·O<sub>2</sub> self-reaction (Eq. 7) is discussed. The simulations case 1–6 are repeated with the reaction rate constant for the ClO·O<sub>2</sub> self-reaction ( $k_7$ ) proposed by Prasad and Lee (1994). An not negligible impact of Eq. (7) on the ozone chemistry is only found for case 1, where up to ≈600 pptv ClO·O<sub>2</sub> is produced and so sufficient ClO·O<sub>2</sub> molecules are available for the ClO·O<sub>2</sub> self-reaction (Eq. 7) (case 7, Table 3, not shown in Fig. 1). The simulated ozone destruction is here a bit higher than the standard case. The effect of Eq. (7) in case 7 is comparable with an increase of  $k_6$  for case 1 discussed above. Also here the simulated ClO mixing ratios (max. ≈800 pptv) are much lower than we know from stratospheric measurements.

We note here that a reaction  $\text{Cl} + \text{ClO} \cdot \text{O}_2 \rightarrow \text{Cl}_2\text{O} + \text{O}_2$  (with  $k = 1.0\text{E}-10$  [ $\text{cm}^3 \text{molecules}^{-1} \text{s}^{-1}$ ], estimated by Prasad and Lee, 1994, and the reactions destroying Cl<sub>2</sub>O ( $\text{Cl}_2\text{O} + \text{O}(^3\text{P}) \rightarrow \text{ClO} + \text{ClO}$  and  $\text{Cl}_2\text{O} + \text{Cl} \rightarrow \text{Cl}_2 + \text{ClO}$ , both with  $k$  values recommended by Sander et al., 2002) have no significant impact on the ozone losses calculated in the model simulations shown before.

#### 4.1.1. Analysis of the ClO dimer equilibrium constant

To analyze if the partitioning between ClO and its dimer (Cl<sub>2</sub>O<sub>2</sub>) in our model simulations is consistent with recently reported values for the equilibrium constant of the Cl<sub>2</sub>O<sub>2</sub> formation ( $K_{\text{eq}1}$ , Eq. 1) derived from stratospheric measurements (Stimpfle, 2004; von Hobe et al., 2005), we calculate a kind of effective equilibrium constant  $K_{\text{eq}}^{\text{eff}}(\text{Cl}_2\text{O}_2)$  from

Reactions (1), (5), (6), and (7):

$$\begin{aligned}
 K_{\text{eq}}^{\text{eff}}(\text{Cl}_2\text{O}_2) &= \frac{[\text{Cl}_2\text{O}_2]_{\text{night}}}{[\text{ClO}]_{\text{night}}^2} \\
 &= K_{\text{eq}1} \times \left( 1 + \epsilon \frac{k_{f5} [\text{O}_2]_{\text{night}}}{k_{f1} [\text{ClO}]_{\text{night}}} \right) \quad (19)
 \end{aligned}$$

with  $\epsilon$  the part of the ClO-O<sub>2</sub> radical-molecule complexes which forms the ClO dimer

$$\epsilon = \frac{k_6[\text{ClO}] + k_7[\text{ClO}\cdot\text{O}_2]}{k_6[\text{ClO}] + k_7[\text{ClO}\cdot\text{O}_2] + \frac{k_{f5}}{K_{\text{eq}5}}M} \quad (20)$$

Here only model data are used for solar zenith angles (SZA)  $\geq 100^\circ$  representing night time conditions. Plenge et al. (2005) found a value of  $K_{\text{eq}1}$  that is lower than current reference data (Sander et al., 2002) and agrees well with high altitude aircraft measurements within their scattering range (Stimpfle, 2004; von Hobe et al., 2005) (see Fig. 2), so that the upper limit of current reference values appears to be too high. The  $K_{\text{eq}}^{\text{eff}}(\text{Cl}_2\text{O}_2)$  values derived from our model results are compared to the values derived by (Stimpfle, 2004; von Hobe et al., 2005) shown in a van't Hoff plot of the equilibrium constant  $K_p$  as a function of  $T^{-1}$  ( $K_p = K_{\text{eq}1}(T)/(RT)$ ) (see Fig. 2). For the standard case without complex chemistry (here  $\epsilon$  is zero), the  $K_{\text{eq}1}$  value is identically with the value derived by Plenge et al. (2005) as expected because this  $K_{\text{eq}1}$  value was used for the model simulations. The  $K_p$  values derived from case 1 are much higher than derived by stratospheric measurements, because here reactive chlorine is stored in the ClO-O<sub>2</sub> complex and therefore the ClO mixing ratios are strongly reduced. This is also valid for case 7, where in addition the ClO-O<sub>2</sub> self-reaction is considered.  $K_p$  values derived from case 3 are almost identical with the standard case and values derived by (Plenge et al., 2005), respectively, because here a negligible amount of

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ClO·O<sub>2</sub> is calculated and thus the ClO mixing ratios are not affected. The K<sub>p</sub> values derived from case 2, 4, 5, and 6 increase with rising the reaction rate constant for the Cl<sub>2</sub>O<sub>2</sub> formation (k<sub>6</sub>), whereby case 2, 4, and 5 are within the scatter range of the results derived by (Stimpfle, 2004; von Hobe et al., 2005). For case 6, the K<sub>p</sub> value is higher than stratospheric measurements (see Fig. 2). Although significant ozone destruction compared to the standard case is taking place in case 6 this case is ruled out because the ClO to Cl<sub>2</sub>O<sub>2</sub> partitioning is unrealistic compared to stratospheric measurements. Thus only for cases 4 and 5, where addition ozone loss is simulated and the K<sub>p</sub> values are within the scatter range of stratospheric measurements, the ozone loss rates are compared to the Match results for the Arctic winter 2002/2003 at a level of 500 K potential temperature shown in Fig. 3. The amount of O<sub>3</sub> loss simulated additionally to the standard case (without complex chemistry) is lower than 0.5 ppb/sunlight h. We note that for the first Match point in Fig. 3 (and also in Fig. 7, see below) we have no simulated ozone loss rates due to the chemical initialization from SLIMCAT which started from early December.

#### 4.1.2. Analysis of the ozone change

Our model calculations show that the simulations case 1–3 yield only up to 2% lower ozone change than the standard case (see Fig. 4, right panel), although the stability of the ClO·O<sub>2</sub> complex is changed (D<sub>0</sub>=7.35–4.96, see Table 3). A detailed analysis of the ozone change show that the partitioning between the different halogen-induced ozone destroying cycles differ in a wide range as shown in Fig. 4 (left panel). In the standard case (without complex chemistry) ≈40% of the ozone destruction is caused by the ClO dimer cycle, ≈34% by the ClO-BrO cycle (McElroy et al., 1986), ≈21% by the ClO-O cycle (Molina and Rowland, 1974), and ≈6% by the ClO-HO<sub>2</sub> cycle (Solomon et al., 1986) at a temperature of 202 K for daylight conditions (SZA≤80°).

For case 1, the ClO·O<sub>2</sub> complex formation is faster than the complex destruction and up to ≈600 pptv ClO·O<sub>2</sub> is produced by the model, so that 60% of the ozone destruction is produced via cycle I (see Fig. 4, left panel). In this case, the efficiency of the other

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halogen-induced ozone destroying cycles are reduced mainly because of decreased free ClO. Thus the rate of the ClO dimer cycle on the total ozone destruction is only 9%, also reduced by a factor of 4 (because the ozone change is proportional to the  $[\text{ClO}]^2$ ), whereby the other cycles are reduced by approximately a factor of 2.

5 In case 2 the equilibrium constant for the ClO-O<sub>2</sub> formation was reduced so that lower ClO-O<sub>2</sub> mixing ratios are calculated by the model. Here only 8% the ozone destruction is caused by cycle I. In case 3, the equilibrium constant for the ClO-O<sub>2</sub> formation was reduced further. Here the rate of cycle I on the total ozone change is negligible, because the formation of the ClO-O<sub>2</sub> complex is too slow compared to the reaction velocity of  
10 the other halogen-induced ozone destroying cycles. Thus the partitioning between the different halogen-induced ozone destroying cycles for case 3 is more or less the same as for the standard case.

In case 5, the same  $K_{\text{eq}5}$  value is used as in case 2, but the reaction rate constant for the ClO-O<sub>2</sub> formation ( $k_6$ ) is increased. In this case, ≈21% more ozone loss is calculated by the model (see Fig. 4, right panel), because the reaction rate of the formation  
15 of the ClO dimer from the ClO-O<sub>2</sub> complex is very fast. Here 41% of the total ozone loss is produced via cycle I (see Fig. 4, left panel). In this case, where in our studies maximal additionally ozone loss is simulated for the ClO-O<sub>2</sub> complex and simultaneously the  $K_p$  values are within the scatter range of stratospheric measurements, the usual  
20 halogen-induced ozone destroying cycles (the ClO dimer cycle, the ClO-BrO cycle, the ClO-O cycle, and the HO<sub>2</sub>-ClO cycle) are strongly depressed compared to the standard case, but not as strongly as in case 1. The sum of the O<sub>3</sub> loss rates for the ClO dimer cycle and cycle I is approximately the same in cases 1 and 5, but reduced ClO mixing ratios in case 1 causes that all other halogen-induced ozone destroying cycles  
25 are slower than in case 5.



## 4.2. The ClO<sub>x</sub> water complexes

### 4.2.1. The ClO·H<sub>2</sub>O complex

Our model simulations show that an additional ozone loss compared to the standard case is only simulated for much higher equilibrium constants for the ClO·H<sub>2</sub>O formation (K<sub>eq8</sub>) (case 2) (cf. Table 4) than theoretically predicted as shown in Fig. 5 (left panel). Simultaneously the simulated ClO mixing ratios decrease and the Cl<sub>2</sub>O<sub>2</sub> mixing ratios increase when increasing the K<sub>eq8</sub> values (case 2). Here the ClO<sub>x</sub> mixing ratio are very close to those for case 1. By further increasing the K<sub>eq8</sub> value (case 3) the ClO mixing ratios still decrease to values which are much lower (max. ClO mixing ratios ≈700 pptv) than we know from stratospheric measurements for activated conditions (cf. Sect. 4.1.1). Simultaneously the Cl<sub>2</sub>O<sub>2</sub> mixing ratios increase further on, but here also the amount of ClO<sub>x</sub> is higher (≈100 pptv) than for case 1 and 2. Thus in case 2, the partitioning between ClO and Cl<sub>2</sub>O<sub>2</sub> is only changed, whereas in case 3 also the partitioning within the chlorine family is affected. This is because in case 3 the ClO mixing ratios are that low that significant lower Cl and HOCl and thus also lower HCl mixing ratios are simulated. In case 3 the simulated ClO mixing ratios are much lower than we know from stratospheric measurements because the reactive chlorine is stored in the complex. Therefore we conclude that K<sub>eq8</sub> values in that range are unrealistic. An increase of the k<sub>9</sub> values in case 3 would yield more ozone loss, but only for k<sub>9</sub> values much faster than gas-kinetic.

For the K<sub>eq8</sub> value from case 2 we perform further sensitivity studies varying the k<sub>9</sub> values (see Fig. 5, right panel). For k<sub>9</sub> values (case 4) lower than in case 1, no additional ozone loss is simulated similar to case 1 that means this k<sub>9</sub> value is too slow compared to K<sub>eq8</sub>, so that no additional ClO dimer mixing ratios are produced and no additional ozone loss is simulated. Increasing the k<sub>9</sub> values (case 5) yield additional ozone loss because additional Cl<sub>2</sub>O<sub>2</sub> is produced. Here the ClO mixing ratios are not so strongly reduced as in case 3, but the k<sub>9</sub> value are high (in the range of the upper limit of our estimation for the gas-kinetic limit). Thus we conclude that only case 2 yield

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an additional ozone loss compared to the standard case under realistic conditions, but with a binding energy for the ClO·H<sub>2</sub>O complex substantial higher than predicted by Francisco and Sander (1995) and Fu et al. (2003), respectively.

A similar analysis for the partitioning between ClO and its dimer in our model simulations as for the ClO·O<sub>2</sub> complex is performed. Here case 3 yields an  $K_{\text{eq}}^{\text{eff}}(\text{Cl}_2\text{O}_2)$  which is above the uncertainty range of the recently reported values for the equilibrium constant of the Cl<sub>2</sub>O<sub>2</sub> formation ( $K_{\text{eq}1}$ , Eq. 1) (Plenge et al., 2005). For all other cases the  $K_{\text{eq}}^{\text{eff}}(\text{Cl}_2\text{O}_2)$  values are within the reported uncertainties, where for case 5 the  $K_{\text{eq}}^{\text{eff}}(\text{Cl}_2\text{O}_2)$  values are at the upper limit.

Ozone loss rates for case 2 and 5 compared to Match results for the whole winter 2003/2003 at a level of 500 K are shown in Fig. 7. The enhancement of the ozone loss rates is  $\approx 0.5$  ppb/sunlight h.

#### 4.2.2. The OClO·H<sub>2</sub>O complex

Analogous sensitivity studies are performed with the OClO·H<sub>2</sub>O complex (see Table 5 and Fig. 6). Also here the equilibrium constant for the formation of the OClO·H<sub>2</sub>O complex ( $K_{\text{eq}11}$ ) is to be increased (case 2) compared to case 1 to simulate ozone loss rates higher than in the standard case (see Fig. 6, left panel). Again the ClO mixing ratios are simultaneously decreased. However, by further increasing the  $K_{\text{eq}11}$  values (case 3) the relation between  $K_{\text{eq}11}$  and  $k_{12}$  is changed so that the OClO·H<sub>2</sub>O complex formation is faster than the complex destruction and up to  $\approx 800$  pptv OClO·H<sub>2</sub>O is produced by the model changing the partitioning within the chlorine family. Therefore less ozone is destroyed in this model simulation than in the standard case. An increase of the  $k_{12}$  values in case 3 would yield more ozone loss, but only for  $k_{12}$  values much faster than gas-kinetic.

For a  $K_{\text{eq}11}$  value of case 2 we decrease the  $k_{12}$  values (case 4) and found the same behavior as in case 3, namely a high formation rate of OClO·H<sub>2</sub>O and less ozone loss than in the standard case (see Fig. 6, right panel). For higher  $k_{12}$  values (case 5), the

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simulations show ozone loss rates a bit higher than in case 2 and the ClO mixing ratios are only decreased by a small amount. However, the  $k_{12}$  values are in the range of the upper limit of our estimation for the gas-kinetic limit, so that we conclude that case 2 yields model results for reasonably realistic conditions, but with a much higher binding energy for the ClO-H<sub>2</sub>O complex than theoretically predicted (Aloisio and Francisco, 1999). For case 2 and 5 the simulated ozone loss rates in comparison to the Match results for the winter 2002/2003 at 500 K potential temperature are shown in Fig. 7. The simulated ozone loss rates are a bit larger than simulated ozone loss rates for the ClO-H<sub>2</sub>O complex (see Fig. 7).

We note that the analysis of the partitioning between ClO and its dimer in our model simulations show that the  $K_{eq}^{eff}(Cl_2O_2)$  values are only marginally affected. Further, for cases 2–5 the simulated OCIO mixing ratios are very low with maximum OCIO mixing ratios up to 4–6 pptv. These mixing ratios are much lower than we know from recent stratospheric nighttime OCIO measurements (Canty et al., 2005).

#### 4.2.3. The OCIO·(H<sub>2</sub>O)<sub>2</sub> complex

The potential impact of the ozone destroying cycle V due to the OCIO·(H<sub>2</sub>O)<sub>2</sub> radical complex is analyzed. For cycle V also the OCIO-H<sub>2</sub>O complex is required to form the OCIO·(H<sub>2</sub>O)<sub>2</sub> complex, so that we have also to consider the uncertainties of the OCIO-H<sub>2</sub>O complex chemistry. Therefore we repeat the model simulations case 1–5 (see Table 5) performed for the OCIO-H<sub>2</sub>O complex plus Eqs. (15) and (16) with kinetic parameters for Eqs. (15) and (16) as shown in Table 2. However no additional ozone loss is simulated for these cases. For case 2 and 3, where OCIO-H<sub>2</sub>O mixing ratios are simulated up to 600 and 800 pptv, respectively, we expect that sufficient OCIO·(H<sub>2</sub>O)<sub>2</sub> molecules are available that the ozone destroying cycle V can proceed. Therefore we increase for these cases the reaction rate constant  $k_{16}$  to enhance the formation of Cl<sub>2</sub>O<sub>2</sub> and therefore to enhance ozone destruction. But also for reaction rate constants much larger than gas-kinetic, simulations yield no additional ozone loss.

In further simulations we assume kinetic parameters for the OCIO-H<sub>2</sub>O complex of

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case 2 and vary the equilibrium constant  $K_{\text{eq}15}$ . We found here the same behavior as for the  $\text{OCIO}\cdot\text{H}_2\text{O}$  complex (see Sect. 4.2.2). Only for equilibrium rate constants  $K_{\text{eq}15}$  much higher than predicted by theoretical calculations of the binding energy of the  $\text{OCIO}\cdot(\text{H}_2\text{O})_2$  complex an additional ozone loss is simulated (see Table 6 and Fig. 8, case 6). Also here the simulated ozone loss is very sensitive on  $k_{16}$  for given  $K_{\text{eq}15}$  values (see case 7). Further increasing the  $K_{\text{eq}15}$  values (case 8) yield an lower ozone loss as in the standard case (without radical complex chemistry), because here reactive chlorine is stored in the  $\text{OCIO}\cdot(\text{H}_2\text{O})_2$  complex. Increasing the  $k_{16}$  values would yield an additional ozone loss to case 2, but only for  $k_{16}$  values much higher than gas-kinetic.

#### 4.2.4. The $\text{ClOO}\cdot\text{H}_2\text{O}$ complex

From the discussion above, we expect the same behavior for the  $\text{ClOO}\cdot\text{H}_2\text{O}$  complex chemistry as for the other  $\text{ClO}_x\cdot(\text{H}_2\text{O})_x$  complexes because we assume that this complex has a collision cross-section in a similar range, which determined the gas-kinetic limit. Therefore we conclude that also the  $\text{ClOO}\cdot\text{H}_2\text{O}$  radical complex molecule has to be fairly stable which is in contrast to theoretically predicted value of  $1.3 \text{ kcal mol}^{-1}$  for the binding energy ( $D_0$ ) (Aloisio and Francisco, 1999). Thus a significant impact of a  $\text{ClOO}\cdot\text{H}_2\text{O}$  complex on stratospheric ozone processes can most likely be excluded.

#### 4.3. The potential impact of $\text{ClO}_x$ complexes on stratospheric in situ measurements

Here the potential impact of a  $\text{ClO}_x$  radical-molecule complexes on stratospheric in situ measurements of  $\text{ClO}$  and  $\text{Cl}_2\text{O}_2$ , respectively, mixing ratios is to be discussed. All available stratospheric in situ  $\text{ClO}$  and  $\text{Cl}_2\text{O}_2$  measurements which were used to infer the equilibrium constant for the  $\text{ClO}$  dimer formation (Stimpfle, 2004; von Hobe et al., 2005) employ the same measurement technique, namely the well-established chemical-conversion resonance-fluorescence technique (Brune et al., 1989). A  $\text{ClO}_x$  complex may react with  $\text{NO}$  in just the same way as  $\text{ClO}$  would, therefore the equilibrium constant for the  $\text{ClO}$  dimer formation ( $K_{\text{eq}1}$ ) derived by stratospheric  $\text{ClO}$  and

dimer measurements have to be lower than  $K_{\text{eq}1}$  values derived by laboratory measurements, if a  $\text{ClO}_x$  radical complexes would exist in a sufficient large amount in the polar stratosphere:

$$[\text{ClO}]_{\text{meas}} = [\text{ClO}]_{\text{real}} + [\text{ClO}_x \text{ complexes}] \quad (21)$$

$$K_{\text{eq}}^{\text{meas}} = \frac{[\text{Cl}_2\text{O}_2]}{[\text{ClO}]_{\text{meas}}^2} \leq \frac{[\text{Cl}_2\text{O}_2]}{[\text{ClO}]_{\text{real}}^2} = K_{\text{eq}}^{\text{real}} \quad (22)$$

Our studies show that for the  $\text{ClO}\cdot\text{O}_2$  complexes for the cases 1 and 7 a sufficient large amount of  $\text{ClO}\cdot\text{O}_2$  is available so that  $K_{\text{eq}}^{\text{meas}}$  is significant lower than  $K_{\text{eq}}^{\text{real}}$  as shown in Fig. 9. However, these cases are unrealistic because both the simulated  $\text{ClO}$  mixing ratios were too low and the  $K_{\text{eq}}^{\text{eff}}(\text{Cl}_2\text{O}_2)$  values were too high. For the  $\text{OCIO}\cdot\text{H}_2\text{O}$  complex only for cases 3 and 4 and for low temperatures ( $\leq 196\text{ K}$ ) a significant difference was found. These cases yield realistic values for the  $\text{ClO}$  mixing ratios and for  $K_{\text{eq}}^{\text{eff}}(\text{Cl}_2\text{O}_2)$ , but too low  $\text{OCIO}$  mixing ratios. We note that all these cases yield no additional ozone loss. However, in this study we present only borderline cases to study the possible impact on stratospheric ozone loss rates. Therefore possibly for other binding energies not analyzed here these complexes could affect the in situ  $\text{ClO}$  and  $\text{Cl}_2\text{O}_2$  measurements, but not the ozone loss rates. Thus the existence of these  $\text{ClO}_x$  radical complexes could explain that the  $K_{\text{eq}1}$  values derived from stratospheric  $\text{ClO}$  and  $\text{Cl}_2\text{O}_2$  in situ measurements by [Stimpfle \(2004\)](#) and [von Hobe et al. \(2005\)](#) differ from the  $K_{\text{eq}1}$  values derived by [Plenge et al. \(2005\)](#). These discrepancies were already discussed by [Plenge et al. \(2005\)](#), but further examinations of this feature would be worthwhile.

## 5. Summary and conclusions

The potential impact of radical complexes on polar stratospheric ozone loss processes was studied performing model simulations with the Chemical Lagrangian Model of the

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stratosphere (CLaMS) including the  $\text{ClO}\cdot\text{O}_2$  and  $\text{ClO}_x$  water radical complexes like  $\text{ClO}\cdot\text{H}_2\text{O}$ ,  $\text{OCIO}\cdot\text{H}_2\text{O}$ ,  $\text{OCIO}\cdot(\text{H}_2\text{O})_2$ , and  $\text{ClOO}\cdot\text{H}_2\text{O}$  in pure gas-phase chemistry. The simulated ozone loss was compared to observed ozone loss rates determined with the Match technique for the Arctic winter 2002/2003 at a level of 500 K potential temperature.

The present sensitivity studies show that the stratospheric polar ozone chemistry is very sensitive on the relation between the equilibrium constant  $K_{\text{eq}}$  of the complex formation and its thermal decay and of the bimolecular reaction rate constant  $k$  of the  $\text{ClO}$  dimer formation from the radical-molecule complex. Our studies show that there exists for each  $\text{ClO}_x$  radical-molecule complex only one ideal range for the equilibrium constant ( $K_{\text{eq}}^{\text{ideal}}$ ) where an additional ozone loss is possible provided that the reaction rate constant  $k$  for the  $\text{Cl}_2\text{O}_2$  formation is not faster than gas-kinetic. If the  $K_{\text{eq}}$  values are lower than  $K_{\text{eq}}^{\text{ideal}}$  no enhanced ozone loss is possible. If the  $K_{\text{eq}}$  are higher than  $K_{\text{eq}}^{\text{ideal}}$  less ozone loss is simulated, because reactive chlorine is stored in the complex. Further, then the partitioning between  $\text{ClO}$  and  $\text{Cl}_2\text{O}_2$  is unrealistic compared to stratospheric measurements. For these  $K_{\text{eq}}$  values higher than  $K_{\text{eq}}^{\text{ideal}}$  an additional ozone loss is possible whether the bimolecular reaction rate constant  $k$  for  $\text{Cl}_2\text{O}_2$  formation from the complex is much faster than gas-kinetic, which is unphysical and therefore can be excluded. Further, the present model simulations show that the simulated ozone loss is very sensitive on the bimolecular reaction rate constant of the  $\text{ClO}$  dimer formation  $k$  from the complex by fixed values for the equilibrium constant ( $K_{\text{eq}}^{\text{ideal}}$ ) for the  $\text{ClO}_x$  complex formation.

The present sensitivity studies for a  $\text{ClO}\cdot\text{O}_2$  complex show that an additional ozone loss is only simulated for binding energies of the  $\text{ClO}\cdot\text{O}_2$  complex in the range of  $\approx 6$  kcal  $\text{mol}^{-1}$  in agreement with Shindell (1996), which is lower than the upper limit of 7.4 kcal  $\text{mol}^{-1}$  recommended by Sander et al. (2002). In addition to the work by Shindell (1996), recently reported values for the equilibrium constant of the  $\text{ClO}$  dimer formation  $K_{\text{eq}}(\text{Cl}_2\text{O}_2)$  from stratospheric measurements (Stimpfle, 2004; von Hobe et al., 2005) are used to restrict the number of possible model results caused by large uncertain-

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ties about radical complex chemistry. Further our studies show, that the reaction rate constant of the ClO dimer formation from the ClO-O<sub>2</sub> complex ( $k_6$ ) has to be faster than assumed by Prasad and Lee (1994) in agreement with Shindell (1996). An upper limit for the  $k_6$  value is that the effective equilibrium constant for the ClO dimer formation ( $K_{\text{eq}}^{\text{eff}}(\text{Cl}_2\text{O}_2)$ ) has to be not higher than recently recommended from field measurements (Stimpfle, 2004; von Hobe et al., 2005). The amount of additionally simulated O<sub>3</sub> loss rates is very small ( $d\text{O}_3/dt \ll 0.5$  ppb/sunlight h).

Our findings show for the ClO<sub>x</sub> water complexes that to produce additionally O<sub>3</sub> loss rates the binding energies of these radical complexes have to be much higher ( $\approx 9$ – $15$  kcal mol<sup>-1</sup>) than theoretically predicted ( $1.3$ – $3.4$  kcal mol<sup>-1</sup>) (Francisco and Sander, 1995; Aloisio and Francisco, 1999; Fu et al., 2003). In addition the Cl<sub>2</sub>O<sub>2</sub> formation has to be very fast (gas-kinetic). The additionally simulated O<sub>3</sub> loss rates is  $\approx 0.5$  ppb/sunlight h. The present work shows that an impact of ClO<sub>x</sub> water radical complexes on polar ozone loss rates is most unlikely considering pure gas-phase chemistry, because the binding energy of these complexes has to be much higher than theoretically predicted.

Moreover our studies show that the existence of ClO<sub>x</sub> radical-molecule complexes could possibly explain discrepancies for the equilibrium constant of the ClO dimer formation found between recent laboratory and stratospheric measurements (Plenge et al., 2005). Thus ClO<sub>x</sub> radical-molecule complexes do not solve the early winter problem of ozone loss rates considering pure gas-phase chemistry. However if another ClO<sub>x</sub> radical-molecule complex formation channel for instance via heterogeneous reactions on polar stratospheric clouds would exist (e.g., McKeachie et al., 2004), the ozone destroying cycles discussed here could have an important impact on stratospheric polar ozone loss processes, especially under cold mid-winter conditions.

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**Table 1.** Kinetic parameters used for the first guess model simulation including the radical complexes ClO-O<sub>2</sub>.

		ClO-O <sub>2</sub>	Reference
A	[cm <sup>3</sup> molecules <sup>-1</sup> ]	2.9E-26	<a href="#">Sander et al. (2002)</a>
B	[K <sup>-1</sup> ]	<3700	<a href="#">Sander et al. (2002)</a>
D <sub>0</sub>	[kcal mol <sup>-1</sup> ]	≡7.4	
K <sub>eq5</sub> (200 K)	[cm <sup>3</sup> molecules <sup>-1</sup> ]	≈3.1E-18	
k <sub>6</sub>	[cm <sup>3</sup> molecules <sup>-1</sup> s <sup>-1</sup> ]	≈1.0E-12	<a href="#">Prasad and Lee (1994)</a>
k <sub>7</sub>	[cm <sup>3</sup> molecules <sup>-1</sup> s <sup>-1</sup> ]	≈5.0E-13	<a href="#">Prasad and Lee (1994)</a>

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**Table 2.** Kinetic parameters used for the first guess model simulation including the radical complexes ClO·H<sub>2</sub>O, OClO·H<sub>2</sub>O, OClO·(H<sub>2</sub>O)<sub>2</sub>, and ClOO·H<sub>2</sub>O.

		ClO·H <sub>2</sub> O	OClO·H <sub>2</sub> O	OClO·(H <sub>2</sub> O) <sub>2</sub>	ClOO·H <sub>2</sub> O
$\Delta_f S_{\text{complex}}$	[cal K <sup>-1</sup> mol <sup>-1</sup> ]	71.0 <sup>a</sup>	71.0 <sup>b</sup>	80.0 <sup>g</sup>	71.0 <sup>b</sup>
$\Delta_f S$	[cal K <sup>-1</sup> mol <sup>-1</sup> ]	-27.9	-35.5	-36.1	-38.4
$D_0$	[kcal mol <sup>-1</sup> ]	3.2 <sup>c</sup>	2.0 <sup>d</sup>	3.4 <sup>d</sup>	1.3 <sup>d</sup>
$K_{\text{eq}}(200\text{ K})$	[cm <sup>3</sup> molecules <sup>-1</sup> ]	$\sim K_{\text{eq8}} = 1.1\text{E-}22$	$\sim K_{\text{eq11}} = 1.1\text{E-}25$	$\sim K_{\text{eq15}} = 2.7\text{E-}24$	$\sim K_{\text{eq17}} = 4.2\text{E-}27$
$\sigma$	[nm]	0.34 <sup>e</sup>	0.5 <sup>f</sup>	0.8 <sup>f</sup>	0.5 <sup>f</sup>
$k$	[cm <sup>3</sup> molecules <sup>-1</sup> s <sup>-1</sup> ]	$\sim k_9 = 1.3\text{E-}10$	$\sim k_{12} = 1.7\text{E-}10$	$\sim k_{16} = 2.7\text{E-}10$	$\sim k_{18} = 1.7\text{E-}10$

<sup>a</sup> estimated by [Francisco and Sander \(1995\)](#)

<sup>b</sup> assumed to be similar to ClO·H<sub>2</sub>O

<sup>c</sup> [Francisco and Sander \(1995\)](#), similar values are calculated with the density functional theory by [Fu et al., 2003](#)

<sup>d</sup> [Aloisio and Francisco \(1999\)](#)

<sup>e</sup> collision cross-section is estimated from geometric parameters calculated by [Fu et al. \(2003\)](#)

<sup>f</sup> collision cross-section is estimated from geometric parameters calculated by [Aloisio and Francisco \(1999\)](#)

<sup>g</sup> assumed

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**Table 3.** Equilibrium constants ( $K_{\text{eq5}}$ ) and reaction reaction rate constants ( $k_6$  and  $k_7$  in  $[\text{cm}^3\text{molecules}^{-1}\text{s}^{-1}]$ ) used for different model simulations (case 1–7) considering ClO·O<sub>2</sub> complex chemistry (see Eqs. 5, 6, and 7). The parameterization of  $K_{\text{eq}}$  is described in Sect. 3.2.

case	$K_{\text{eq5}}$ [ $\text{cm}^3\text{molecules}^{-1}$ ]				$k_6$	$k_7$	additional $d\text{O}_3/dt$
	A [ $\text{cm}^3\text{molecules}^{-1}$ ]	B [ $\text{K}^{-1}$ ]	$D_0$ [ $\text{kcal mol}^{-1}$ ]	$K_{\text{eq5}}(200\text{ K})$			
1	2.9 E-26	3700.0	7.35	3.1 E-18	1.0 E-12	0.0	–
2	2.9 E-26	3000.0	5.69	9.5 E-20	1.0 E-12	0.0	0
3	2.9 E-26	2500.0	4.96	7.8 E-21	1.0 E-12	0.0	0
4	2.9 E-26	3000.0	5.69	9.5 E-20	5.0 E-12	0.0	+
5	2.9 E-26	3000.0	5.69	9.5 E-20	1.0 E-11	0.0	+
6	2.9 E-26	3000.0	5.69	9.5 E-20	5.0 E-11	0.0	+
7	2.9 E-26	3700.0	7.35	3.1 E-18	1.0 E-12	5.0E-13	+

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**Table 4.** Equilibrium constants ( $K_{\text{eq8}}$ ) and reaction rate constants ( $k_9$ ) used for different model simulations (case 1–5) considering ClO·H<sub>2</sub>O complex chemistry (see Eqs. 8 and 9). The parameterization of  $K_{\text{eq}}$  is described in Sect. 3.2.

case	$K_{\text{eq8}}$ [cm <sup>3</sup> molecules <sup>-1</sup> ]				$k_9$ [cm <sup>3</sup> molecules <sup>-1</sup> s <sup>-1</sup> ]	additional dO <sub>3</sub> /dt
	A [cm <sup>3</sup> molecules <sup>-1</sup> ]	B [K <sup>-1</sup> ]	D <sub>0</sub> [kcal mol <sup>-1</sup> ]	$K_{\text{eq8}}$ (200 K)		
1	3.3 E-26	1611.4	3.2	1.1 E-22	1.3 E-10	0
2	3.3 E-26	4500.0	8.9	1.9 E-16	1.3 E-10	+
3	3.3 E-26	5000.0	9.9	2.4 E-15	1.3 E-10	+
4	3.3 E-26	4500.0	8.9	1.9 E-16	1.0 E-11	0
5	3.3 E-26	4500.0	8.9	1.9 E-16	3.0 E-10	+

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**Table 5.** Equilibrium constants ( $K_{\text{eq}11}$ ) and reaction rate constants ( $k_{12}$ ) used for different model simulations (case 1–5) considering OCIO- $\text{H}_2\text{O}$  complex chemistry (see Eqs. 11 and 12). The parameterization of  $K_{\text{eq}}$  is described in Sect. 3.2.

case	$K_{\text{eq}11}$ [ $\text{cm}^3 \text{molecules}^{-1}$ ]				$k_{12}$ [ $\text{cm}^3 \text{molecules}^{-1} \text{s}^{-1}$ ]	additional $\text{dO}_3/\text{dt}$
	A [ $\text{cm}^3 \text{molecules}^{-1}$ ]	B [ $\text{K}^{-1}$ ]	$D_0$ [ $\text{kcal mol}^{-1}$ ]	$K_{\text{eq}11}(200 \text{ K})$		
1	7.2 E-28	1007.1	2.0	1.1 E-25	1.7 E-10	0
2	7.2 E-28	7500.0	14.9	1.4 E-11	1.7 E-10	+
3	7.2 E-28	8000.0	15.9	1.7 E-10	1.7 E-10	–
4	7.2 E-28	7500.0	14.9	1.4 E-11	1.0 E-11	–
5	7.2 E-28	7500.0	14.9	1.4 E-11	3.0 E-10	+

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**Table 6.** Equilibrium constants ( $K_{\text{eq}15}$ ) and reaction rate constants ( $k_{16}$ ) used for different model simulations (case 6–8) considering  $\text{OCIO}\cdot(\text{H}_2\text{O})_2$  complex chemistry (see Eqs. 15 and 16). The parameterization of  $K_{\text{eq}}$  is described in Sect. 3.2.

case	$K_{\text{eq}15}$ [ $\text{cm}^3\text{molecules}^{-1}$ ]				$k_{16}$ [ $\text{cm}^3\text{molecules}^{-1}\text{s}^{-1}$ ]	additional $\text{dO}_3/\text{dt}$
	A [ $\text{cm}^3\text{molecules}^{-1}$ ]	B [ $\text{K}^{-1}$ ]	$D_0$ [ $\text{kcal mol}^{-1}$ ]	$K_{\text{eq}15}(200\text{ K})$		
6	5.2 E-28	6800.0	13.5	3.0 E-13	2.7 E-10	+
7	5.2 E-28	6800.0	13.5	3.0 E-13	5.0 E-10	+
8	5.2 E-28	7500.0	14.9	1.0 E-11	2.7 E-10	-

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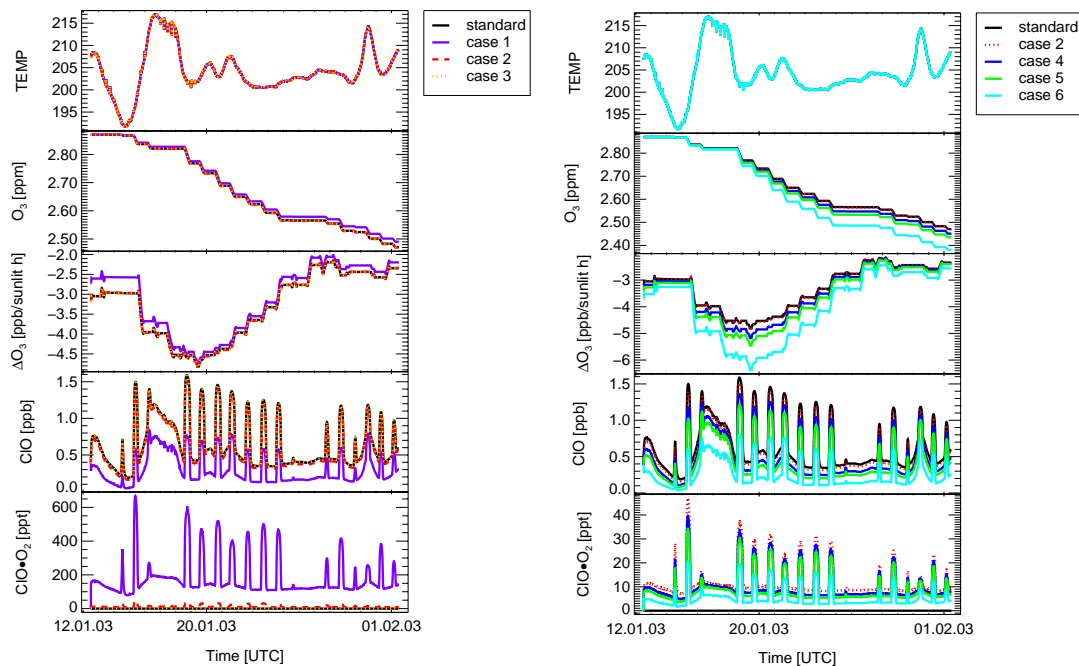
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**Fig. 1.** Temperature,  $O_3$ , ClO, and ClO- $O_2$  mixing ratios as well as the ozone depletion per sunlight hour are shown along one Match trajectory starting in mid-January until the beginning of February 2003 for different sensitivity studies considering the ClO- $O_2$  complex chemistry in model simulations. The sensitivity of  $K_{eq5}$  values (left panel) and of  $k_6$  values for a given  $K_{eq5}$  value (right panel) on polar ozone chemistry was analyzed.

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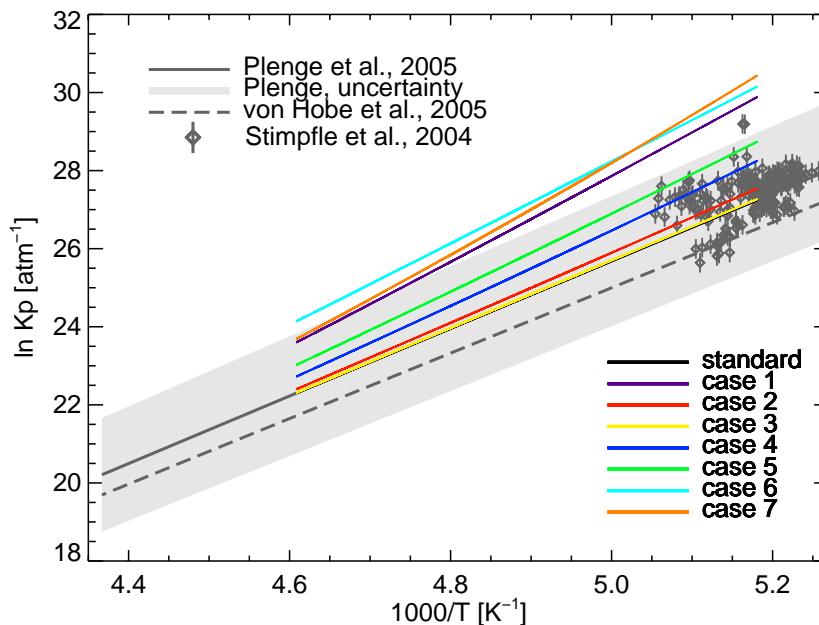
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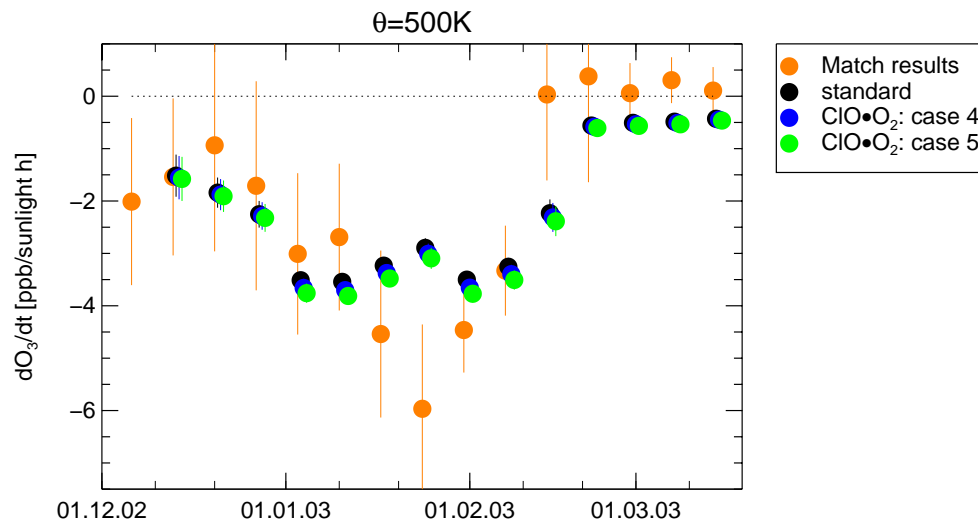
**Fig. 2.** Temperature dependence of the equilibrium constant  $K_p$  of the termolecular ClO dimer formation (Eq. 1) as a function of the reciprocal temperature (van't Hoff plot). Current experimental results (Plenge et al., 2005), results from field measurements (Stimpfle, 2004; von Hobe et al., 2005), and  $K_p$  values calculated from model simulations included ClO $\cdot$ O $_2$  complex chemistry are compared (see Sect. 4.1.1 and Table 3).

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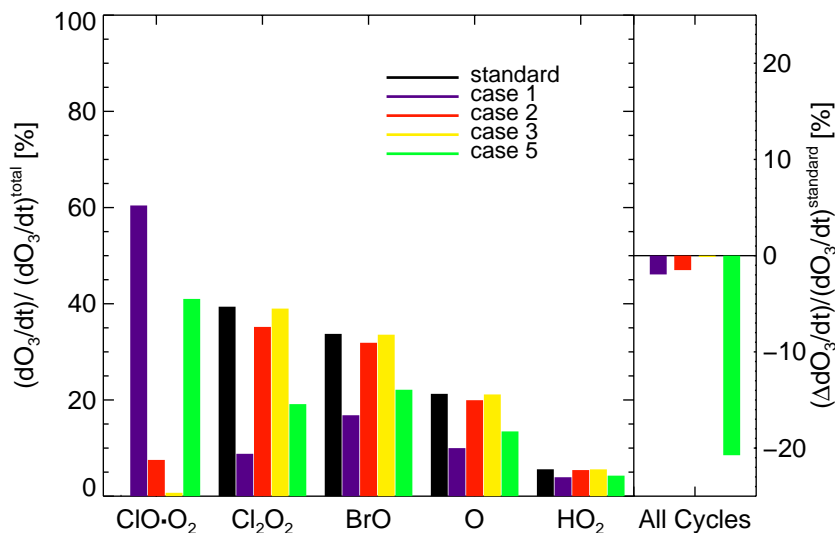
**Fig. 3.** Ozone loss rates derived with the Match technique for the Arctic winter 2002/2003 at a level of 500 K potential temperature compared to different model simulations including  $ClO\cdot O_2$  complex chemistry (see Table 3). The standard case is without radical complex chemistry. Note that the symbols for the model simulations are shifted a bit to the right in order to better distinguish between the different model cases.

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**Fig. 4.** The partitioning between the different halogen-induced ozone destroying cycles:  $ClO \cdot O_2$  (Cycle I), the  $ClO$  dimer cycle, the  $ClO$ - $BrO$  cycle, the  $ClO$ - $O$  cycle, and the  $HO_2$ - $ClO$  cycle for different simulations (case 1, 2, 3, and 5) including  $ClO \cdot O_2$  chemistry are compared to the standard case (without complex chemistry) (left panel). The total ozone loss rates of the different cases are compared to the standard case (right panel). The model results are analyzed for daylight conditions ( $SZA \leq 80^\circ$ ) and at a temperature of 202 K.

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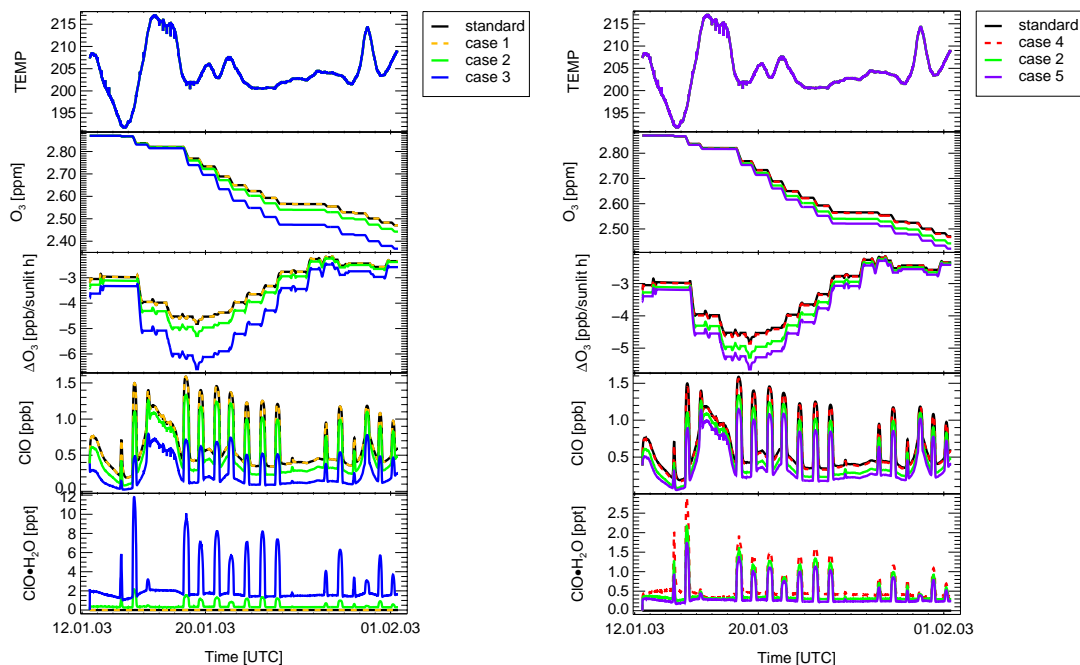
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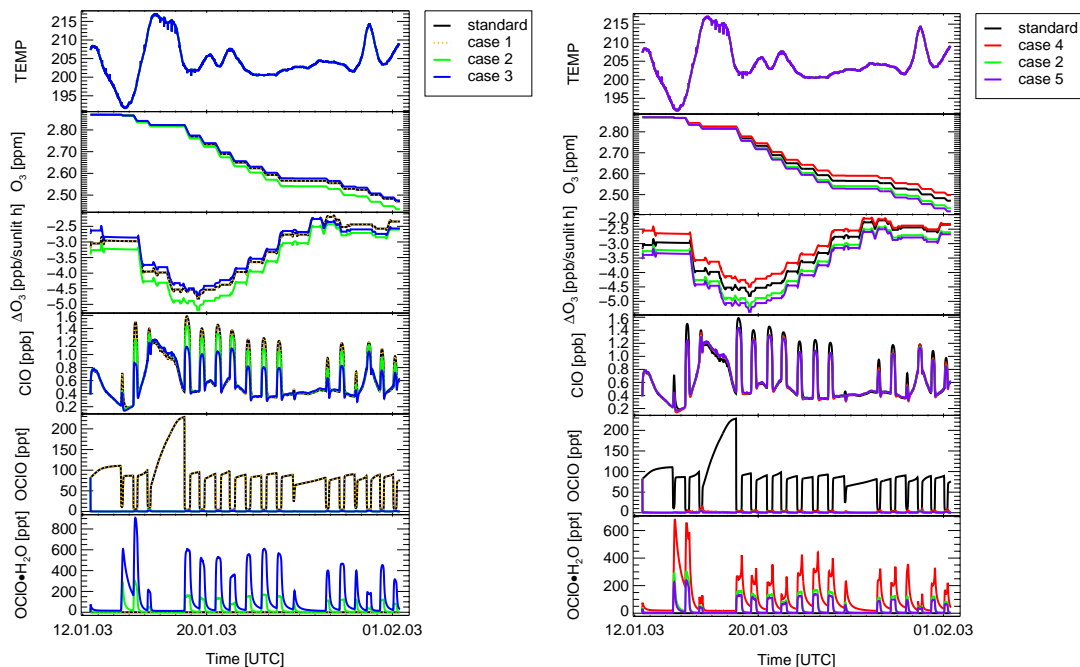
**Fig. 5.** Temperature,  $O_3$ , ClO, and ClO·H<sub>2</sub>O mixing ratios as well as the ozone depletion per sunlit hour are shown along one Match trajectory starting in mid-January until the beginning of February 2003 for different sensitivity studies considering the ClO·H<sub>2</sub>O complex chemistry in model simulations. The sensitivity of  $K_{eq8}$  values (left panel) and of  $k_9$  values for a given  $K_{eq8}$  value (right panel) on polar ozone chemistry was analyzed.

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**Fig. 6.** Temperature, O<sub>3</sub>, ClO, ClO<sub>2</sub>, and OCIO·H<sub>2</sub>O mixing ratios as well as the ozone depletion per sunlight hour are shown along one Match trajectory starting in mid-January until the beginning of February 2003 for different sensitivity studies considering the OCIO·H<sub>2</sub>O complex chemistry in model simulations. The sensitivity of  $K_{eq11}$  values (left panel) and of  $k_{12}$  values for a given  $K_{eq11}$  value (right panel) on polar ozone chemistry was analyzed.

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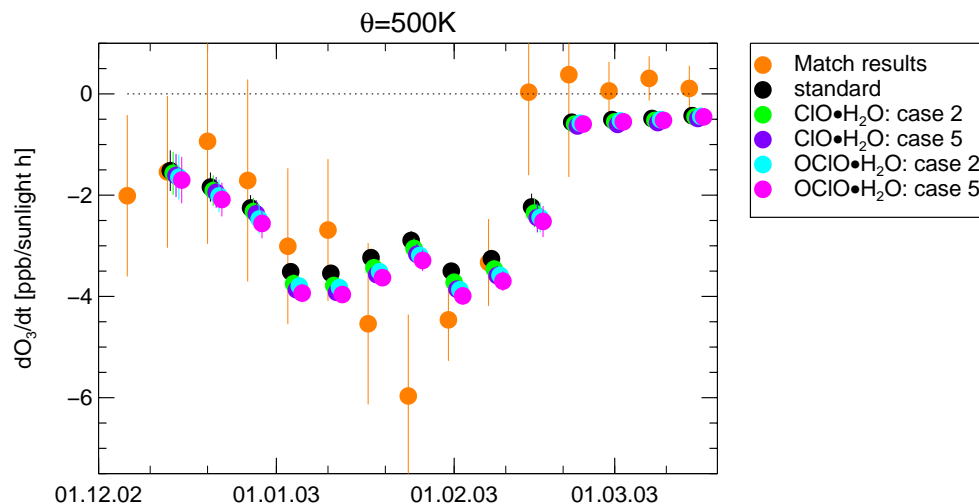
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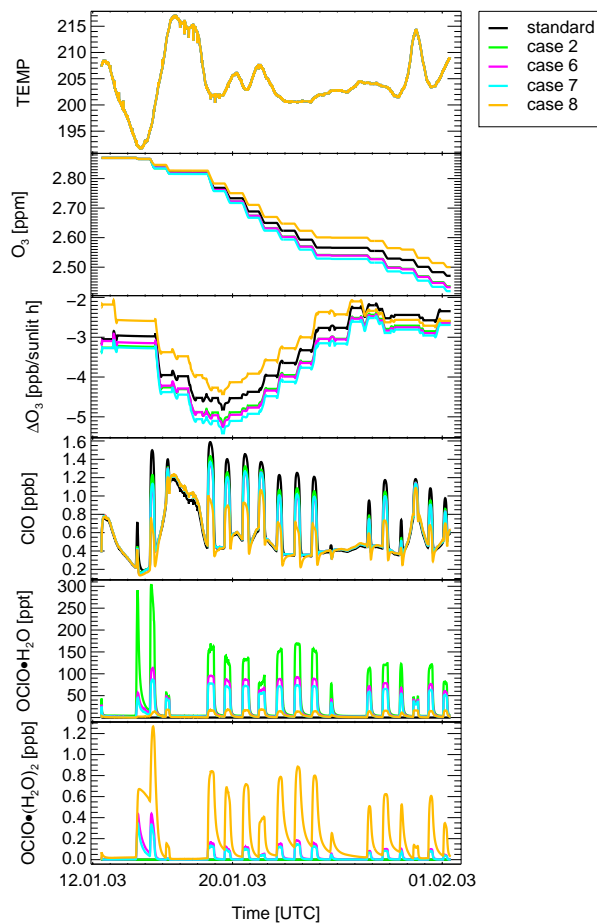
**Fig. 7.** Ozone loss rates derived with the Match technique for the Arctic winter 2002/2003 at a level of 500 K potential temperature compared to different model simulations including ClO<sub>x</sub> water radical complex chemistry (see Tables 4 and 5). The standard case is without radical complex chemistry. We note that the symbols for the model simulations are shifted a bit to the right in order to better distinguish between the different model cases.

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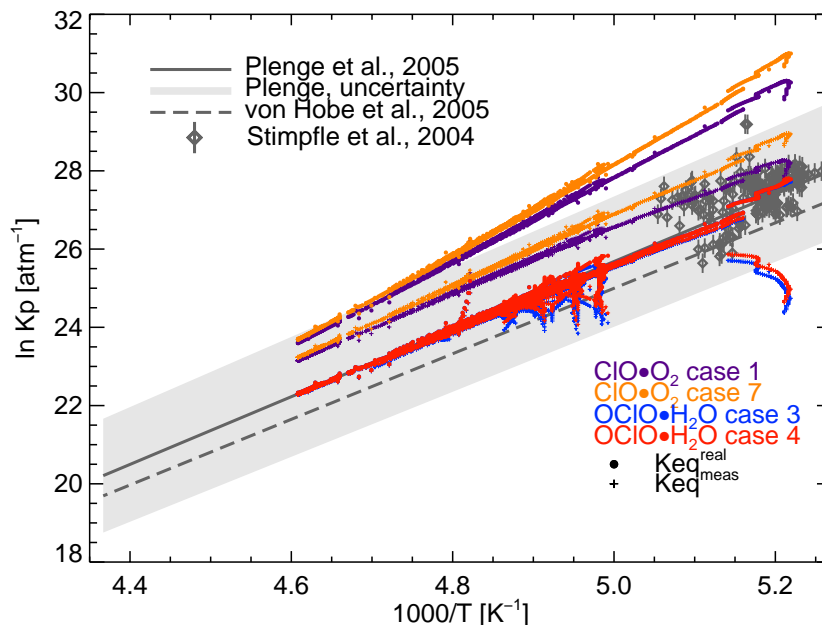


**Fig. 8.** Temperature, O<sub>3</sub>, ClO, OCIO•H<sub>2</sub>O, and OCIO•(H<sub>2</sub>O)<sub>2</sub> mixing ratios as well as the ozone depletion per sunlight hour are shown along one Match trajectory starting in mid-January until the beginning of February 2003 for different sensitivity studies considering the OCIO•(H<sub>2</sub>O)<sub>2</sub> complex chemistry in model simulations.

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**Fig. 9.** Temperature dependence of the equilibrium constant  $K_p$  of the termolecular ClO dimer formation (Eq. 1) as a function of the reciprocal temperature (van't Hoff plot). Current experimental results (Plenge et al., 2005), results from field measurements (Stimpfle, 2004; von Hobe et al., 2005), and  $K_p$  values calculated from model simulations included  $\text{ClO}_x$  complex chemistry are compared with  $K_{\text{eq}}^{\text{meas}} = \frac{[\text{Cl}_2\text{O}_2]}{([\text{ClO}] + [\text{ClO}_x\text{complex}])^2}$  and  $K_{\text{eq}}^{\text{real}} = \frac{[\text{Cl}_2\text{O}_2]}{[\text{ClO}]^2}$  for  $\text{SZA} \leq 100^\circ$ .

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