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The potential impact of 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 $ClO{\cdot}O_2$ and ClO_x water radical complexes like $ClO{\cdot}H_2O$, $OClO{\cdot}H_2O$, $OClO{\cdot}(H_2O)_2$, and $ClOO{\cdot}H_2O$ could play a role in enhancing the ClO dimer (Cl_2O_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 $ClO{\cdot}O_2$ on polar ozone loss processes is small ($dO_3/dt \ll 0.5$ ppb/sunlight h) provided that the $ClO{\cdot}O_2$ complex is only weakly stable. Assuming that the binding energies of the ClO_x water complexes are much higher than theoretically predicted an enhancement of the ozone loss rate by up to ≈0.5 ppb/sunlight h is simulated. Because it is unlikely that the 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 ClO_x radical molecule complexes on polar stratospheric ozone loss processes is very small considering pure gas-phase chemistry. However the existence of 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.

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[1]). 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 $ClO{\cdot}O_2$ complex could have a major role in chlorine catalyzed ozone depletion chemistry. He found that either: (1) the $ClO{\cdot}O_2$ is fairly stable, but does not significantly enhance ClO dimer formation and therefore has a negligible effect on ozone loss rates, or (2) the $ClO{\cdot}O_2$ 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 $ClO{\cdot}O_2$ complex would impact the ClO/Cl_2O_2 ratio, but at that time no measurements of Cl_2O_2 were available. Today such measurements are made (Stimpfle, 2004; von Hobe et al., 2005) so that more constraints exists. Further, Francisco and Sander (1995) proposed that a $ClO{\cdot}H_2O$

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[1] 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 Stroh, F.: Chlorine activation, denitrification and ozone depletion in the cold Arctic winter 2004–05, Geophys. Res. Lett., to be submitted, 2006.

complex could possibly enhance the ClODimer (Cl_2O_2) formation. In addition, theoretical studies predict the existence of $OClO{\cdot}H_2O$, $ClOO{\cdot}H_2O$, and $OClO{\cdot}(H_2O)_2$ radical-molecule complexes (Aloisio and Francisco, 1999; Hansen and Francisco, 2002).

Here, we analyze if such 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[2]).

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 Cl_2O_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

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[2] Feng, W., Chipperfield, M., Backmann, L., Godin, S., Lehmann, R., and Müller, R.: Intercomparison of European stratospheric chemical transport models during the Arctic and Antarctic Match campaigns, in preparation, 2006.

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 (Cl_2O_2) cycle (Molina and Molina, 1987) and ClO-BrO cycle (McElroy et al., 1986). The ClO dimer cycle

$$\mathrm{ClO + ClO + M} \overset{k_{f_1},K_{eq_1}}{\rightleftharpoons} \mathrm{Cl_2O_2 + M}, \quad (1)$$

$$\mathrm{Cl_2O_2} + h\nu \rightarrow \mathrm{ClOO + Cl} \quad (2)$$

$$\mathrm{ClOO + M \rightarrow Cl + O_2 + M} \quad (3)$$

$$2 \times (\mathrm{Cl + O_3 \rightarrow ClO + O_2}) \quad (4)$$

$$\overline{\hspace{12em}}$$

$$\mathrm{net: 2\,O_3 \rightarrow 3\,O_2}$$

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 $ClO{\cdot}O_2$ complex via (Shindell, 1996) cycle I:

$$
\begin{aligned}
ClO + O_2 + M &\overset{k_{f5},K_{eq5}}{\rightleftharpoons} ClO{\cdot}O_2 + M && (5)\\
ClO{\cdot}O_2 + ClO &\overset{k_6}{\rightarrow} Cl_2O_2 + O_2 && (6)\\
Cl_2O_2 + h\nu &\rightarrow ClOO + Cl && (2)\\
ClOO + M &\rightarrow Cl + O_2 + M && (3)\\
2 \times (Cl + O_3 &\rightarrow ClO + O_2) && (4)\\
\hline
\text{net}: 2\,O_3 &\rightarrow 3\,O_2
\end{aligned}
$$

and cycle II:

$$
\begin{aligned}
2 \times (ClO + O_2 + M &\overset{k_{f5},K_{eq5}}{\rightleftharpoons} ClO{\cdot}O_2 + M) && (5)\\
ClO{\cdot}O_2 + ClO{\cdot}O_2 &\overset{k_7}{\rightarrow} Cl_2O_2 + 2O_2 && (7)\\
Cl_2O_2 + h\nu &\rightarrow ClOO + Cl && (2)\\
ClOO + M &\rightarrow Cl + O_2 + M && (3)\\
2 \times (Cl + O_3 &\rightarrow ClO + O_2) && (4)\\
\hline
\text{net}: 2\,O_3 &\rightarrow 3\,O_2
\end{aligned}
$$

Further, the following reaction scheme (cycle III) involving the $ClO{\cdot}H_2O$ complex for stratospheric ozone depletion was proposed by Francisco and Sander (1995):

$$\mathrm{ClO + H_2O + M} \overset{k_{f_8},K_{eq_8}}{\rightleftharpoons} \mathrm{ClO{\cdot}H_2O + M} \tag{8}$$

$$\mathrm{ClO{\cdot}H_2O + ClO} \overset{k_9}{\rightarrow} \mathrm{Cl_2O_2 + H_2O} \tag{9}$$

$$\mathrm{Cl_2O_2} + h\nu \rightarrow \mathrm{ClOO + Cl} \tag{2}$$

$$\mathrm{ClOO + M \rightarrow Cl + O_2 + M} \tag{3}$$

$$2 \times (\mathrm{Cl + O_3 \rightarrow ClO + O_2}) \tag{4}$$

$$\overline{\qquad\qquad\qquad\qquad\qquad\qquad}$$

$$\mathrm{net: 2\,O_3 \rightarrow 3\,O_2}$$

The reaction of ClO with BrO has three reaction channels Br +Cl +O_2, BrCl +O_2, and OClO +Br, where the latter one normally results in a null cycle for ozone destruction. However, the following cycles including OClO·H_2O, OClO·$(H_2O)_2$, and ClOO·H_2O could enhance the ozone depletion due to the reaction ClO+BrO→OClO+Br via cycle IV:

$$2 \times (\mathrm{BrO + ClO \rightarrow OClO + Br}) \tag{10}$$

$$\mathrm{OClO + H_2O + M} \overset{k_{f_{11}},K_{eq_{11}}}{\rightleftharpoons} \mathrm{OClO{\cdot}H_2O + M} \tag{11}$$

$$\mathrm{OClO{\cdot}H_2O + OClO} \overset{k_{12}}{\rightarrow} \mathrm{Cl_2O_2 + O_2 + H_2O} \tag{12}$$

$$\mathrm{Cl_2O_2} + h\nu \rightarrow \mathrm{2Cl + O_2} \tag{2+3}$$

$$2 \times (\mathrm{Br + O_3 \rightarrow BrO + O_2}) \tag{13}$$

$$2 \times (\mathrm{Cl + O_3 \rightarrow ClO + O_2}) \tag{14}$$

$$\overline{\qquad\qquad\qquad\qquad\qquad\qquad}$$

$$\mathrm{net: 4\,O_3 \rightarrow 6\,O_2}$$

cycle V:

$$2 \times (\mathrm{BrO} + \mathrm{ClO} \rightarrow \mathrm{OClO} + \mathrm{Br}) \tag{10}$$

$$\mathrm{OClO} + \mathrm{H_2O} + \mathrm{M} \overset{k_{f_{11}},K_{eq_{11}}}{\rightleftharpoons} \mathrm{OClO{\cdot}H_2O} + \mathrm{M} \tag{11}$$

$$\mathrm{OClO{\cdot}H_2O} + \mathrm{H_2O} + \mathrm{M} \overset{k_{f_{15}},K_{eq_{15}}}{\rightleftharpoons} \mathrm{OClO{\cdot}(H_2O)_2} + \mathrm{M} \tag{15}$$

$$\mathrm{OClO{\cdot}(H_2O)_2} + \mathrm{OClO} \overset{k_{16}}{\rightarrow} \mathrm{Cl_2O_2} + 2\mathrm{H_2O} + \mathrm{O_2} \tag{16}$$

$$\mathrm{Cl_2O_2} + h\nu \rightarrow 2\mathrm{Cl} + \mathrm{O_2} \tag{2+3}$$

$$2 \times (\mathrm{Br} + \mathrm{O_3} \rightarrow \mathrm{BrO} + \mathrm{O_2}) \tag{13}$$

$$2 \times (\mathrm{Cl} + \mathrm{O_3} \rightarrow \mathrm{ClO} + \mathrm{O_2}) \tag{14}$$

$$\text{net} : 4\,\mathrm{O_3} \rightarrow 6\,\mathrm{O_2}$$

and cycle VI:

$$\mathrm{BrO + ClO \rightarrow OClO + Br} \tag{10}$$

$$\mathrm{ClO + ClO + M \overset{k_{f_1},K_{eq_1}}{\rightleftharpoons} Cl_2O_2 + M} \tag{1}$$

$$\mathrm{Cl_2O_2} + h\nu \rightarrow \mathrm{ClOO + Cl} \tag{2}$$

$$\mathrm{ClOO + H_2O + M \overset{k_{f_{17}},K_{eq_{17}}}{\rightleftharpoons} ClOO{\cdot}H_2O + M} \tag{17}$$

$$\mathrm{ClOO{\cdot}H_2O + OClO \overset{k_{18}}{\rightarrow} Cl_2O_2 + H_2O + O_2} \tag{18}$$

$$\mathrm{Cl_2O_2} + h\nu \rightarrow \mathrm{2Cl + O_2} \tag{2+3}$$

$$\mathrm{Br + O_3 \rightarrow BrO + O_2} \tag{13}$$

$$3 \times \mathrm{(Cl + O_3 \rightarrow ClO + O_2)} \tag{14}$$

$$\mathrm{net: 4\,O_3 \rightarrow 6\,O_2}$$

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_{eq}=K_{eq5}, K_{eq8}, K_{eq11}, K_{eq15}, or K_{eq17}) 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_x radical complexes

In stratospheric chemistry models a parameterization of the form $K_{eq}(T)$ [$cm^3 molecules^{-1}$]=$A\times \exp(\frac{B}{T})$ is usually used to describe the equilibrium constant. The parameters A and B are calculated from the reactions entropy ($\Delta_r S$) and enthalpy ($\Delta_r H$) (Sander et al., 2002):

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

with R'=82.1 cm^3 atm $molecules^{-1}$ 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 ClO_x radical complex ($\Delta_r H=-D_0$) (see Tables 1 and 2).

For the $ClO{\cdot}O_2$ radical complex we used parameter A and B to calculated K_{eq5} 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 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 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 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 ClO dimer formation (Eq. 1). Because large uncertainties about the radical complex chemistry exist, we perform sensitivity studies varying k_f, K_{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.

4. Results

For the 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_{eq} and k (see Figs. 1, 5, 6 and 8). In the following, we will discuss this for each 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 ClO_x complexes on stratospheric in situ measurements.

4.1. The $ClO{\cdot}O_2$ complex

To study the impact of a $ClO{\cdot}O_2$ 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 $ClO{\cdot}O_2$ 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 $ClO{\cdot}O_2$ complex formation is faster than the complex destruction and up to ≈600 pptv $ClO{\cdot}O_2$ is produced by the model changing the partioning 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 ClO mixing ratios would likewise decrease compared to case 1 (not shown in Fig. 1), so that the simulated ClO mixing ratios would be much lower than what we know from stratospheric measurements which is most unlikely. Therefore the K_{eq5} values, that mean the stability of the $ClO{\cdot}O_2$ complex, have to be decreased (case 2) to simulate an ozone loss similar to the standard case as shown in Fig. 1 (left panel).

Further decreasing the K_{eq5} value (case 3) yield a bit lower $ClO{\cdot}O_2$ values as for case 2 (Fig. 1, left panel). But taking the K_{eq5} 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 $ClO{\cdot}O_2$ self-reaction (Eq. 7) is discussed. The simulations case 1–6 are repeated with the reaction rate constant for the $ClO{\cdot}O_2$ 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 $ClO{\cdot}O_2$ is produced and so sufficient $ClO{\cdot}O_2$ molecules are available for the $ClO{\cdot}O_2$ 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 $Cl+ClO{\cdot}O_2 \rightarrow Cl_2O+O_2$ (with k=1.0E-10 [$cm^3 molecules^{-1} s^{-1}$], estimated by Prasad and Lee, 1994, and the reactions destroying Cl_2O ($Cl_2O+O(^3P) \rightarrow ClO+ClO$ and $Cl_2O+Cl \rightarrow Cl_2+ClO$, 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 partioning between ClO and its dimer (Cl_2O_2) in our model simulations is consistent with recently reported values for the equilibrium constant of the Cl_2O_2 formation (K_{eq1}, Eq. 1) derived from stratospheric measurements (Stimpfle, 2004; von Hobe et al., 2005), we calculate a kind of effective equilibrium constant $K_{eq}^{eff}(Cl_2O_2)$ from

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

$$K_{eq}^{eff}(Cl_2O_2) = \frac{[Cl_2O_2]_{night}}{[ClO]^2_{night}} = K_{eq_1} \times \left(1 + \epsilon \frac{k_{f5}}{k_{f1}} \frac{[O_2]_{night}}{[ClO]_{night}}\right) \tag{19}$$

with ϵ the part of the ClO·O$_2$ radical-molecule complexes which forms the ClO dimer

$$\epsilon = \frac{k_6[ClO] + k_7[ClO{\cdot}O_2]}{k_6[ClO] + k_7[ClO{\cdot}O_2] + \frac{k_{f5}}{K_{eq_5}}M} \tag{20}$$

Here only model data are used for solar zenith angels (SZA) ≥100° representing night time conditions. Plenge et al. (2005) found a value of K_{eq1} 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 $K_{eq}^{eff}(Cl_2O_2)$ 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} ($K_p = K_{eq1}(T)/(R\,T)$) (see Fig. 2). For the standard case without complex chemistry (here ϵ is zero), the K_{eq1} value is identically with the value derived by Plenge et al. (2005) as expected because this K_{eq1} 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$_2$ complex and therefore the ClO mixing ratios are strongly reduced. This is also valid for case 7, where in addition the ClO·O$_2$ 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

$ClO{\cdot}O_2$ is calculated and thus the ClO mixing ratios are not affected. The K_p values derived from case 2, 4, 5, and 6 increase with rising the reaction rate constant for the Cl_2O_2 formation (k_6), 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_p 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_2O_2 partioning is unrealistic compared to stratospheric measurements. Thus only for cases 4 and 5, where addition ozone loss is simulated and the K_p 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_3 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 $ClO{\cdot}O_2$ complex is changed (D_0=7.35–4.96, see Table 3). A detailed analysis of the ozone change show that the partioning 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_2 cycle (Solomon et al., 1986) at a temperature of 202 K for daylight conditions ($SZA \leq 80^\circ$).

For case 1, the $ClO{\cdot}O_2$ complex formation is faster than the complex destruction and up to ≈600 pptv $ClO{\cdot}O_2$ 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 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 $[\mathrm{ClO}]^2$), whereby the other cycles are reduced by approximately a factor of 2.

In case 2 the equilibrium constant for the $\mathrm{ClO{\cdot}O_2}$ formation was reduced so that lower $\mathrm{ClO{\cdot}O_2}$ mixing ratios are calculated by the model. Here only 8% the ozone destruction is cause by cycle I. In case 3, the equilibrium constant for the $\mathrm{ClO{\cdot}O_2}$ formation was reduced further. Here the rate of cycle I on the total ozone change is negligible, because the formation of the $\mathrm{ClO{\cdot}O_2}$ complex is too slow compared to the reaction velocity of the other halogen-induced ozone destroying cycles. Thus the partioning 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_{eq5} value is used as in case 2, but the reaction rate constant for the $\mathrm{ClO{\cdot}O_2}$ 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 of the ClO dimer from the $\mathrm{ClO{\cdot}O_2}$ 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 $\mathrm{ClO{\cdot}O_2}$ complex and simultaneously the K_p values are within the scatter range of stratospheric measurements, the usual halogen-induced ozone destroying cycles (the ClO dimer cycle, the ClO-BrO cycle, the ClO-O cycle, and the $\mathrm{HO_2}$-ClO cycle) are strongly depressed compared to the standard case, but not as strongly as in case 1. The sum of the $\mathrm{O_3}$ 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 are slower than in case 5.

4.2. The ClO_x water complexes

4.2.1. The $ClO{\cdot}H_2O$ 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 $ClO{\cdot}H_2O$ formation (K_{eq8}) (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_2O_2 mixing ratios increase when increasing the K_{eq8} values (case 2). Here the ClO_x mixing ratio are very close to those for case 1. By further increasing the K_{eq8} 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_2O_2 mixing ratios increase further on, but here also the amount of ClO_x is higher (≈100 pptv) than for case 1 and 2. Thus in case 2, the partioning between ClO and Cl_2O_2 is only changed, whereas in case 3 also the partioning 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_{eq8} values in that range are unrealistic. An increase of the k_9 values in case 3 would yield more ozone loss, but only for k_9 values much faster than gas-kinetic.

For the K_{eq8} value from case 2 we perform further sensitivity studies varying the k_9 values (see Fig. 5, right panel). For k_9 values (case 4) lower than in case 1, no additional ozone loss is simulated similar to case 1 that means this k_9 value is too slow compared to K_{eq8}, so that no additional ClO dimer mixing ratios are produced and no additional ozone loss is simulated. Increasing the k_9 values (case 5) yield additional ozone loss because additional Cl_2O_2 is produced. Here the ClO mixing ratios are not so strongly reduced as in case 3, but the k_9 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 an additional ozone loss compared to the standard case under realistic conditions, but with a binding energy for the $ClO{\cdot}H_2O$ complex substantial higher than predicted by Francisco and Sander (1995) and Fu et al. (2003), respectively.

A similar analysis for the partioning between ClO and its dimer in our model simulations as for the $ClO{\cdot}O_2$ complex is performed. Here case 3 yields an $K_{eq}^{eff}(Cl_2O_2)$ which is above the uncertainty range of the recently reported values for the equilibrium constant of the Cl_2O_2 formation (K_{eq1}, Eq. 1) (Plenge et al., 2005). For all other cases the $K_{eq}^{eff}(Cl_2O_2)$ values are within the reported uncertainties, where for case 5 the $K_{eq}^{eff}(Cl_2O_2)$ 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 ≈0.5 ppb/sunlight h.

4.2.2. The $OClO{\cdot}H_2O$ complex

Analogous sensitivity studies are performed with the $OClO{\cdot}H_2O$ complex (see Table 5 and Fig. 6). Also here the equilibrium constant for the formation of the $OClO{\cdot}H_2O$ complex (K_{eq11}) 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_{eq11} values (case 3) the relation between K_{eq11} and k_{12} is changed so that the $OClO{\cdot}H_2O$ complex formation is faster than the complex destruction and up to ≈800 pptv $OClO{\cdot}H_2O$ is produced by the model changing the partioning 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_{eq11} 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 $OClO{\cdot}H_2O$ and less ozone loss than in the standard case (see Fig. 6, right panel) . For higher k_{12} values (case 5), the 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} value 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 condition, but with a much higher binding energy for the $ClO{\cdot}H_2O$ 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 $ClO{\cdot}H_2O$ complex (see Fig. 7).

We note that the analysis of the partioning 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 OClO mixing ratios are very low with maximum OClO mixing ratios up to 4–6 pptv. These mixing ratio are much lower than we know from recent stratospheric nighttime OClO measurements (Canty et al., 2005).

4.2.3. The $OClO{\cdot}(H_2O)_2$ complex

The potential impact of the ozone destroying cycle V due to the $OClO{\cdot}(H_2O)_2$ radical complex is analyzed. For cycle V also the $OClO{\cdot}H_2O$ complex is required to form the $OClO{\cdot}(H_2O)_2$ complex, so that we have also to consider the uncertainties of the $OClO{\cdot}H_2O$ complex chemistry. Therefore we repeat the model simulations case 1–5 (see Table 5) performed for the $OClO{\cdot}H_2O$ 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 $OClO{\cdot}H_2O$ mixing ratios are simulated up to 600 and 800 pptv, respectively, we expect that sufficient $OClO{\cdot}(H_2O)_2$ 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_2O_2 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 $OClO{\cdot}H_2O$ complex of case 2 and variate the equilibrium constant K_{eq15}. We found here the same behavior as for the OClO·H_2O complex (see Sect. 4.2.2). Only for equilibrium rate constants K_{eq15} much higher than predicted by theoretical calculations of the binding energy of the OClO·$(H_2O)_2$ 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_{eq15} values (see case 7). Further increasing the K_{eq15} 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 OClO·$(H_2O)_2$ 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 ClOO·H_2O complex

From the discussion above, we expect the same behavior for the ClOO·H_2O complex chemistry as for the other ClO_x·$(H_2O)_x$ 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 ClOO·H_2O radical complex molecule has to be fairly stable which is in contrast to theoretically predicted value of 1.3 kcal mol^{-1} for the binding energy (D_0) (Aloisio and Francisco, 1999). Thus a significant impact of a ClOO·H_2O complex on stratospheric ozone processes can most likely be excluded.

4.3. The potential impact of ClO_x complexes on stratospheric in situ measurements

Here the potential impact of a ClO_x radical-molecule complexes on stratospheric in situ measurements of ClO and Cl_2O_2, respectively, mixing ratios is to discussed. All available stratospheric in situ ClO and Cl_2O_2 measurements which were used to infer the equilibrium constant for the 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 ClO_x complex may react with NO in just the same way as ClO would, therefore the equilibrium constant for the ClO dimer formation (K_{eq1}) derived by stratospheric ClO and dimer measurements have to be lower than K_{eq1} values derived by laboratory measurements, if a ClO_x radical complexes would exist in a sufficient large amount in the polar stratosphere:

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

$$K_{eq}{}^{meas} = \frac{[Cl_2O_2]}{[ClO]^2_{meas}} \leq \frac{[Cl_2O_2]}{[ClO]^2_{real}} = K_{eq}{}^{real} \quad (22)$$

Our studies show that for the $ClO{\cdot}O_2$ complexes for the cases 1 and 7 a sufficient large amount of $ClO{\cdot}O_2$ is available so that $K_{eq}{}^{meas}$ is significant lower than $K_{eq}{}^{real}$ as shown in Fig. 9. However, these cases are unrealistic because both the simulated ClO mixing ratios were too low and the $K^{eff}_{eq}(Cl_2O_2)$ values were too high. For the $OClO{\cdot}H_2O$ complex only for cases 3 and 4 and for low temperatures (≤196 K) a significant difference was found. These cases yield realistic values for the ClO mixing ratios and for $K^{eff}_{eq}(Cl_2O_2)$, but too low OClO 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 ClO and Cl_2O_2 measurements, but not the ozone loss rates. Thus the existence of these ClO_x radical complexes could explain that the K_{eq1} values derived from stratospheric ClO and Cl_2O_2 in situ measurements by Stimpfle (2004) and von Hobe et al. (2005) differ from the K_{eq1}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 stratosphere (CLaMS) including the $ClO{\cdot}O_2$ and ClO_x water radical complexes like $ClO{\cdot}H_2O$, $OClO{\cdot}H_2O$, $OClO{\cdot}(H_2O)_2$, and $ClOO{\cdot}H_2O$ 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_{eq} of the complex formation and its thermal decay and of the bimolecular reaction rate constant k of the ClO dimer formation from the radical-molecule complex. Our studies show that there exists for each ClO_x radical-molecule complex only one ideal range for the equilibrium constant (K_{eq}^{ideal}) where an additional ozone loss is possible provided that the reaction rate constant k for the Cl_2O_2 formation is not faster than gas-kinetic. If the K_{eq} values are lower than K_{eq}^{ideal} no enhanced ozone loss is possible. If the K_{eq} are higher than K_{eq}^{ideal} less ozone loss is simulated, because reactive chlorine is stored in the complex. Further, then the partioning between ClO and Cl_2O_2 is unrealistic compared to stratospheric measurements. For these K_{eq} values higher than K_{eq}^{ideal} an additional ozone loss is possible whether the bimolecular reaction rate constant k for Cl_2O_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 ClO dimer formation k from the complex by fixed values for the equilibrium constant (K_{eq}^{ideal}) for the ClO_x complex formation.

The present sensitivity studies for a $ClO{\cdot}O_2$ complex show that an additional ozone loss is only simulated for binding energies of the $ClO{\cdot}O_2$ complex in the range of ≈6 kcal mol^{-1} in agreement with Shindell (1996), which is lower than the upper limit of 7.4 kcal 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 ClO dimer formation $K_{eq}(Cl_2O_2)$ from stratospheric measurements (Stimpfle, 2004; von Hobe et al., 2005) are used to restrict the number of possible model results caused by large uncertainties about radical complex chemistry. Further our studies show, that the reaction rate constant of the ClO dimer formation from the ClO·O_2 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 ($K_{eq}^{eff}(Cl_2O_2)$) has to be not higher than recently recommended from field measurements (Stimpfle, 2004; von Hobe et al., 2005). The amount of additionally simulated O_3 loss rates is very small ($dO_3/dt \ll 0.5$ ppb/sunlight h).

Our findings show for the ClO_x water complexes that to produce additionally O_3 loss rates the binding energies of these radical complexes have to be much higher (≈9–15 kcal mol^{-1}) than theoretically predicted (1.3–3.4 kcal mol^{-1}) (Francisco and Sander, 1995; Aloisio and Francisco, 1999; Fu et al., 2003). In addition the Cl_2O_2 formation has to be very fast (gas-kinetic). The additionally simulated O_3 loss rates is ≈0.5 ppb/sunlight h. The present work shows that an impact of ClO_x 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_x 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_x radical-molecule complexes do not solve the early winter problem of ozone loss rates considering pure gas-phase chemistry. However if another ClO_x 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 $ClO{\cdot}O_2$.

		$ClO{\cdot}O_2$	Reference
A	[$cm^3 molecules^{-1}$]	2.9E-26	Sander et al. (2002)
B	[K^{-1}]	<3700	Sander et al. (2002)
D_0	[$kcal\ mol^{-1}$]	≡7.4	
K_{eq5}(200 K)	[$cm^3 molecules^{-1}$]	$\curvearrowright$3.1E-18	
k_6	[$cm^3 molecules^{-1} s^{-1}$]	≈1.0E-12	Prasad and Lee (1994)
k_7	[$cm^3 molecules^{-1} s^{-1}$]	≈5.0E-13	Prasad and Lee (1994)

Table 2. Kinetic parameters used for the first guess model simulation including the radical complexes $ClO{\cdot}H_2O$, $OClO{\cdot}H_2O$, $OClO{\cdot}(H_2O)_2$, and $ClOO{\cdot}H_2O$.

		$ClO{\cdot}H_2O$	$OClO{\cdot}H_2O$	$OClO{\cdot}(H_2O)_2$	$ClOO{\cdot}H_2O$
$\Delta_f S_{complex}$	[cal $K^{-1}mol^{-1}$]	71.0[a]	71.0[b]	80.0[g]	71.0[b]
$\Delta_r S$	[cal K^{-1} mol^{-1}]	−27.9	−35.5	−36.1	−38.4
D_0	[kcal mol^{-1}]	3.2[c]	2.0[d]	3.4[d]	1.3[d]
K_{eq}(200 K)	[cm^3molecules^{-1}]	$\curvearrowright K_{eq8}$ = 1.1E-22	$\curvearrowright K_{eq11}$ = 1.1E-25	$\curvearrowright K_{eq15}$ = 2.7E-24	$\curvearrowright K_{eq17}$ = 4.2E-27
σ	[nm]	0.34[e]	0.5[f]	0.8[f]	0.5[f]
k	[cm^3molecules$^{-1}s^{-1}$]	$\curvearrowright k_9$= 1.3E-10	$\curvearrowright k_{12}$= 1.7E-10	$\curvearrowright k_{16}$= 2.7E-10	$\curvearrowright k_{18}$= 1.7E-10

[a] estimated by Francisco and Sander (1995)

[b] assumed to be similar to $ClO{\cdot}H_2O$

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

[d] Aloisio and Francisco (1999)

[e] collision cross-section is estimated from geometric parameters calculated by Fu et al. (2003)

[f] collision cross-section is estimated from geometric parameters calculated by Aloisio and Francisco (1999)

[g] assumed

Table 3. Equilibrium constants (K_{eq5}) and reaction reaction rate constants (k_6 and k_7 in [$cm^3 molecules^{-1} s^{-1}$]) used for different model simulations (case 1–7) considering $ClO{\cdot}O_2$ complex chemistry (see Eqs. 5, 6, and 7). The parameterization of K_{eq} is described in Sect. 3.2.

case	K_{eq5} [$cm^3 molecules^{-1}$]				k_6	k_7	additional dO_3/dt
	A [$cm^3 molecules^{-1}$]	B [K^{-1}]	D_0 [$kcal\ mol^{-1}$]	K_{eq5}(200 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	+

Table 4. Equilibrium constants (K_{eq8}) and reaction reaction rate constants (k_9) used for different model simulations (case 1–5) considering $ClO{\cdot}H_2O$ complex chemistry (see Eqs. 8 and 9). The parameterization of K_{eq} is described in Sect. 3.2.

case	K_{eq8} [cm^{3}molecules^{-1}]				k_9 [cm^{3}molecules^{-1}s^{-1}]	additional dO_3/dt
	A [cm^{3}molecules^{-1}]	B [K^{-1}]	D_0 [kcal mol^{-1}]	K_{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	+

Table 5. Equilibrium constants (K_{eq11}) and reaction rate constants (k_{12}) used for different model simulations (case 1–5) considering $OClO{\cdot}H_2O$ complex chemistry (see Eqs. 11 and 12). The parameterization of K_{eq} is described in Sect. 3.2.

case	K_{eq11} [$cm^3 molecules^{-1}$]				k_{12} [$cm^3 molecules^{-1} s^{-1}$]	additional dO_3/dt
	A [$cm^3 molecules^{-1}$]	B [K^{-1}]	D_0 [$kcal\ mol^{-1}$]	K_{eq11}(200 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	+

Table 6. Equilibrium constants (K_{eq15}) and reaction reaction rate constants (k_{16}) used for different model simulations (case 6–8) considering $OClO{\cdot}(H_2O)_2$ complex chemistry (see Eqs. 15 and 16). The parameterization of K_{eq} is described in Sect. 3.2.

case	K_{eq15} [cm^{3}molecules^{-1}]				k_{16} [cm^{3}molecules^{-1}s^{-1}]	additional dO_3/dt
	A [cm^{3}molecules^{-1}]	B [K^{-1}]	D_0 [kcal mol^{-1}]	K_{eq15}(200 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	–

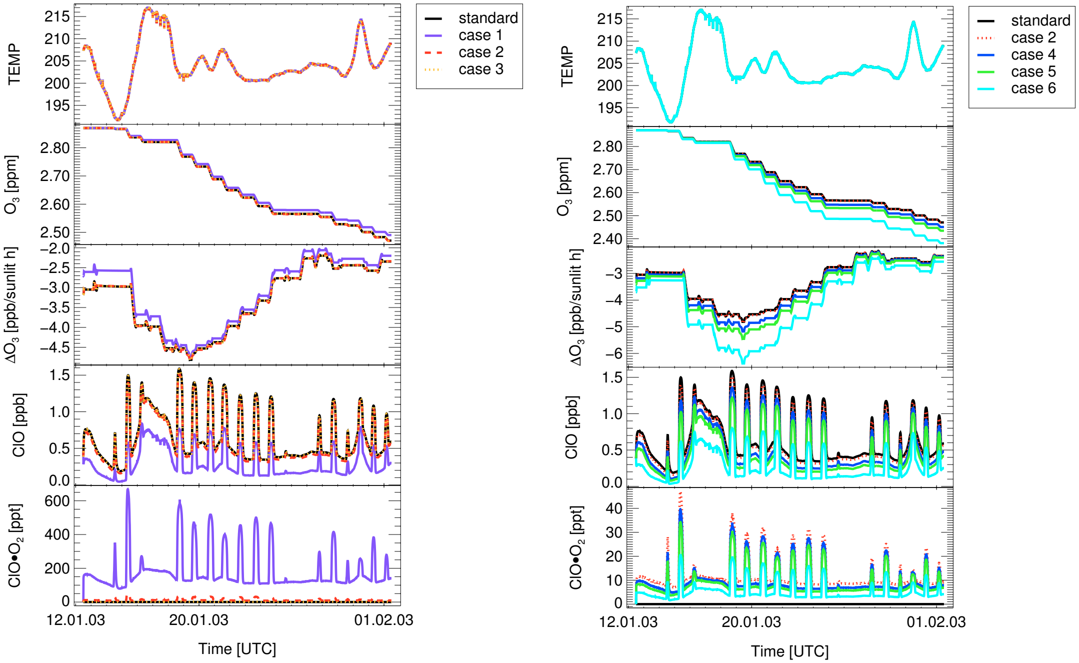

Fig. 1. Temperature, O_3, ClO, and ClO·O_2 mixing ratios as well as the ozone depletion per sunlight hour are shown along one Match trajectory starting in mid-January until the beginning of February 2003 for different sensitivity studies considering the ClO·O_2 complex chemistry in model simulations. 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.

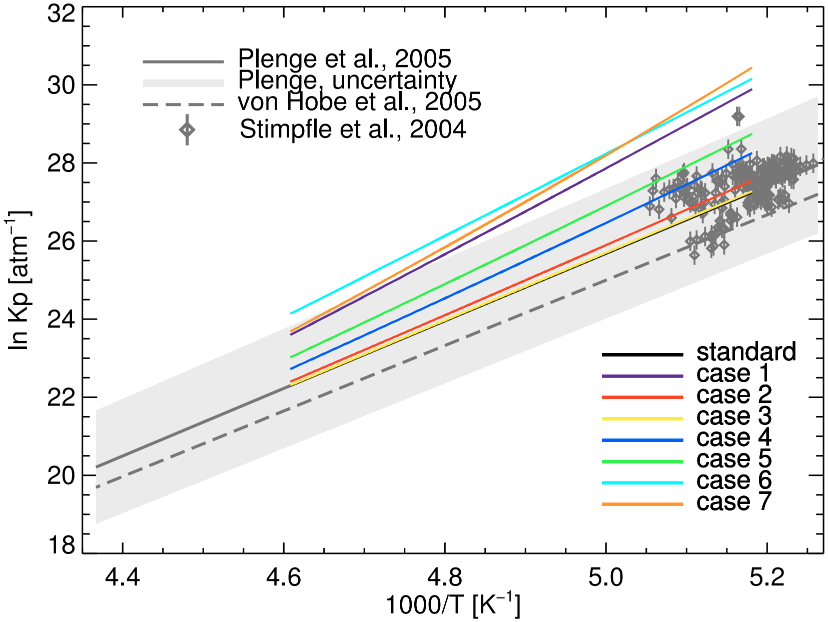

Fig. 2. Temperature dependence of the equilibrium constant K_p of the termolecular ClO dimer formation (Eq. 1) as a function of the reciprocal temperature (vant't Hoff plot). Current experimental results (Plenge et al., 2005), results from field measurements (Stimpfle, 2004; von Hobe et al., 2005), and K_p values calculated from model simulations included ClO·O_2 complex chemistry are compared (see Sect. 4.1.1 and Table 3).

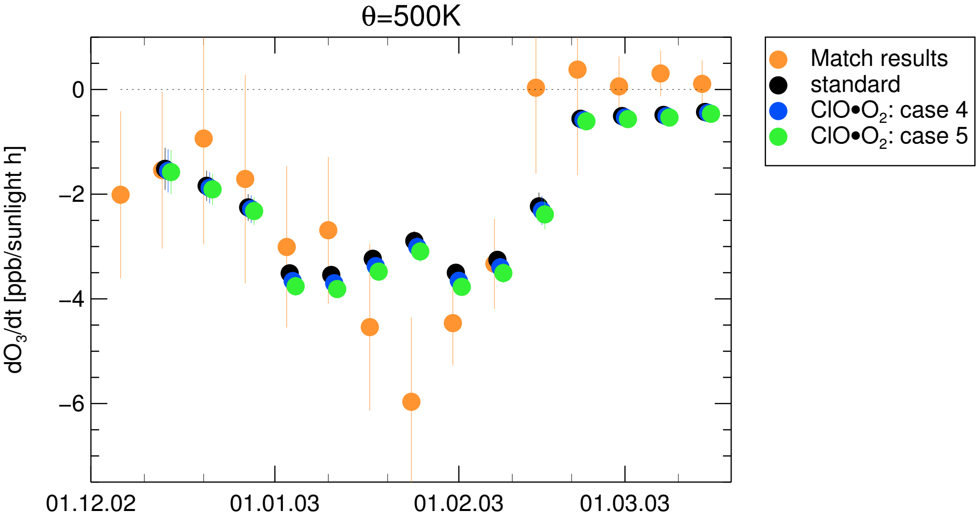

Fig. 3. Ozone loss rates derived with the Match technique for the Arctic winter 2002/2003 at a level of 500 K potential temperature compared to different model simulations including $ClO{\cdot}O_2$ complex chemistry (see Table 3). The standard case is without radical complex chemistry. Note that the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

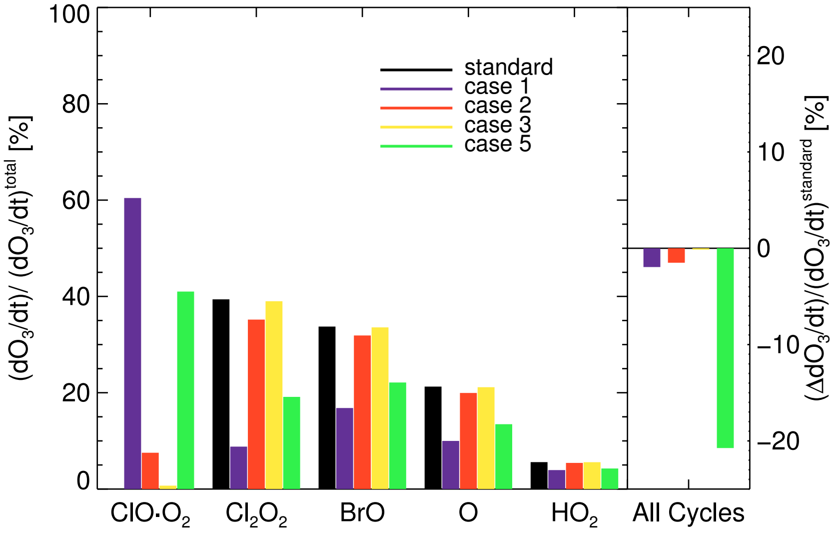

Fig. 4. The partioning between the different halogen-induced ozone destroying cycles: $ClO{\cdot}O_2$ (Cycle I), the ClO dimer cycle, the ClO-BrO cycle, the ClO-O cycle, and the HO_2-ClO cycle for different simulations (case 1, 2, 3, and 5) including $ClO{\cdot}O_2$ chemistry are compared to the standard 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≤80°) and at a temperature of 202 K.

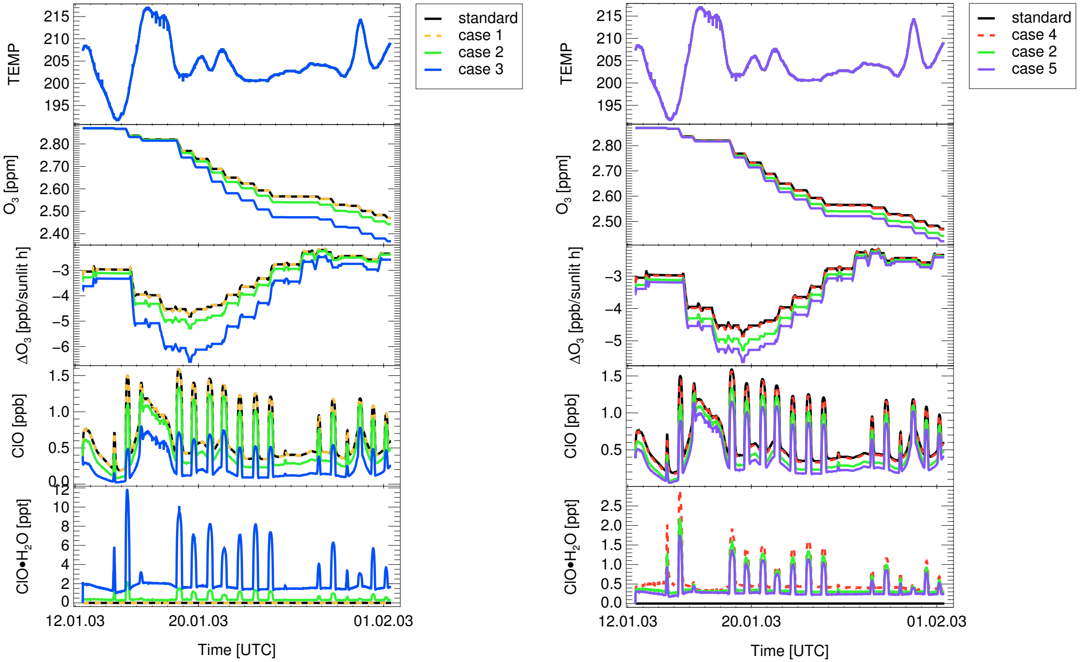

Fig. 5. Temperature, O_3, ClO, and ClO·H_2O mixing ratios as well as the ozone depletion per sunlight hour are shown along one Match trajectory starting in mid-January until the beginning of February 2003 for different sensitivity studies considering the ClO·H_2O complex chemistry in model simulations. 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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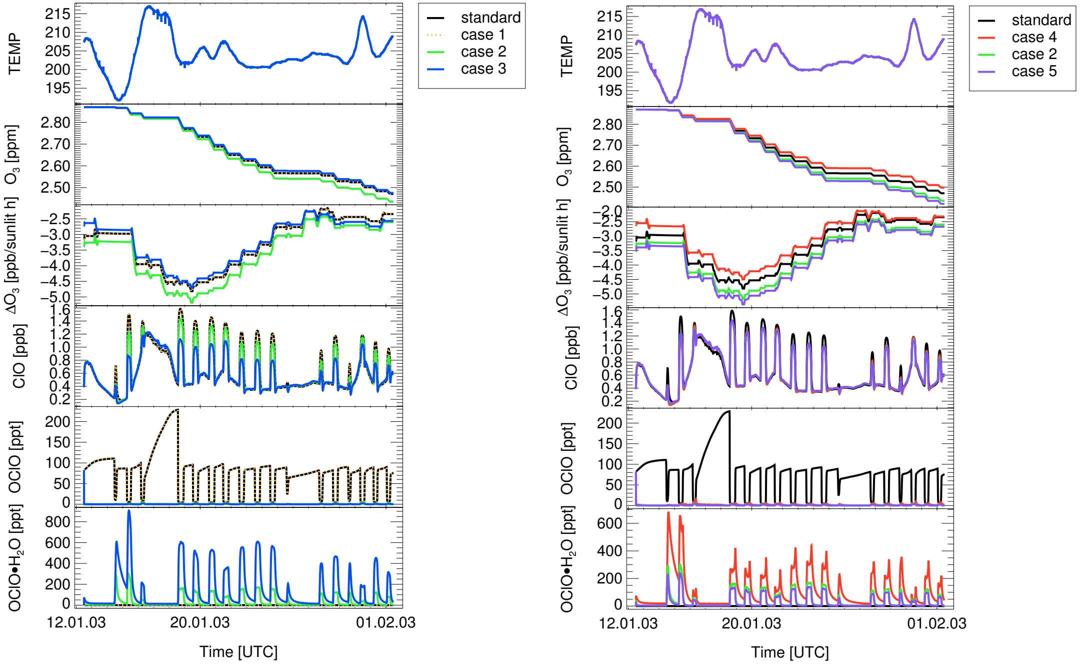

Fig. 6. Temperature, O_3, ClO, OClO, and $OClO{\cdot}H_2O$ mixing ratios as well as the ozone depletion per sunlight hour are shown along one Match trajectory starting in mid-January until the beginning of February 2003 for different sensitivity studies considering the $OClO{\cdot}H_2O$ complex chemistry 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.

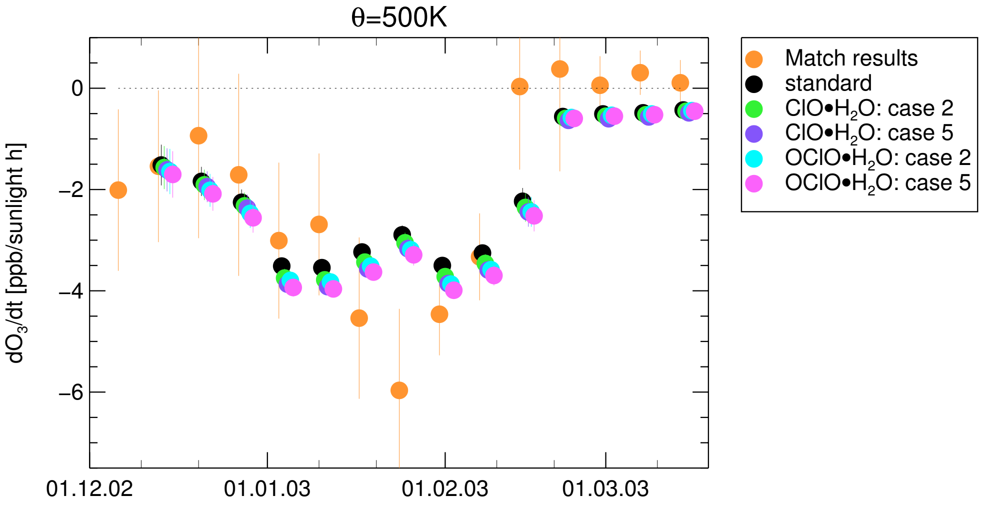

Fig. 7. Ozone loss rates derived with the Match technique for the Arctic winter 2002/2003 at a level of 500 K potential temperature compared to different model simulations including ClO$_x$ water radical complex chemistry (see Tables 4 and 5). The standard case is without radical complex chemistry. We 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.

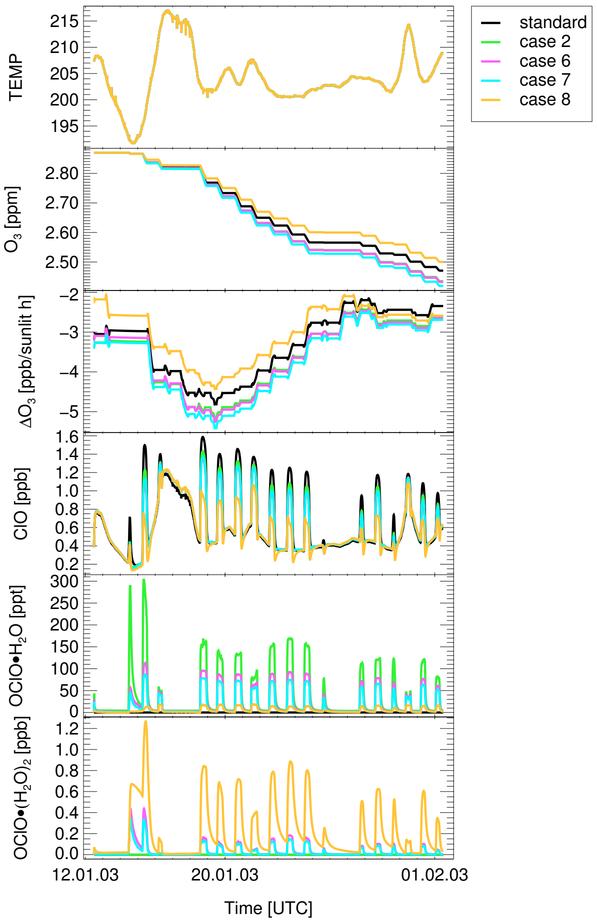

Fig. 8. Temperature, O_3, ClO, OClO·H_2O, and OClO·$(H_2O)_2$ mixing ratios as well as the ozone depletion per sunlight hour are shown along one Match trajectory starting in mid-January until the beginning of February 2003 for different sensitivity studies considering the OClO·$(H_2O)_2$ complex chemistry in model simulations.

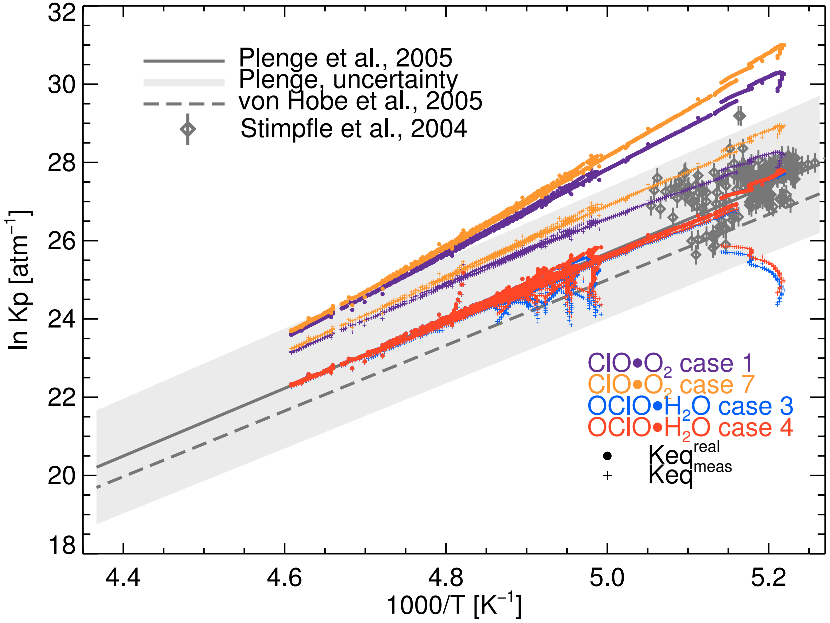

Fig. 9. Temperature dependence of the equilibrium constant K_p of the termolecular ClO dimer formation (Eq. 1) as a function of the reciprocal temperature (vant't Hoff plot). Current experimental results (Plenge et al., 2005), results from field measurements (Stimpfle, 2004; von Hobe et al., 2005), and K_p values calculated from model simulations included ClO_x complex chemistry are compared with $K_{eq}^{meas}=\frac{[Cl_2O_2]}{([ClO]+[ClO_{x\,complex}])^2}$ and $K_{eq}^{real}=\frac{[Cl_2O_2]}{[ClO]^2}$ for SZA ≤100°.