**Atmospheric
Chemistry
and Physics**

Understanding the kinetics of the ClO dimer cycle

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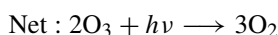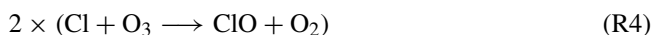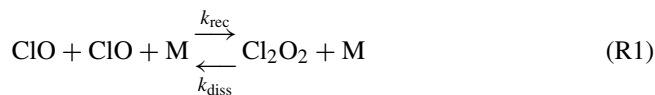
Abstract. Among the major factors controlling ozone loss in the polar vortices in winter/spring is the kinetics of the ClO dimer catalytic cycle. Here, we propose a strategy to test and improve our understanding of these kinetics by comparing and combining information on the thermal equilibrium between ClO and Cl_2O_2, the rate of Cl_2O_2 formation, and the Cl_2O_2 photolysis rate from laboratory experiments, theoretical studies and field observations. Concordant with a number of earlier studies, we find considerable inconsistencies of some recent laboratory results with rate theory calculations and stratospheric observations of ClO and Cl_2O_2. The set of parameters for which we find the best overall consistency – namely the ClO/Cl_2O_2 equilibrium constant suggested by Plenge et al. (2005), the Cl_2O_2 recombination rate constant reported by Nickolaisen et al. (1994) and Cl_2O_2 photolysis rates based on absorption cross sections in the range between the JPL 2006 assessment and the laboratory study by Burkholder et al. (1990) – is not congruent with the latest recommendations given by the JPL and IUPAC panels and does not represent the laboratory studies currently regarded as the most reliable experimental values. We show that the incorporation of new Pope et al. (2007) Cl_2O_2 absorption cross sections into several models, combined with best estimates for other key parameters (based on either JPL and IUPAC evaluations or on our study), results in severe model underestimates of observed ClO and observed ozone loss rates. This finding suggests either the existence of an unknown process that drives the partitioning of ClO and Cl_2O_2, or else some unidentified problem with either the laboratory study or numerous measurements of atmospheric ClO. Our mechanistic understanding of the ClO/Cl_2O_2 system is grossly lacking, with severe implications for our ability to simulate both present and future polar ozone depletion.

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1 Introduction

The ClO dimer cycle is one of the most important catalytic cycles destroying ozone in the polar vortices in late winter/early spring (Molina and Molina, 1987):

$$ClO + ClO + M \underset{k_{diss}}{\overset{k_{rec}}{\rightleftharpoons}} Cl_2O_2 + M \qquad (R1)$$

$$Cl_2O_2 + h\nu \xrightarrow{J} Cl + ClOO \qquad (R2)$$

$$ClOO + M \longrightarrow Cl + O_2 + M \qquad (R3)$$

$$\underline{2 \times (Cl + O_3 \longrightarrow ClO + O_2)} \qquad (R4)$$

$$Net : 2O_3 + h\nu \longrightarrow 3O_2$$

In darkness thermal equilibrium of Reaction (R1) is established with

$$K_{eq} = \frac{k_{rec}}{k_{diss}} = \frac{[Cl_2O_2]}{[ClO]^2} \quad . \qquad (1)$$

The terms k_{rec} and k_{diss} refer to rate constants for the recombination of ClO and ClO and the dissociation of Cl_2O_2 (unless stated otherwise, Cl_2O_2 here refers to the chlorine peroxide isomer, ClOOCl, the only isomer that leads to ozone loss upon photolysis), respectively; K_{eq} refers to the equilibrium constant and J is the Cl_2O_2 photolysis frequency. For a given amount of active chlorine ($[ClO_x] \sim [ClO] + 2[Cl_2O_2]$) the rate at which this catalytic cycle destroys ozone is determined by the dimer formation rate constant k_{rec} and the photolysis rate J. The combined ozone loss rate from all catalytic cycles (see e.g. Solomon, 1999) is more sensitive to J than to k_{rec}: increasing J leads to a faster dimer cycle as well as to higher [ClO], which largely determines the rates of other catalytic cycles, in particular the ClO-BrO cycle (McElroy et al., 1986). On the other hand, the enhanced

Table 1. Vibrational frequencies and uncertainties of ClOOCl.

Vibrational mode	ν, cm^{-1}
Torsion	127^{+0}_{-13} [a]
ClOO symmetric bend	321^{+21}_{-11} [b]
ClOO antisymmetric bend	418.5[c]
Cl–O symmetric stretch	543.0[c]
Cl–O antisymmetric stretch	647.7[c]
O–O stretch	754.0[c]

[a] $127\pm20\,\mathrm{cm}^{-1}$ represents the only measurement of the torsional wave number (Birk et al., 1989). As all reported values from ab initio (e.g. Lee et al., 1992) and force field calculations (Jacobs et al., 1994) fall below $127\,\mathrm{cm}^{-1}$, we deem it unlikely that the frequency should be higher. The lower limit used here represents the lowest value found in the literature (Jacobs et al., 1994).
[b] $321\,\mathrm{cm}^{-1}$ and upper limit of $342\,\mathrm{cm}^{-1}$ from different ab initio calculations (Lee et al., 1992), lower limit of $310\,\mathrm{cm}^{-1}$ from force field calculations (Jacobs et al., 1994).
[c] measured by (Jacobs et al., 1994), in good agreement with other experiments (Burkholder et al., 1990; Cheng and Lee, 1989). Measurements are rather exact and uncertainties of these higher frequencies are not significant for the calculations in the temperature range relevant to this study.

overall rate of the dimer cycle induced by increasing k_{rec} is partly offset due to the effect of reduced [ClO] on other catalytic cycles.

A large number of laboratory studies have addressed K_{eq} (Basco and Hunt, 1979; Cox and Hayman, 1988; Nickolaisen et al., 1994; Ellermann et al., 1995; Plenge et al., 2005), k_{rec} (Sander et al., 1989; Trolier et al., 1990; Nickolaisen et al., 1994; Bloss et al., 2001; Boakes et al., 2005) and σ_{ClOOCl} (Basco and Hunt, 1979; Molina and Molina, 1987; Permien et al., 1988; Cox and Hayman, 1988; DeMore and Tschuikow-Roux, 1990; Burkholder et al., 1990; Huder and DeMore, 1995; Pope et al., 2007). For each of these parameters, large discrepancies exist that often cannot be explained by the reported uncertainty limits. The appearance of new studies has not always led to a better understanding, at least quantitatively. With the latest values reported for k_{rec} by Boakes et al. (2005) and for σ_{ClOOCl} by Pope et al. (2007) falling outside the limits of all previously published values, the uncertainties for the dimer formation and photolysis rates seem larger than ever. Some proposed parameters or combinations thereof are inconsistent in the thermodynamic properties they imply (e.g. Golden, 2003), and studies testing the consistency with atmospheric observations (Shindell and de Zafra, 1995; Shindell and de Zafra, 1996; Solomon et al., 2000; Avallone and Toohey, 2001; Solomon et al., 2002; Stimpfle et al., 2004; von Hobe et al., 2005) have shown that some of the constants determined in the laboratory cannot be reconciled with atmospheric ClO and Cl$_2$O$_2$ measurements. But hitherto laboratory, field and theoretical data on all rele-

vant parameters have not been considered together in a comprehensive way.

Here we integrate the available information from laboratory studies, atmospheric data and theoretical calculations, pointing out the existing inconsistencies and their possible implications. Based on the currently accepted chemistry and reaction mechanisms, we attempt to identify a set of values for K_{eq}, k_{rec}, and σ_{ClOOCl} that are consistent with each other and with atmospheric observations while still being reconcilable with theoretically feasible thermodynamic and energy transfer properties. We start by using statistical thermodynamics to constrain K_{eq}, and exploit the result together with corresponding thermodynamic properties to successively constrain k_{diss} and k_{rec} with the help of unimolecular rate theory as developed by Troe (1977a, b, 1979). Two independent analyses – photochemical steady state analysis and a chemical box model study – are carried out to discern which Cl$_2$O$_2$ photolysis cross sections can best explain simultaneous ClO and Cl$_2$O$_2$ observations made during several Arctic aircraft missions in the stratosphere.

2 Enthalpies and entropies of ClO and Cl$_2$O$_2$ and the equilibrium constant K_{eq}

The equilibrium of Reaction (R1) and its temperature dependence have been addressed in numerous studies. Laboratory measurements of K_{eq} have been carried out by Basco and Hunt (1979), Cox and Hayman (1988), Nickolaisen et al. (1994) and Ellermann et al. (1995). Avallone and Toohey (2001) and von Hobe et al. (2005) have inferred K_{eq} from field observations of ClO and Cl$_2$O$_2$. A value for K_{eq} was determined from analysis of atmospheric measurements of ClO and Cl$_2$O$_2$ by von Hobe et al. (2005). Avallone and Toohey (2001) also estimated a value for K_{eq}, based on atmospheric measurements of ClO and estimates of the concentration of Cl$_2$O$_2$ deduced assuming complete chlorine activation.

K_{eq} is related to the standard reaction enthalpy $\Delta_r H^\circ$ and entropy $\Delta_r S^\circ$:

$$K_{\mathrm{eq}} = \frac{RT}{N_A} e^{\Delta_r S^\circ/R} e^{-\Delta_r H^\circ/RT} \tag{2}$$

with the factor RT/N_A (R in cm^3 atm K^{-1} mol^{-1}) converting K_{eq} into units of molecules^{-1} cm^3. $\Delta_r S^\circ$ can be calculated from the third law entropies of ClO and Cl$_2$O$_2$ (see below). $\Delta_r H^\circ$ has been determined in the laboratory (Plenge et al., 2005) and estimated in ab initio calculations (McGrath et al., 1990; Lee et al., 1992; Zhu and Lin, 2003).

The kinetic laboratory studies (Cox and Hayman, 1988; Nickolaisen et al., 1994) can be interpreted either by third law analysis (i.e. obtaining $\Delta_r S^\circ$ from third law entropies and fitting $\Delta_r H^\circ$) or by second law analysis (i.e. both $\Delta_r H^\circ$ and $\Delta_r S^\circ$ are obtained from a linear least squares fit to the observed K_{eq} values at different temperatures). The two
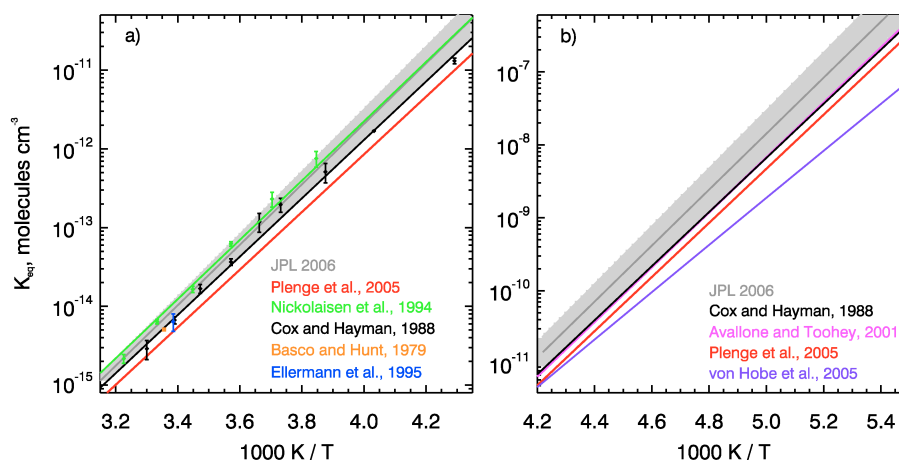
Fig. 1. Temperature dependence of K_{eq} **(a)** in the temperature range of laboratory measurements and **(b)** at stratospheric temperatures. Note that the lines corresponding to the Cox and Hayman (1988) and Nickolaisen et al. (1994) data are based on the fits obtained in this study and not on the fits reported in the original papers. The uncertainty range given by JPL 2006 is shown by the gray areas.

methods may yield significantly different values for the temperature dependence of K_{eq}, but as the entropies of ClO and Cl_2O_2 are reasonably well constrained by available spectroscopic data, third law analysis is the preferred method (Nickolaisen et al., 1994). The JPL 2006 recommendation for K_{eq} is based on third law analysis of the laboratory data given by Cox and Hayman (1988) and Nickolaisen et al. (1994) using a value for $S°$ (300 K) of Cl_2O_2 equal to $302.2 \, \mathrm{J\,K^{-1}\,mol^{-1}}$ to obtain the value of $RT/N_A \exp(\Delta_r S°/R)$, the so-called pre-exponential factor.

Here, standard entropies $S°$ for ClO and Cl_2O_2 and the standard enthalpy of formation $\Delta_f H°$ for ClO are determined using statistical thermodynamics as described in Chase (1998). The uncertainty in these parameters for ClO is small with $S°(298.15 \, \mathrm{K}) = 225.07 \pm 0.5 \, \mathrm{J\,K^{-1}\,mol^{-1}}$ and $\Delta_f H°(298.15 \, \mathrm{K}) = 101.63 \pm 0.1 \, \mathrm{kJ\,mol^{-1}}$. When computing $S°$ for Cl_2O_2 a larger uncertainty arises, because some of the vibrational frequencies used in the calculation are not exactly known. Using the frequencies and uncertainties given in Table 1 results in $S°(298.15 \, \mathrm{K}) = 302.08^{+1.11}_{-0.42} \, \mathrm{J\,K^{-1}\,mol^{-1}}$. The temperature dependence of $\Delta_f H°$ for Cl_2O_2, $d(\Delta_f H°)/dT$, may also be calculated from statistical thermodynamics with a relatively small uncertainty (using the same vibrational frequencies as for computing $S°$). If we express $\Delta_r H°$ as the sum of $\Delta_r H°(0 \, \mathrm{K})$ and a temperature dependent thermal correction, Eq. (2) becomes

$$K_{eq}(T) = \frac{RT}{N_A} e^{\Delta_r S°/R} e^{-\left(\Delta_r H°(0\mathrm{K}) + \int_{0\mathrm{K}}^T \frac{\partial(\Delta_r H°)}{\partial T} dT\right)/RT}$$

$$= \frac{RT}{N_A} e^{\Delta_r S°/R} e^{-\left(\int_{0\mathrm{K}}^T \frac{\partial(\Delta_r H°)}{\partial T} dT\right)/RT} e^{-\Delta_r H°(0\mathrm{K})/RT} \quad (3)$$

All quantities in Eq. (3) are either constant or can be calculated from statistical thermodynamics, except for $\Delta_r H°$ (0 K). The value of $\Delta_r H°$ can be taken from direct laboratory measurements or deduced from laboratory measure-

ments of K_{eq} at different temperatures by a logarithmic fit, corresponding to third law analysis but taking into account the temperature dependence of $\Delta_r H°$ and $\Delta_r S°$. The major uncertainty in this calculation arises from the uncertainties in the vibrational frequencies of Cl_2O_2 (Table 1). However, this results in less than $0.2 \, \mathrm{kJ\,mol^{-1}}$ error in the calculated $\Delta_r H°$ (0 K) values and less than 10% error in K_{eq} below 300 K.

Figure 1a shows various laboratory measurements of K_{eq} at different temperatures, and the temperature dependence resulting from the analysis of these data described above. Basco and Hunt (1979) and Ellermann et al. (1995) only measured K_{eq} at 298 K so that no robust determination of the temperature dependence of K_{eq} and thus $\Delta_r H°$ can be obtained from these studies. Even though concerns have been raised about their reliability (Crowley, 2006), they are included for completeness and seem to be in good agreement with Cox and Hayman (1988). Also included in Fig. 1a is the temperature dependence deduced from $\Delta_r H°$ measured by Plenge et al. (2005) and the recommendation and uncertainty given in JPL 2006. A comparison with K_{eq} deduced from stratospheric observations is shown in Fig. 1b. The values obtained for $\Delta_r H°$ (0 K) from the temperature dependent third law analysis of the laboratory data shown in Fig. 1a are given in Table 2, together with other values found in the literature. We note three arguments that support the lower $\Delta_r H°$ (0 K) obtained from Cox and Hayman (1988):

1. Cox and Hayman (1988) actually establish equilibrium between ClO and Cl_2O_2 while Nickolaisen et al. (1994) determine K_{eq} from measured values of k_{rec} and k_{diss} that are somewhat dependent on each other,

2. in Nickolaisen et al. (1994) the Cl_2O_2 entropies obtained by second and third law analyses disagree beyond the error margins of both methods, and

Table 2. Standard reaction enthalpies $\Delta_r H°$ for Reaction (R1) and corresponding heat of formation $\Delta_f H°$ for Cl_2O_2 at 0 K deduced from laboratory and theoretical studies.

	$\Delta_r H°$ (0 K) kJ mol^{-1}	$\Delta_f H°$ (0 K) for Cl_2O_2 kJ mol^{-1}
Direct determination by photoionisation mass spec.		
Plenge et al. (2005)	-68.0 ± 2.8	134.1 ± 2.8
Deduced from measurements of K_{eq} as described[a]		
Cox and Hayman (1988)	-68.9 ± 0.2	133.2 ± 0.2
Nickolaisen et al. (1994)	-70.0 ± 0.2	132.1 ± 0.2
Ab initio studies		
McGrath et al. (1990)	-66.1 ± 17.6	136.5 ± 13.4
Lee et al., 1992	-65.2	136.9
Li and Ng (1997)	-73.9	128.2
Zhu and Lin (2003)	-78.0 ± 4.2	123.1 ± 4.2

[a] Given are values and errors derived using Eq. (3) with entropies/thermal corrections with Cl_2O_2 vibrational frequencies and uncertainties given in Table 1. Because these uncertainties are small and only $\Delta_r H°$ (0 K) is fitted, its resulting uncertainty is small.

3. K_{eq} resulting from the Cox and Hayman (1988) data is in excellent agreement with atmospheric measurements (Fig. 1b). At stratospheric temperatures, it corresponds almost exactly to the function inferred from aircraft observations of ClO inside the Arctic polar vortex by Avallone and Toohey (2001), which represents an upper limit to K_{eq} because their assumption of full chlorine activation means that they used maximum possible values for [Cl_2O_2]. Stimpfle et al. (2004) could best reproduce their simultaneous observations of ClO and Cl_2O_2 in darkness using the Cox and Hayman (1998) value for K_{eq}, which is further supported by a number of nighttime ClO measurements (Berthet et al., 2005; Glatthor et al., 2004; Pierson et al., 1999; von Clarmann et al., 1997). Observations of ClO and Cl_2O_2 presented in von Hobe et al. (2005) suggest a value for K_{eq} even lower by a factor of 2 to 4, but equilibrium may not have been established considering lower rates of Cl_2O_2 formation than assumed in their study (cf. Sect. 4) and their Cl_2O_2 measurements may be biased low (cf. Sect. 5).

Table 3 gives an overview of K_{eq} values given in the literature. While the upper (Nickolaisen et al., 1994) and lower (von Hobe et al., 2005) limits at stratospheric temperatures differ by a factor of 9 at 200 K, the values given by Plenge et al. (2005) and Avallone and Toohey (2001) and deduced here for the laboratory data of Cox and Hayman (1988) lie only 30% apart and are consistent with most observations of atmospheric ClO and Cl_2O_2 (e.g. Glatthor et al., 2004; Stimpfle et al., 2004; Berthet et al., 2005; and, within error limits, even von Hobe et al., 2005).
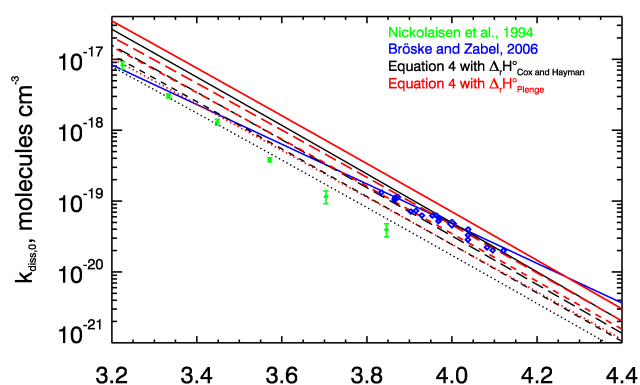

Fig. 2. Temperature dependence of $k_{diss,0}$. For the theoretical values (Eq. 4), solid lines show $k_{diss,0}^{sc}$, long dashed, short dashed and dotted lines $k_{diss,0}^{wc}$ with β_c (300 K) of 0.60, 0.45 and 0.30 respectively. Only the experimental data from Bröske and Zabel (2006) obtained at pressures below 10 hPa, where falloff behavior is assumed to be negligible (cf. Sect. 4), are included.

3 The Cl_2O_2 dissociation rate constant k_{diss}

Explicit values for k_{diss} from laboratory experiments are only given by Nickolaisen et al. (1994) and by Bröske and Zabel (2006). Bröske and Zabel (2006) prepared Cl_2O_2 and monitored its loss whereas Nickolaisen et al. (1994) obtained k_{diss} from fitting the observed decay of ClO to an overall reaction mechanism. Neither study extends to stratospheric temperatures, and at 260 K they disagree by a factor of about 3 as obvious from Fig. 2. We compare the low pressure limiting rate constants $k_{diss,0}$ from these studies to theoretical calculations using unimolecular rate theory described by the following formalism (Troe, 1977a; Troe, 1977b; Troe, 1979;

Table 3. K_{eq} values given in the literature. Given are pre-exponential factors and temperature dependence using the JPL format $K = A \times \exp(B/T)$.

	A	B
JPL 2006[a]	9.3×10^{-28}	8835
Cox and Hayman (1988)	$(4.10 \pm 0.31) \times 10^{-30} \times T$	8720 ± 360
Nickolaisen et al. (1994) (3rd law anal.)	$(1.24 \pm 0.18) \times 10^{-27}$	8820 ± 440
Avallone and Toohey (2001)	$1.99 \times 10^{-30} \times T$	8854
von Hobe et al. (2005)	3.61×10^{-27}	8167
Plenge et al. (2005)	1.92×10^{-27}	8430 ± 326

[a] Factor of 1.2 uncertainty at 298 K and factor of 2 uncertainty at 200 K.

Patrick and Golden, 1983):

$$k_{diss,0} = \beta_c k_{diss,0}^{sc} = \beta_c Z_{LJ} \left[\rho_{vib,h} (E_0) RT/Q_{vib} \right]$$
$$e^{-E_0/RT} F_{anh} F_E F_{rot} F_{rot\,int} F_{corr} \qquad (4)$$

The hypothetical strong collision rate constant $k_{diss,0}^{sc}$ forms an upper limit, which is multiplied by a collision efficiency term β_c to take weak collision effects into account. Z_{LJ} is the Lennard-Jones collision frequency, $\rho_{vib,h} (E_0)$ the harmonic oscillator density of states, Q_{vib} the vibrational partition function, $E_0 \cong \Delta_r H^\circ$ (0 K) the reaction threshold energy (note that in Table 2, $\Delta_r H^\circ$ values are given for the forward direction of Reaction (R1), so the sign has to be reversed here), F_{anh} the anharmonicity correction, F_E the energy dependence of the density of states and F_{rot} the external rotational contribution. The correction factor for internal rotation, $F_{rot\,int}$, is not considered here because internal rotors are not significant at low temperatures for these calculations (Patrick and Golden, 1983). Following Troe (1977b) we neglect the final factor F_{corr} introduced to correct for the coupling between the various factors and the approximations made in the calculation. A summary of the parameters in Eq. (4) and their uncertainties at various temperatures is given in Table 4. The exact calculation is described in detail by Troe (1977a, b). As for K_{eq}, the uncertainties arising from the vibrational frequencies of Cl_2O_2 are small ($<7\%$ error for $k_{diss,0}^{sc}$) because the temperature dependence is determined mainly by E_0 and the effects of using different vibrational frequencies on $\rho_{vib,h} (E_0)$ and Q_{vib} partially cancel. Of all input parameters in Eq. (4), E_0 introduces the largest uncertainty, which is easily rationalised by the exponential dependency and clearly shows in the comparison of $k_{diss,0}^{sc}$ using only marginally different values of $\Delta_r H^\circ$ (0 K) (Fig. 2).

Using $\Delta_r H^\circ$ (0 K) from Plenge et al. (2005) and β_c (300 K)=0.6, the theoretical value of $k_{diss,0}$ derived from Eq. (4) is in excellent agreement with the results of Bröske and Zabel (2006) (Fig. 2). The values of $k_{diss,0}$ derived in the Nickolaisen et al. (1994) study fall significantly below even the lowest theoretical value using $\Delta_r H^\circ$ (0 K) derived from Cox and Hayman (1988) and β_c (300 K)=0.3 (Fig. 2).

In their paper, Bröske and Zabel (2006) also compare their results to theoretical predictions of the low pressure rate constant using the formalism by Troe (1977a, b) described above (Eq. 4). However, they fix β_c (250 K)=0.3 and derive $\Delta_r H^\circ$ (0 K)=66.4±3.0 kJ mol^{-1} to fit their data. This value is lower than the laboratory values presented in Table 2 and would imply an equilibrium constant similar to von Hobe et al. (2005). On the other hand, when multiplying $k_{diss,0}$ with $k_{rec,0}$ recommended by JPL 2006 they obtain K_{eq} between Cox and Hayman (1988) and Plenge et al. (2005). Obviously the agreement with the rate theory calculations is much better for the results of Bröske and Zabel (2006) compared to those of Nickolaisen et al. (1994). We also feel that the potential sources of error in the method employed by Bröske and Zabel (2006) are smaller, because the data are much easier to interpret and the only other loss mechanism for Cl_2O_2 in this experiment are wall effects that were not apparent over the pressure range used (Bröske and Zabel, 2006). However, one major drawback of the Bröske and Zabel study is the limited temperature range over which the experiment was conducted. The uncertainty of the temperature extrapolation from their fit to the data becomes rather large well below or above 242–261 K. We propose to use the rate theory calculations for a more robust temperature extrapolation by fitting an exponential function to $k_{diss,0}$ obtained from Eq. (4) with $\Delta_r H^\circ$ (0 K) from Plenge et al. (2005) and β_c (300 K)=0.6 that best fits the Bröske and Zabel (2006) measurements, giving

$$k_{diss,0} = 1.66 \times 10^{-6} e^{-7821/T}. \qquad (5)$$

As pointed out by Patrick and Golden (1983) and stressed in Crowley (2006) and Golden (2006), rate theory is far from being perfect and Eq. (4) involves a number of approximations. In particular the calculations of F_{anh} and F_{rot} can not be regarded as exact and may introduce considerable uncertainty (Golden, 2006). Therefore the results of these calculations need to be treated with care and the good agreement with rate theory calculations does not prove the Bröske and Zabel (2006) study right. Nevertheless, rate theory adds rather than reduces confidence in the results of Bröske and

Table 4. Overview of parameters used or calculated in Eq. (4) for $M=N_2$. Except for β_c, errors given arise mainly from uncertainties in Cl_2O_2 vibrational frequencies (Table 1).

T K	Z_{LJ}^a 10^{-10} cm^3 molecule^{-1}s^{-1}	$\rho_{vib,h}(E_0)^b$ kJ^{-1} mol	Q_{vib}	E_0^b kJ mol^{-1}	F_{anh}	F_E^c	F_{rot}^c	$\beta_c^{c,d}$
200	3.30	$2689^{+387}_{-147}(2831^{+408}_{-154})$	$2.02^{+0.16}_{-0.03}$	68.0 (68.9)	1.52	1.11	12.1	0.55±0.15
250	3.45		$2.73^{+0.25}_{-0.05}$			1.14	9.4	0.49± 0.15
300	3.59		$3.75^{+0.37}_{-0.10}$			1.17	7.6	0.45±0.15

^{a} Lennard-Jones parameters for Cl_2O_2 from Bloss et al. (2001) were used.
^{b} $\Delta_r H^\circ$ (0 K) from Plenge et al. (2005) is used for E_0 (with values based on the Cox and Hayman data, 1988, given in parentheses).
^{c} F_E, F_{rot} and β_c are only marginally affected by the choice of E_0.
^{d} we use values of 0.3, 0.45 and 0.6 for β_c (300 K) and derive the temperature dependence as described in (Troe, 1979) with $\beta_c/(1-\beta_c)$ $\cong -<\Delta E>/F_E kT$, where $<\Delta E>$ is the enegry transferred in all up and down transitions.
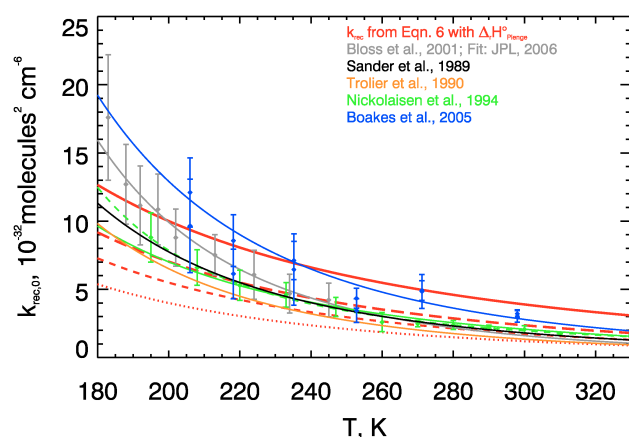

Fig. 3. Temperature dependence of $k_{rec,0}$. For the theoretical values (Eq. 6), collision efficiencies β_c are represented by line styles as in Fig. 2. For Nickolaisen et al. (1994), the solid line represents the T^n treatment, the dashed line the $e^{-E/T}$ treatment. For Boakes et al. (2005) the two points at each temperature represent their results with and without incorporating an intercept in the falloff curves.

Zabel (2006), and in our opinion is helpful for extrapolating their measurements to lower temperatures.

4 The Cl_2O_2 formation rate constant k_{rec}

The Cl_2O_2 formation rate constant k_{rec} has been determined in a number of laboratory studies employing flash photolysis with time resolved UV absorption spectroscopy (Sander et al., 1989; Trolier et al., 1990; Nickolaisen et al., 1994; Bloss et al., 2001; Boakes et al., 2005). Except for the most recent investigation (Boakes et al., 2005), the values given for the low pressure limit $k_{rec,0}$ at temperatures above about 240 K agree well, but at stratospheric temperatures between 180 and 220 K there is a large discrepancy as shown in Fig. 3.

Trolier et al. (1990) and Boakes et al. (2005) find higher ClO recombination rates at low pressures than expected from typical falloff behaviour (cf. below), with the resulting intercept in the falloff curves inversely related to temperature. A number of possible reasons for this behaviour are discussed in both studies. However, the issue has not been fully resolved, accentuating the extant shortcomings in our understanding of the Cl_2O_2 formation kinetics.

Using Eq. (1), $k_{rec,0}$ can be calculated by multiplying K_{eq} obtained from Eq. (3) and $k_{diss,0}$ from Eq. (4). As long as the choice of $\Delta_r H^\circ$ (0 K) is consistent, the $e^{-\Delta_r H^\circ(0K)/RT}$ and $e^{-E_0/RT}$ terms in Eqs. (3) and (4) cancel and the remaining dependency on E_0 (mainly through $\rho_{vib,h}$) and hence on the choice of the equilibrium constant is small (Patrick and Golden, 1983). The following expression is obtained:

$$k_{rec,0} = \frac{R^2 T^2}{N_A} \beta_c \rho_{vib,h} Z_{LJ} \frac{1}{Q_{vib}} F_{anh} F_E F_{rot}$$
$$e^{\Delta_r S^\circ/R} e^{-\left(\int_{0K}^T \frac{\partial(\Delta_r H^\circ)}{\partial T} dT\right)/RT} \quad (6)$$

R, N_A, $\rho_{vib,h}$ and F_{anh} are independent of temperature. The temperature dependence of the remaining terms is calculated or fitted over the temperature range 170 to 320 K to the functional form T^n, giving $T^{-1.5\pm0.3}$ for $1/Q_{vib}$, $T^{-1.1\pm0.1}$ for F_{rot}, $T^{-0.9\pm0.4}$ for $e^{\Delta_r S^\circ/R}$, $T^{-1.2\pm0.2}$ for $e^{-\left(\int_{0K}^T \frac{\partial(\Delta_r H^\circ)}{\partial T} dT\right)/RT}$ and $T^{0.2\pm0.1}$ for $\beta_c Z_{LJ} F_E$ combined (the individual temperature dependence of these three terms is complicated but small, cf. Table 4). The uncertainties in the exponents incorporate uncertainties of the parameters used (e.g. vibrational frequencies) as well as uncertainties from the fits, in some cases taking the extremes at either end of the temperature range as upper and lower limits. Together with the T^2 term, this yields an overall temperature dependence of $T^{-2.9\pm0.6}$ for $k_{rec,0}$. The uncertainty in the vibrational frequencies has a larger effect on $k_{rec,0}$ than on K_{eq} and $k_{diss,0}$ due to the sensitivity of $\rho_{vib,h}$ and Q_{vib} (Table 4)

as well as $e^{\Delta_r S^\circ/R}$ and $e^{-\left(\int_{0K}^{T} \frac{\partial(\Delta_r H^\circ)}{\partial T} dT\right)/RT}$, resulting in an error for $k_{\text{rec},0}$ of up to 15% from the uncertainties given in Table 1. As pointed out in Sect. 3, an additional uncertainty is introduced by the approximations made in the Troe calculations.

It is evident from Fig. 3 that at stratospheric temperatures, these calculations raise concern over the validity of values of $k_{\text{rec},0}$ from Bloss et al. (2001) and Boakes et al. (2005). Values of $k_{\text{rec},0}$ from these two studies are both higher than $k_{\text{rec},0}$ calculated from Eq. (6), even for β_c=1, and both laboratory values display a stronger temperature dependence than theory. On the other hand, using β_c=0.6 (most consistent with $k_{\text{diss},0}$ observed by Bröske and Zabel (2006), cf. Sect. 3) yields a $k_{\text{rec},0}$ corresponding almost exactly to the T^n treatment of Nickolaisen et al. (1994), which is in reasonable agreement with Sander et al. (1989) and Trolier et al. (1990). Moreover, the temperature exponent of –3.01±0.20 given by Nickolaisen et al. (1994) is in excellent agreement with the –2.9±0.6 deduced from Eq. (6).

A value for $k_{\text{rec},0}$ higher than the derived $k_{\text{rec},0}^{sc}$ (i.e. β_c=1.0) is difficult to rationalize: thermal decomposition faster than $k_{\text{diss},0}^{sc}$ derived in Sect. 3 is unlikely on theoretical grounds (Golden, 2003) and would contradict both available laboratory studies (Bröske and Zabel, 2006; Nickolaisen et al., 1994). A significantly higher value for K_{eq} is incompatible with most field observations of ClO and Cl_2O_2. This is not in conflict with the notion of Bröske and Zabel (2006) that K_{eq} calculated from their k_{diss} and k_{rec} from Bloss et al. (2001) is consistent with Cox and Hayman (1988) and Plenge et al. (2005), because over the temperature range of their experiment, i.e. 242–261 K, k_{rec} from Bloss et al. (2001) and Nickolaisen et al. (1994) are equivalent (Fig. 3).

These studies were carried out by the same laboratory and, as pointed out in Crowley (2006), the more recent Bloss et al. (2001) results supersedes the older Nickolaisen et al. (1994) value because of an improvement in how the ClO cross section (σ_{ClO}) was used to infer $k_{\text{rec},0}$ at low temperature. Compared to the low temperature extrapolation of σ_{ClO} measured by Sander and Friedl (1989) that was used by Nickolaisen et al. (1994), Bloss et al. (2001) measured a steeper increase of σ_{ClO} at low temperatures. However, the cross sections may not be directly comparable, because the earlier study used absolute cross sections at 275.2 nm while Bloss et al. (2001) relied on differential cross sections (peak at 275.2 nm, trough at 276.4 nm). This could explain why the cross sections calculated by the two formulae for temperature dependence of σ_{ClO}, both given in Bloss et al. (2001), are always lower in Bloss et al. (2001) compared to Nickolaisen et al. (1994) for T>155 K. The steeper increase of σ_{ClO} towards lower temperatures observed by Bloss et al. would then be explained by the significant increase of peak-to-valley ratios with decreasing temperature observed by Sander and Friedl (1989), the study on which the cross sections used in Nickolaisen et al. (1994) are based. While the use of dif-

ferential cross sections has certainly advantages and deems Bloss et al. (2001) more reliable, it does not conclusively invalidate the earlier Nickolaisen et al. (1994) study, especially given the significant scatter between various σ_{ClO} determinations from different chemical systems described in Bloss et al. (2001).

From the laboratory point of view, Bloss et al. (2001) is certainly the preferred value for $k_{\text{rec},0}$ (Golden, 2003; Atkinson et al., 2006; Crowley, 2006; Golden, 2006; Sander et al., 2006) with the very recent Boakes et al. (2005) study suggesting an even higher value. And clearly, the disagreement with rate theory calculations does not invalidate these results because of 1) the uncertainty inherent to the theory itself and 2) the possibility of Reaction (R1) proceeding by a different mechanism (e.g. chaperone mechanism, Golden, 2003) or forming a product mix including different Cl_2O_2 isomers (Bloss et al., 2001), both not being compatible with rate theory calculations as applied above. However, to test if there exists any combination of laboratory parameters consistent with both "available" theory and atmospheric observations, the results for the atmospheric steady state and modelling studies presented in Section 5 use only the Nickolaisen et al. (1994) value of $k_{\text{rec},0}$ because it presents the least discrepancies for the suite of parameters discussed in Sects. 2, 3 and 4.

In the atmosphere somewhat lower values than the low pressure limits are usually observed for rate constants such as k_{diss} and k_{rec} due to falloff behaviour with increasing pressure. Effective rate constants are estimated using the following expression (Troe, 1979; Patrick and Golden, 1983):

$$k = \frac{k_0[\text{M}]}{1 + k_0[\text{M}]/k_\infty} F^{\left[1+\left(\log\left\{\frac{k_0[\text{M}]}{k_\infty}\right\}\right)^2\right]^{-1}} \qquad (7)$$

where k_∞ is the high pressure limiting rate constant and $F \sim 0.6$ is the broadening parameter. Parameterizations for $k_{\text{rec},\infty}$ given in the laboratory studies mentioned above are compared in Fig. 4. The largest difference at stratospheric temperatures is about a factor of two. We choose to follow the JPL 2006 recommendation for $k_{\text{rec},\infty}$, because it provides an intermediate estimate at stratospheric temperatures with a temperature dependence of $T^{-2.4}$. Uncertainties in $k_{\text{rec},\infty}$ are not as critical as the choice for $k_{\text{rec},0}$ at stratospheric pressures. Below 150 hPa, variation of $k_{\text{rec},\infty}$ by a factor of two changes the resulting k_{rec} by 10% at most. Falloff behavior also applies to k_{diss}. Because no reliable measurement of $k_{\text{diss},\infty}$ exists (Bröske and Zabel, 2006, state that the uncertainty of their proposed $k_{\text{diss},\infty}$ is large because measurements were only made at low pressures), it is calculated from $k_{\text{rec},\infty}$ through K_{eq}.
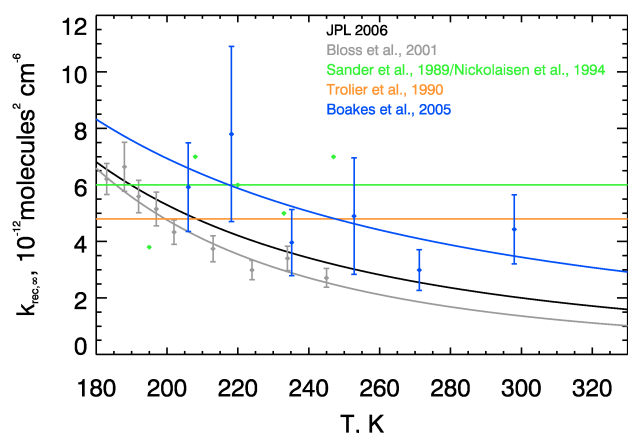
Fig. 4. Temperature dependence of $k_{rec,\infty}$.

Fig. 5. Comparison of UV–Vis absorption spectra of ClOOCl. Solid lines show actual experimental data, dashed lines are based on log-linear extrapolation.

5   The Cl_2O_2 absorption cross section σ_{ClOOCl} and photolysis frequency J

When light is available Cl_2O_2 is readily photolysed, and it has been demonstrated that between 90 and 100% of the product yield is comprised of Cl and ClOO as in Reaction (R2), out to wavelengths of 308 nm (Moore et al., 1999; Plenge et al., 2004). No laboratory measurements of product yields are available for wavelengths longer than 308 nm, which represents a considerable gap in laboratory confirmation of ozone loss by the ClO+ClO cycle.

The absorption cross section of Cl_2O_2, σ_{ClOOCl}, has been determined in a number of laboratory studies (Basco and Hunt, 1979; Molina and Molina, 1987; Permien et al., 1988; Cox and Hayman, 1988; DeMore and Tschuikow-Roux, 1990; Burkholder et al., 1990; Huder and DeMore, 1995; Pope et al., 2007). The spectra obtained by Basco and Hunt (1979) and Molina and Molina (1987) are significantly different in shape from the other studies and have been proposed to be influenced by Cl_2O_3 and possibly other impurities. As shown in Fig. 5, the other studies agree extremely well in the peak region around 245 nm, but disagree by up to a factor of 20 at higher wavelengths, i.e. the wavelengths controlling J in the atmosphere.

The JPL 2006 recommendation for σ_{ClOOCl} also shown in Fig. 5 is based on an average of the values reported by Permien et al. (1988), Cox and Hayman (1988), DeMore and Tschuikow-Roux (1990) and Burkholder et al. (1990). The latest recommendation by the IUPAC Subcommittee on Gas Kinetic Data Evaluation (Atkinson et al., 2006) is based solely on the Huder and DeMore (1995) study with the notion that the authors prefer these data over the earlier study by the same group (DeMore and Tschuikow-Roux, 1990). However, for wavelengths greater than 310 nm, the Huder and DeMore (1995) cross section is based on a log-linear extrapolation of data obtained at shorter wavelengths, which may be problematic if there exist any ClOOCl absorption bands centred at higher wavelength.
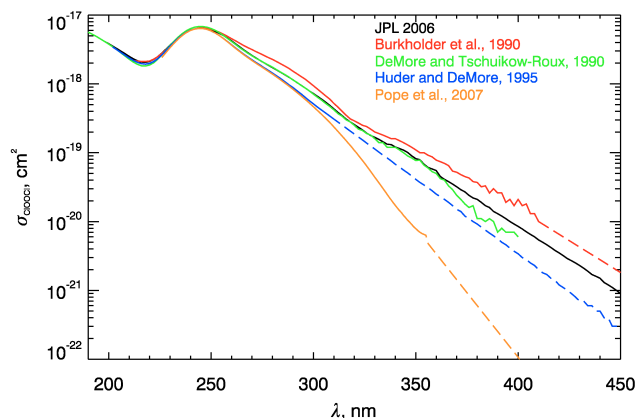
Several ab initio studies suggest that the ClOOCl cross sections might not fall off in log-linear manner at long wavelength. Toniolo et al. (2000) calculated a theoretical photoabsorption spectrum of ClOOCl and predict two electronic excited states producing small absorption bands centered at about 340 nm. Peterson and Francisco (2004) suggest the presence of a weakly absorbing, dissociative triplet state at about 385 nm. These calculations may explain the structure observed by Burkholder et al. (1990) and DeMore and Tschuikow-Roux (1990) in this wavelength region. On the other hand, a recent study by Pope et al. (2007) suggests cross sections significantly lower compared to Huder and DeMore (1995) in the atmospherically relevant region of wavelengths longer than 300 nm. Pope et al. (2007) obtained cross section measurements out to $\sim$355 nm and explicitly avoided some of the interferences from impurities causing uncertainties in the former laboratory studies. Therefore, the Pope et al. (2007) study should be regarded as the most reliable experiment from the laboratory point of view.

Photolysis frequencies of Cl_2O_2 are obtained by multiplying the absorption cross section by the actinic flux and integrating over all atmospherically relevant wavelengths. Here we use a full radiative model that takes into account solar zenith angle (SZA), ambient pressure, overhead ozone and albedo (Salawitch et al., 1994). This is the same radiative transfer model used by Stimpfle et al. (2004) to examine the SOLVE observations of ClO and ClOOCl. Variations in albedo along the flight track of the ER-2 and Geophysica aircraft are obtained primarily from TOMS reflectivity maps. However, measurements from a UV/Vis spectrometer aboard the ER-2 are used when these data are available (Stimpfle et al., 2004). The ozone profiles used to constrain the radiative model are obtained primarily from an assimilation of satellite profiles scaled to match total ozone column measured by TOMS along the flight track. Partial ozone columns from the onboard UV/Vis spectrometer are used for some portions

of the ER-2 simulations (Stimpfle et al., 2004). Under typical stratospheric conditions, J values based on the cross sections by Burkholder et al. (1990) are higher compared to JPL 2006, Huder and DeMore (1995) and Pope et al. (2007) by factors of about 1.3, 2.5 and 10 respectively. The variation in J due to the various cross sections is much larger than typical differences due to reasonable uncertainties in albedo and overhead ozone.

5.1 Photochemical steady state analysis of field data

As described by Avallone and Toohey (2001), effective atmospheric J values can be estimated from atmospheric mixing ratios of ClO and Cl_2O_2 assuming photochemical steady state:

$$J = k_{rec}[M] \left(\frac{[ClO]^2}{[Cl_2O_2]} - \frac{1}{K_{eq}} \right) \qquad (8)$$

The resulting J values depend critically on the choice of k_{rec}. We utilize the second order rate constant from Eq. (7) (that replaces the $k_{rec}[M]$ term in Eq. 8) using $k_{rec,0}$ from Nickolaisen et al. (1994) and $k_{rec,\infty}$ from JPL 2006, for the reasons explained in Sect. 4. K_{eq} is calculated according to Plenge et al. (2005) (cf. Sect. 2). This choice is critical at high solar zenith angles where the contribution from thermal dissociation to the overall rate of Cl_2O_2 removal becomes significant.

Equation (8) only yields reliable J values when the steady state assumption holds. To test this, we employ a time dependent diurnal box model containing the relevant photochemical reactions that govern the partitioning of active chlorine and bromine in the perturbed polar vortex (Canty et al., 2005). We compare J derived from the simulated abundances of ClO and Cl_2O_2 using Eq. (8) to the values of J used in the photochemical model, which are based on radiative transfer calculations. The results shown in Fig. 6 indicate that the steady state assumption is valid at SZA$<82°$, but significant deviations exist at higher SZA. During early morning, Cl_2O_2 accumulated during the night needs time to photolyse until steady state is reached, and J deduced from Eq. (8) falls below J calculated by the radiative model. During late evening, Cl_2O_2 needs time to reform causing J from Eq. (8) to lie above the radiative J. The difference between J found using Eq. (8) and the radiative J is larger at lower temperatures, because of the temperature effect on k_{rec} and K_{eq}. For larger cross sections that lead to faster photolysis (i.e., Burkholder et al., 1990), the relative difference between the two values of J is smaller than for smaller cross sections that lead to slower photolysis (i.e., Huder and DeMore, 1995; Pope et al., 2007). For air parcels that reach SZA of $\sim82°$ to 90° at noon, the difference between J found using Eq. (8) and radiative J is smaller than shown in Fig. 6. Under these conditions, air masses spend more time at high SZA, resulting in a chemical evolution that is close to instantaneous steady state. Equation (8) will yield reliable results provided the data analysis is focused on SZA$<82°$.
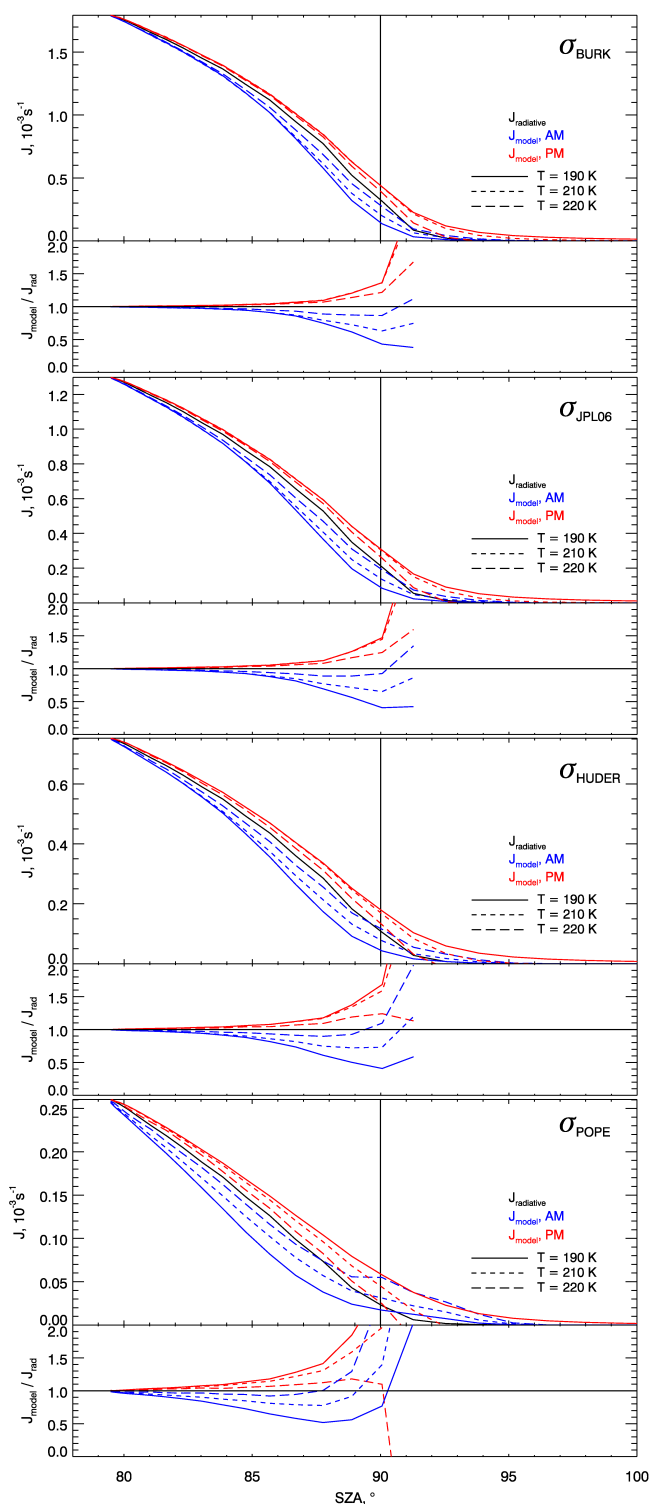

Fig. 6. Comparison of J derived from the simulated abundances of [ClO] and [Cl_2O_2] using Eq. (8) to the values from the radiative model for different Cl_2O_2 absorption cross sections.
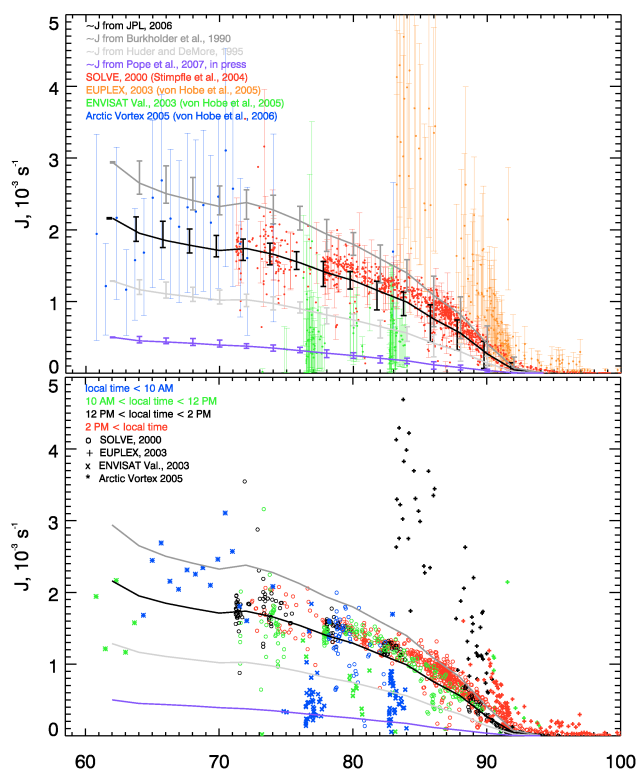
Fig. 7. J values deduced from simultaneous [ClO] and [Cl$_2$O$_2$] observations (only when [ClO$_x$] >200 ppt and $P < 120$ hPa) assuming photochemical steady state color coded for the different campaigns with propagated error bars (top panel) and for different times of day (bottom panel). For comparison, average J values calculated using a radiative model with different σ_{ClOOCl} are given for 2° SZA bins, with error indicating maximum and minimum J in each 2° bin.

In Fig. 7, J values estimated from observations of [ClO] and [Cl$_2$O$_2$] made during field campaigns in several Arctic winters (SOLVE, 1999/2000: Stimpfle et al., 2004; EUPLEX and ENVISAT Arctic Validation, 2002/3: von Hobe et al., 2005; Arctic Vortex flight 2005: von Hobe et al., 2006) using Eq. (8) are plotted as a function of SZA with error bars propagated from measurement errors for [ClO] and [Cl$_2$O$_2$]. The uncertainties can be rather large, especially at low concentrations where the relative measurement error is usually larger. At high zenith angles Cl$_2$O$_2$ thermal dissociation becomes comparable to photolysis and [ClO]^2/[Cl$_2$O$_2$] approaches $1/K_{eq}$, resulting in a large relative error for the difference and hence J. Also shown in Fig. 7 are J values based on the radiative model for the different cross sections given by Burkholder et al. (1990), Huder and DeMore (1995), Pope et al. (2007) and JPL 2006. Variations along the aircraft flight track of overhead ozone, albedo, and pressure cause the radiative J values to vary in a manner that is not strictly monotonic with SZA. The error bars on Fig. 7 for radiative J represent the maximum and minimum values for 2° wide SZA bins, considering the actual variations in albedo, overhead ozone and pressure.

A large number of data points, particularly from the SOLVE data (Stimpfle et al., 2004), follow a dependence on SZA very similar to J_{JPL2006} and $J_{\text{Burkholder}}$. However, numerous points diverge from the compact relationship with SZA, especially at high SZA. Partly, these deviations can be explained by the non-steady state effects described above. In the bottom panel of Fig. 7, data are marked according to the time of day when the measurement was made. At SZA$>85°$, the SOLVE data cluster around two separate lines, the higher one containing almost all points measured in the evening. This is consistent with expectation, as shown in Fig. 6.

Even though all flights carried out during the ENVISAT Arctic Validation Campaign occurred in the morning and hence are expected to fall below the steady state curve, and most EUPLEX flights were evening flights expected to fall above the curve, for the data from these two campaigns the discrepancy is often too large to be explained by non steady state effects alone. As observed in the empirical fit used to obtain K_{eq} from nighttime measurements (von Hobe et al., 2005), [Cl$_2$O$_2$]/[ClO]^2 ratios observed during the EUPLEX campaign are considerably lower than during other field campaigns, which via Eq. (8) translates into faster photolysis rates. For many data points the discrepancy with respect to the JPL06 model lies within the error bounds of the data, but the reason for this obvious underestimation of [Cl$_2$O$_2$]/[ClO]^2 on the order of $\sim$40% is unresolved. Indeed, it is unclear why the EUPLEX measurements of [Cl$_2$O$_2$]/[ClO]^2 can differ substantially even compared to other measurements by the same instrument (HALOX). As mentioned above, a 40% relative error on [Cl$_2$O$_2$]/[ClO]^2 can produce a much larger relative error for J derived from Eq. (8) at high zenith angles often encountered during EUPLEX. A source of error leading to an underestimation of J may be present in the data from the ENVISAT Validation campaign. Von Hobe et al. (2005) state that contribution from ClONO$_2$ at the dimer dissociation temperature in their measurement is less than 1%. However, at the end of the Arctic winter after significant deactivation and hence high ClONO$_2$ and moderate to low levels of active chlorine, this may introduce a significant error in the measurement of Cl$_2$O$_2$.

For the SOLVE data and the Vortex 2005 flight, the ratio $J_{\text{Eq. (8)}}/J_{\text{radiative}}$ is plotted as a function of solar zenith angle (SZA) in Fig. 8. As described above, the steady state assumption does not hold at SZA$>82°$, and the uncertainties can be ascribed to non-steady state effects. Below 82°, uncertainties in J inferred from Eq. (8) still exist, and J cannot be deduced conclusively from the observations used. However, it can be said that the cross sections presented by Huder and DeMore (1995) and even more so Pope et al. (2007) are clearly inconsistent with these atmospheric observations.

Avallone and Toohey (2001) presented a steady state analysis of ClO observations during the AASE field campaigns in the Arctic vortex during the winters 1988/89 and 1991/92. In contrast to the results presented here, their steady state

J values support the cross section measurements by Huder and DeMore (1995). However, they used Cl_2O_2 concentrations based on the assumption that all available inorganic chlorine is activated and in the form of either ClO or Cl_2O_2 (cf. Sect. 2), thus representing an upper limit for $[Cl_2O_2]$ resulting via Eq. (8) in a lower limit for J. Deviations from their assumption will have a larger impact on their J value than on their K_{eq} because the relative change of $[Cl_2O_2]$ would be greater at lower concentrations during the day.

5.2 Box model studies

The results of our photochemical steady state analysis are in good agreement with the results from the comparison of the SOLVE data with box model studies by Stimpfle et al. (2004), where $J_{JPL2006}$ was too small and $J_{Burkholder}$ was too large when using $k_{rec,0}$ from JPL 2000 (Sander et al., 2000), which is basically the same as $k_{rec,0}$ from Nickolaisen et al. (1994).

We also carried out a box model study similar to Stimpfle et al. (2004) to provide a further test independent of any non-steady-state-effects. Observations were taken from the Arctic vortex 2005 flight (von Hobe et al., 2006). These are probably the most reliable HALOX measurements due to high ClO_x and low $ClONO_2$ levels and stronger chlorine emission lamps than were available in the 2002/03 winter (lamp output strongly influences sensitivity of the chemical conversion reference fluorescence technique used by HALOX). Due to the wide range of solar zenith angles encountered, the flight is also most suitable to constrain J. Simulations were carried out using CLaMS (Chemical Lagrangian Model of the Stratosphere, McKenna et al., 2002) along back trajectories from ECMWF wind fields initialized at 04:00 a.m. UTC on the flight day with $[ClO_x]=[ClO]_{obs}+2[Cl_2O_2]_{obs}$ and values of ClO and Cl_2O_2 calculated using K_{eq} from Plenge et al. (2005). This K_{eq} was used in the model together with $k_{rec,0}$ from Nickolaisen et al. (1994) and $k_{rec,\infty}$ from JPL 2002. Four model runs using different parameterizations for σ_{ClOOCl} were carried out (Fig. 9). In agreement with the steady state analysis presented in Sect. 5.1, the results using σ_{ClOOCl} from Pope et al. (2007) always lie far outside the margin of measurement error, and results from Huder and DeMore (1995) mostly lie outside the error margins. It should be noted that the results of both, steady state analysis and box model studies, are insensitive to the choice of K_{eq} for zenith angles below 85°.

6 Conclusions

Figure 10 summarises our results concerning k_{rec} and J that govern the rate of the ClO dimer cycle during daytime and thus ozone loss rates. Under typical stratospheric conditions, k_{rec} given by Bloss et al. (2001), currently regarded as the most reliable laboratory experiment (Golden, 2003; Atkin-
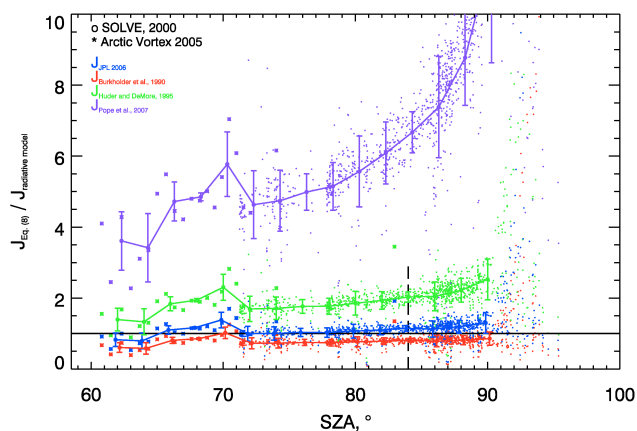

Fig. 8. Ratio of J calculated from SOLVE and VORTEX 2005 observations using Eq. (8) to J from the radiative model using different σ_{ClOOCl} vs. SZA.

son et al., 2006; Crowley, 2006; Golden, 2006; Sander et al., 2006), falls just outside the range rationalised by theoretical calculations (cf. Bloss et al., 2001; Golden, 2003). Even with the imperfection of rate theory in mind, the difference is large enough to at least put a question mark on either our mechanistic understanding of Reaction R1 or the Bloss et al. (2001) data at low temperatures. When considering observed atmospheric ClO_x partitioning, the Bloss et al. (2001) k_{rec} is consistent only with J based on the Burkholder et al. (1990) cross sections (Stimpfle et al., 2004). The value for k_{rec} given by Boakes et al. (2005) is inconsistent with both rate theory and atmospheric observations (at least for any published ClOOCl cross section data). While the cross sections given by JPL 2006 still produce realistic ClO_x partitioning (i.e. within given uncertainties) in combination with lower k_{rec} values (Trolier et al., 1990; Nickolaisen et al., 1994), the Huder and DeMore (1995) and Pope et al. (2007) cross sections are clearly too low to be consistent with atmospheric observations, including earlier studies of ClO in the Antarctic vortex (Shindell and de Zafra, 1995; Shindell and de Zafra, 1996; Solomon et al., 2002).

Nevertheless, Huder and DeMore (1995) and Pope et al. (2007) represent the most recent and probably most reliable laboratory measurements of σ_{ClOOCl}. Accepting the cross sections from either of these studies and that the available observational techniques do not generally overestimate [ClO] in the polar vortices means that either some unidentified loss process converts Cl_2O_2 to ClO in the polar vortex or the formation of Cl_2O_2 from ClO proceeds much slower than even at the lowest rates reported based on laboratory studies.

Recent studies (Chipperfield et al., 2005; Frieler et al., 2006; Tripathi et al., 2006) show that observed ozone loss is underestimated by models using ClOOCl absorption cross sections lower than JPL 2006 and that the best agreement is actually achieved when using the higher Burkholder et
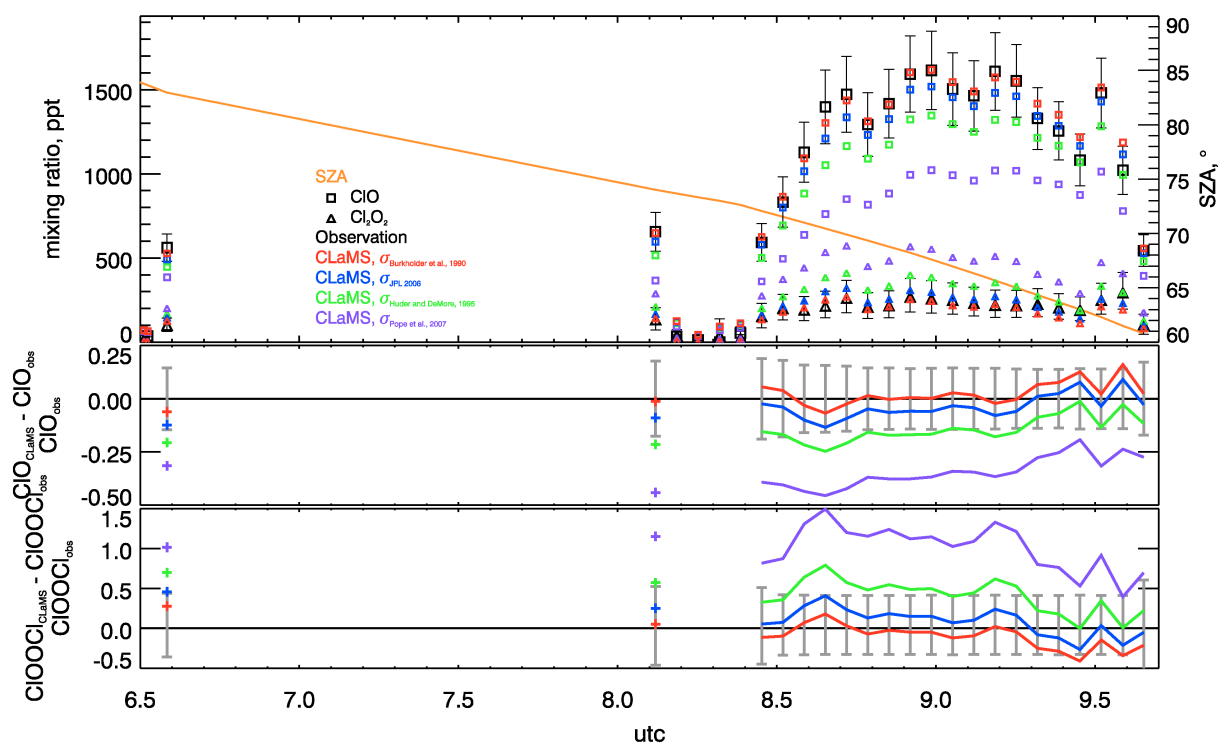
Fig. 9. Comparison of simulated ClO and Cl_2O_2 using different parameterizations with observations from the Arctic Vortex 2005 flight (von Hobe et al., 2006). For each σ_{ClOOCl} used in the simulation, the relative difference of the simulated ClO and Cl_2O_2 mixing ratios to the observed values is shown in the bottom two panels (except where $[ClO_x] < 200$ ppt).
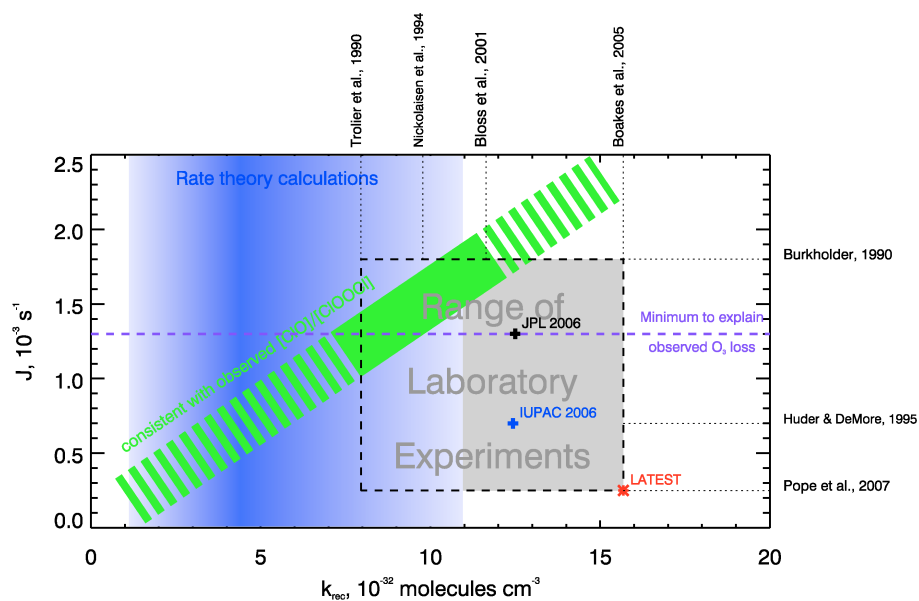

Fig. 10. "Map" of kinetic parameters $k_{rec,0}$ and J from various laboratory experiments (grey area) and deduced from atmospheric observations (green line, thickness indicates approximately the uncertainty). Shown in blue is the range of $k_{rec,0}$ values consistent with unimolecular rate theory calculations ($0.1 < \beta_c$ (300 K) < 1.0 with the darkest blue at β_c (300 K)=0.3). The plot is shown for T=190 K and SZA=80°, but the results are qualitatively insensitive to T and SZA within the temperature range observed in the polar vortices and for SZA<93°.

al. (1990) cross sections. This is further illustrated in Fig. 11 that shows ozone loss simulated by CLaMS along a typical trajectory over the Antarctic winter 2003, when a cold and stable vortex was observed (meaning that possible uncertainties due to atmospheric dynamics are minimised). At 450 K potential temperature, near complete ozone loss was observed over much of the vortex by the end of the winter (Tilmes et al., 2006; Tripathi et al., 2006). This is not reproduced by the model runs using Huder and DeMore (1995) or Pope et al. (2007) cross sections. With Pope et al. (2007), Cl_2O_2 photolysis becomes so slow that increasing k_{rec} significantly reduces ozone loss indicating that ClO concentrations become low enough to effectively slow the ClO–BrO catalytic cycle. Thus, cross sections lower than JPL 2006 would imply additional yet unidentified ozone loss processes.

By looking at all kinetic and thermodynamic parameters of the ClO dimer cycle synergistically and taking into account information from laboratory experiments, theoretical studies and field observations, we have presented a new strategy for understanding the kinetics of the ClO dimer cycle, which we hope complements the evaluations by the JPL and IUPAC panels that are based almost exclusively on laboratory measurements and focus on individual reactions rather than on complete reaction systems (such as the ClO dimer cycle). We can identify an internally consistent set of kinetic parameters

- K_{eq} from Avallone and Toohey (2001), Cox and Hayman (1988) or Plenge et al. (2005),

- $k_{diss,0}$ measured by Bröske and Zabel (2006) and extrapolated using unimolecular rate theory,

- $k_{rec,0}$ and $k_{rec,\infty}$ given by Nickolaisen et al. (1994) and JPL 2006 respectively,

- J values in the range of JPL 2006 and Burkholder (1990)

that falls within the constraints given by theoretical considerations and reproduces stratospheric observations of chlorine oxides reasonably well. However, this set of parameters is not consistent with the recommendations given by the JPL and IUPAC panels, which are based solely on evaluation of laboratory studies of individual processes. In particular, for k_{rec} and J, values from Bloss et al. (2001) and Huder and DeMore (1995)/Pope et al. (2007) respectively are currently regarded as the most reliable experimental values.

A number of open questions remain and we cannot claim to have reached full understanding of the kinetics of the ClO dimer catalytic cycle as given by Reactions (R1) to (R4). This has profound implications for our understanding of polar ozone loss. Most importantly, the uncertainty regarding the Cl_2O_2 absorption cross section at wavelengths longer than 310 nm needs to be resolved. It is also critical to explain the substantial differences between reported ClO recombination rates at cold temperatures. Any processes that possibly cause faster loss of ClO in the studies by Bloss et
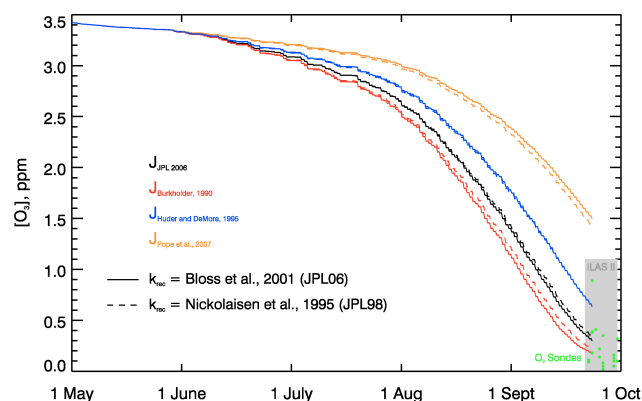

Fig. 11. Simulated ozone loss in the Antarctic winter 2003 along a single trajectory ending on the 450 K isentrope on 23 September. This trajectory was selected such that its ozone loss (using JPL 2006 kinetics) corresponds to the mean ozone loss of a 3-D CLaMS simulation for this winter (Grooß et al., in preparation). The simulation was initialised using MIPAS and HALOE satellite observations and tracer correlations. For comparison, ozone sonde data from six stations south of 66° S (Tripathi et al., 2006) and the range of ILAS-II O_3 observations within the Antarctic Vortex at 450 K potential temperature (Tilmes et al., 2006) near the end of the simulation are shown.

al. (2001) and Boakes et al. (2005) need to be identified, because it cannot be excluded that these processes play a role in the atmosphere under certain conditions. An enhancement of the ClO recombination rate due to a chaperone mechanism in the presence of Cl_2 has been suggested by Nickolaisen et al. (1994). Similar effects due to other molecules or even heterogeneous processes can occur. The possibility of pressure and temperature dependent formation of other Cl_2O_2 isomers than ClOOCl has been proposed in several studies (Bloss et al., 2001; Boakes et al., 2005; Bröske and Zabel, 2006; Golden, 2003; Nickolaisen et al., 1994; von Hobe et al., 2005). Finally, there may be yet unidentified reactions involving ClO and Cl_2O_2 that are fast enough to alter the partitioning of these species.

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