

**A re-evaluation of the  
ClO/Cl<sub>2</sub>O<sub>2</sub>  
equilibrium constant**

M. von Hobe et al.

# **A re-evaluation of the ClO/Cl<sub>2</sub>O<sub>2</sub> equilibrium constant based on stratospheric in-situ observations**

**M. von Hobe, J.-U. Grooß, R. Müller, S. Hrechanyy, U. Winkler, and F. Stroh**

Institut für Chemie und Dynamik der Geosphäre I: Stratosphäre (ICG-I), Forschungszentrum  
Jülich, Jülich, Germany

Received: 3 August 2004 – Accepted: 16 August 2004 – Published: 7 September 2004

Correspondence to: M. von Hobe (m.von.hobe@fz-juelich.de)

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2004

## Abstract

In-situ measurements of ClO and its dimer carried out during the SOLVE II/VINTERSOL-EUPLEX and ENVISAT Validation campaigns in the Arctic winter 2003 suggest that the thermal equilibrium between the dimer formation and dissociation is shifted significantly towards the monomer compared to the current JPL 2002 recommendation. Detailed analysis of observations made in thermal equilibrium was used to re-evaluate the magnitude and temperature dependence of the equilibrium constant. A fit of the JPL format for equilibrium constants yields  $K_{EQ}=4.06\times 10^{-23}\exp(6201/T)$ , but to reconcile the observations made at low temperatures with the existing laboratory studies at room temperature, a modified equation,  $K_{EQ}=2.31\times 10^{-13}(T/300)^{-34.9}\exp(-1118/T)$ , is required. This format can be rationalised by a strong temperature dependence of the reaction enthalpy possibly induced by Cl<sub>2</sub>O<sub>2</sub> isomerism effects. At stratospheric temperatures, both equations are practically equivalent. Using the equilibrium constant reported here rather than the JPL 2002 recommendation in atmospheric models does not have a large impact on simulated ozone loss. Solely at large zenith angles after sunrise, a small decrease of the ozone loss rate due to the ClO dimer cycle and an increase due to the ClO-BrO cycle (attributed to the enhanced equilibrium ClO concentrations) is observed, the net effect being a slightly stronger ozone loss rate. The effects of Cl<sub>2</sub>O<sub>2</sub> isomerism are not studied in detail, but the presence of isomers other than ClOOCi would be expected to lead to reduced ozone loss.

## 1. Introduction

ClO and its dimer (Cl<sub>2</sub>O<sub>2</sub>) are the key species involved in the most efficient ozone destruction cycle in the cold polar winter stratosphere (Molina and Molina, 1987):



ACPD

4, 5075–5102, 2004

## A re-evaluation of the ClO/Cl<sub>2</sub>O<sub>2</sub> equilibrium constant

M. von Hobe et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2004

with

$$K_{EQ} = [\text{Cl}_2\text{O}_2]/[\text{ClO}] \quad (1)$$



While at small solar zenith angles the forward reaction of (R1) and dimer photolysis (R2) dominate and  $k_f$  and  $J$  control both the partitioning between ClO and  $\text{Cl}_2\text{O}_2$  and the overall rate of the catalytic cycle, the thermal equilibrium (1) of Reaction (R1) controls the ClO/ $\text{Cl}_2\text{O}_2$  partitioning at night.

10 The equilibrium constant  $K_{EQ}$  depends inversely on temperature.  $K_{EQ}$  has been quantified in numerous laboratory studies (e.g. Cox and Hayman, 1988; Horowitz et al., 1994; Nickolaisen et al., 1994), but all were carried out at temperatures above those prevailing in the stratosphere. The current recommendation (Sander et al., 2003, referred to as JPL 2002 hereafter) extrapolates these studies to stratospheric temperatures. However, a substantial amount of evidence suggests that this procedure does not yield realistic values for  $K_{EQ}$ . Higher ClO concentrations at night than can be explained by the JPL 2002 equilibrium constant have been reported in several studies (Glatthor et al., 2004; Pierson et al., 1999; Ricaud et al., 2004; von Clarmann et al., 1997). Avallone and Toohey (2001) give a lower estimate of  $K_{EQ}$  employing Eq. (1) on field measurements of ClO and estimated  $\text{Cl}_2\text{O}_2$  concentrations based on the total amount of active chlorine calculated from tracer correlations and assuming total activation. The only previous study based on simultaneous observations of ClO and  $\text{Cl}_2\text{O}_2$  (Stimpfle et al., 2004) also makes a strong case, that JPL 2002 overestimates  $K_{EQ}$  at stratospheric temperatures, but no effort was made to derive  $K_{EQ}$  from these measurements. Finally, a recent laboratory study presented by Plenge et al. (submitted,

25

---

**A re-evaluation of the  
ClO/ $\text{Cl}_2\text{O}_2$   
equilibrium constant**

M. von Hobe et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

2004b)<sup>1</sup> using photoionisation mass spectrometry yields a parameterisation giving values for  $K_{EQ}$  in the range as found by Avallone and Toohey (2001), significantly lower than JPL 2002.

During the Arctic winter 2002/2003, we carried out simultaneous in-situ measurements of ClO and Cl<sub>2</sub>O<sub>2</sub>. Based on observations made in darkness, we report a new parameterisation for  $K_{EQ}$  that lies significantly below the JPL 2002 recommendation. An attempt is made to identify possible problems with the extrapolation of the laboratory determinations of  $K_{EQ}$  (Cox and Hayman, 1988; Horowitz et al., 1994; Nickolaisen et al., 1994) to stratospheric temperatures, that might explain the discrepancies between  $K_{EQ}$  deduced from the observations and the value recommended in JPL 2002. Furthermore, possible implications of the reduced  $K_{EQ}$  for the chemistry of the polar stratosphere and ozone loss rates in particular are discussed.

## 2. Observations

Measurements of ClO and Cl<sub>2</sub>O<sub>2</sub> were carried out during the SOLVE II/VINTERSOL-EUPLEX and ENVISAT Validation campaigns from January to March 2003, utilising the HALOX instrument situated in a pod under the left wing of the stratospheric research aircraft M55-Geophysica. For the study of the ClO/Cl<sub>2</sub>O<sub>2</sub> equilibrium, only observations made under equilibrium conditions (cf. Sect. 3) were used, which include data from five flights carried out between 19 January and 2 March. The temperatures encountered during these flights range from 191 to 212 K.

The HALOX instrument employs the chemical conversion resonance fluorescence (CCRF) technique for measuring ClO described by Brune et al. (1989). This technique uses NO added to the sampled air via needle arrays placed in each measurement duct to produce chlorine atoms via the fast reaction ClO+NO→Cl+NO<sub>2</sub>. The chlorine

<sup>1</sup>Plenge, J., Köhl, S., Vogel, B., Müller, R., Stroh, F., Flesch, R., and Rühl, E.: Bond strength of the ClO dimer, Geophys. Res. Lett., submitted, 2004b.

## A re-evaluation of the ClO/Cl<sub>2</sub>O<sub>2</sub> equilibrium constant

M. von Hobe et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

atoms are detected by resonance fluorescence at 118.9 nm, using low pressure gas discharge lamps containing trace amounts of chlorine in 5 hPa helium as light source and VUV photomultiplier tubes (EMR 541J-09-17) as detectors. The NO addition is switched on and off in cycles of 10 to 20 s, and the ClO concentration is calculated from the ratio of the fluorescence signal to the intensity of the background light scatter, correcting for the ClO to Cl conversion efficiency, which is calculated based on NO and O<sub>3</sub> concentrations, flow rate, temperature and pressure using FACSIMILE and is typically about 80 to 90%. As shown in Fig. 1, HALOX consists of two parallel measurement ducts. The open duct A, in which the flow velocity is regulated to within 10–20 m s<sup>-1</sup> by a butterfly valve (MKS 253B), is used to measure ClO with a detection limit of 5 ppt and an accuracy of approximately 15%. To improve precision, 3 to 10 NO addition cycles are averaged. Error limits for [ClO] are computed taking into account accuracy and the standard error resulting from data averaging. In the pumped measurement duct B, the sum of ClO and Cl<sub>2</sub>O<sub>2</sub> is measured after thermal dissociation of the dimer in a heated inlet nozzle depicted in Fig. 2. As the temperature, measured by a thermocouple placed behind the inlet, is raised, an increasing amount of Cl<sub>2</sub>O<sub>2</sub> (if present) dissociates and the signal increases until reaching a constant level at about 370 K where therefore dimer dissociation may be assumed to be complete, as demonstrated in Fig. 3. Because in this way in duct B the sum of 2 Cl<sub>2</sub>O<sub>2</sub> + ClO is measured, to extract the Cl<sub>2</sub>O<sub>2</sub> concentration present in the atmosphere, the ClO background has to be subtracted. This is done using the ClO measurement of duct A, which is compared to the signal in duct B at regular intervals without heating. ClO measurements in ducts A and B agreed to within 5–10% indicating that no radicals are lost in the cold nozzle. Small differences (<20%) observed during some flights (that could usually be traced to ambiguous lamp calibration parameters) were corrected for by scaling the ClO measurement of duct A to that of B. The accuracy of the Cl<sub>2</sub>O<sub>2</sub> measurement results from the propagation of the accuracies of A and B and depends to some extent on the relative amounts of ClO and Cl<sub>2</sub>O<sub>2</sub> present. Typically it lies around 20–30%. If the inlet temperature is raised to above 410 K, the ClO signal starts to increase again due to

# A re-evaluation of the ClO/Cl<sub>2</sub>O<sub>2</sub> equilibrium constant

M. von Hobe et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

dissociation of chlorine nitrate,  $\text{ClONO}_2$  (Fig. 3b). Laboratory tests have shown that less than 1% of any  $\text{ClONO}_2$  present dissociates at 390 K, so that an overestimation of the  $\text{Cl}_2\text{O}_2$  concentration due to a possible contribution of  $\text{ClONO}_2$  can be ruled out. During SOLVE II/VINTERSOL-EUPLEX and the ENVISAT validation campaign, the inlet heater was cycled between the dimer and  $\text{ClONO}_2$  dissociation temperatures, with occasional periods of no heating to check the consistency between ducts A and B.

The conversion efficiency of the inlet heater with respect to  $\text{Cl}_2\text{O}_2$  has been tested in the laboratory employing the system shown in Fig. 4. Molecular chlorine (5% in He) is dissociated by an ohmically heated Pt/Rh filament, and the chlorine atoms are converted to ClO by reaction with ozone produced by flowing molecular oxygen gas through a high voltage field. This ClO source was shown to be stable over the timescales of the experiments (up to 2 h). The ClO is diluted with molecular nitrogen and directed through the unheated inlet into HALOX duct B, which on the exhaust side is connected to a vacuum line containing a butterfly valve (MKS 253B) used to regulate the pressure inside the system. When the nitrogen is cooled by immersing the supply line into a dewar filled with liquid nitrogen, the fluorescence signal produced by the ClO decreases; when the inlet heater is turned to  $100^\circ\text{C}$ , the fluorescence signal returns quantitatively as illustrated in Fig. 5. We ascribe this to formation of  $\text{Cl}_2\text{O}_2$  upon cooling, and dissociation in the heated inlet. However, a small proportion of ClO may be removed by wall loss, especially at low pressures and flow rates. Turning the inlet heater on while the calibration gas is not cooled does not affect measured ClO concentration. The laboratory studies do not suggest any problems with incomplete dimer conversion in the heated inlet. A lower limit for the conversion efficiency is estimated to 80% based on the accuracy and precision of the laboratory measurements. The combined error limits given for  $[\text{Cl}_2\text{O}_2]$  measured during the flights incorporate the uncertainty of the conversion efficiency together with the accuracy and the standard error estimated from data averaging.

Figure 6 shows the results for an afternoon flight (30 January 2003), in which the same air masses probed on the outbound leg were resampled during the return leg.

---

## A re-evaluation of the $\text{ClO}/\text{Cl}_2\text{O}_2$ equilibrium constant

M. von Hobe et al.

---

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)

Although this flight could not be used for the calculation of  $K_{EQ}$  below because the  $\text{ClO}/\text{Cl}_2\text{O}_2$  does not reach thermal equilibrium, the data demonstrate how the  $\text{ClO}$  monomer is slowly reacting into the dimer as the solar zenith angle (SZA) increases. This flight also provides a further test of the dimer measurement: the observed decrease in  $[\text{ClO}]$  between two measurements of the same air mass is matched within error limits by the corresponding increase in  $2[\text{Cl}_2\text{O}_2]$ .

Temperature measurements were carried out by the Central Aerological Observatory, Russia, employing Rosemount sensors (estimating the maximum error to  $\pm 0.6\text{ K}$ ), while static pressure was taken from the UCSE aircraft system. SZA is calculated using position and geometric altitude data provided by the onboard GPS system together with the exact time.

### 3. Derivation of the $\text{ClO}/\text{Cl}_2\text{O}_2$ equilibrium constant

The equilibrium constant of Reaction (R1) can be inferred from observations using Eq. (1). However, this relation is valid only when  $\text{ClO}$  and  $\text{Cl}_2\text{O}_2$  are in equilibrium, and the rate of dimer photolysis (R2) is zero. This is usually the case at night when the excess  $\text{ClO}$  monomer produced photochemically during daytime has relaxed back into thermal equilibrium. The relaxation time needed for the active chlorine species ( $\text{ClO}_x = \text{ClO} + 2\text{Cl}_2\text{O}_2$ ) to go from the point where practically all  $\text{ClO}_x$  is in the form of  $\text{ClO}$  to  $\text{ClO}/\text{Cl}_2\text{O}_2$  equilibrium strongly depends on temperature, pressure and  $\text{ClO}_x$  concentration (Fig. 7). Measurements of these parameters are used to calculate the relaxation time for the EUPLEX and ENVISAT validation data points. Strictly,  $\text{ClO}$  and its dimer are assumed to be in equilibrium when the relaxation time calculated using the JPL 2002 equilibrium constant is smaller than the time past local sunset. Because this “strict” equilibrium criterion limits the data base to only a few points from two flights, a second, “soft” equilibrium criterion is installed that allows including more points. For this criterion, equilibrium is assumed when the relaxation time calculated using the new equilibrium constant inferred from our observations (cf. below) is smaller than the time

## A re-evaluation of the $\text{ClO}/\text{Cl}_2\text{O}_2$ equilibrium constant

M. von Hobe et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

that has passed since the sun was 5° above the horizon, thus taking into account that relaxation into equilibrium starts before sunset (cf. Fig. 6). With the soft equilibrium criterion, data from 5 flights qualify for the thermal equilibrium situation.

The temperature dependence of  $K_{EQ}$  is given by the Van't Hoff equation:

$$\frac{d \ln K}{dT} = \frac{\Delta H^0}{RT^2} \quad \text{or} \quad \frac{d \ln K}{d(1/T)} = \frac{-\Delta H^0}{R}. \quad (2)$$

If  $\Delta H^0$  is assumed to be independent of  $T$ , integration yields:

$$K_{EQ} = A \exp(B/T) \quad \text{with} \quad B = -\Delta H^0/R. \quad (3)$$

The inferred values for  $K_{EQ}$  are plotted against  $1/T$  in Fig. 8. Initially (Fig. 8a), least squares fits of  $\ln(K_{EQ})$  against  $1/T$  were carried out separately for both, the points satisfying the strict equilibrium and the soft equilibrium criteria. Because individual data points have a considerable influence on the fit to the “strict equilibrium” data, and the statistical significance of this fit is rather low, the fit to “soft equilibrium” data was used in the following analysis, which is justified through the observation, that points obeying only the soft equilibrium criterion are not significantly lower (as would be expected if photolysis effects were still significant) than those obeying the strict one.

At stratospheric temperatures,  $K_{EQ}$  derived from our observations lies substantially below the JPL 2002 recommendation (Fig. 8b), which is further supported by the observation that the theoretical amount of  $\text{ClO}_x$  inferred from measured  $\text{ClO}$  and the JPL 2002  $K_{EQ}$  would be as high as 7.6 ppb, which is unrealistic even if all available chlorine was activated. A fit of Eq. (3) through the observed  $[\text{Cl}_2\text{O}_2]/[\text{ClO}]^2$  ratios (fit 2 in Fig. 8) further suggests a weaker temperature dependence of  $K_{EQ}$  than JPL 2002.

Clearly, this discrepancy lies outside the error margins of either the observations or the laboratory studies on which the JPL 2002 recommendation is based (Cox and Hayman, 1988; Nickolaissen et al., 1994). However, if we integrate the Van't Hoff equation under the assumption that  $\Delta H^0$  depends linearly on  $T$ , we obtain

$$K_{EQ} = AT^n \exp(-\Delta H^0/RT), \quad (4a)$$

## A re-evaluation of the $\text{ClO}/\text{Cl}_2\text{O}_2$ equilibrium constant

M. von Hobe et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion



which can be expressed in the more convenient form

$$K_{EQ} = A'(T/300)^n \exp(B/T) \quad \text{with} \quad A' = A \cdot 300^n \quad \text{and} \quad B = -\Delta H^0/R. \quad (4b)$$

A three parameter fit of Eq. (4) through both our observations and the laboratory data, brings them to good agreement (fit 3 in Fig. 8b). Because the three fitting parameters in a function of this form are highly correlated, their individual uncertainty is rather large.

Reaction enthalpies do indeed depend on temperature, but this effect is very small and negligible for most reactions, so that a temperature dependence as strong as suggested by fit 3 in Fig. 8b is not easily justified. One possible explanation could be the formation of different isomers of  $\text{Cl}_2\text{O}_2$ , which has been suggested in numerous theoretical (Fangstrom et al., 1998; Golden, 2003; Han et al., 1998; Lee et al., 1992; Li and Ng, 1997; McGrath et al., 1990; Stanton et al., 1991; Zhu and Lin, 2003) and experimental (Jacobs et al., 1994; Muller and Willner, 1992; Plenge et al., 2004a; Schwell et al., 1996) studies on the stability of the three stable  $\text{Cl}_2\text{O}_2$  isomers, namely chlorine peroxide ( $\text{ClOOCI}$ ), chloryl chloride ( $\text{ClClO}_2$ ) and chlorine chlorite ( $\text{ClOCIO}$ ). Slanina and Uhlík have presented calculations showing that the relative stabilities of the  $\text{Cl}_2\text{O}_2$  isomers and hence the composition of the equilibrium isomeric mixture depends on temperature (Slanina and Uhlík, 1991b), and that this has direct effects on the temperature dependence of  $K_{EQ}$  (Slanina, 1992; Slanina and Uhlík, 1991a). They present yet another functional form to extrapolate the laboratory observations of  $K_{EQ}$  also resulting in a reduced value at stratospheric temperatures (Slanina, 1992).

Regardless of any hypothetical physical explanation for the observed behaviour of the temperature dependence of  $K_{EQ}$ , it is obvious that the JPL 2002 recommendation for  $K_{EQ}$  should be adjusted downwards. In the temperature range prevailing in the lower stratosphere, fits 2 and 3 to the observations yield very similar values, and any of the resulting functions (Table 1) can be used in atmospheric models. Fit 2 is used in the following, because it obeys the given JPL 2002 format for the temperature dependence of equilibrium constants and thus only the fitting parameters  $A$  and  $B$  need to be

---

**A re-evaluation of the  
 $\text{ClO/Cl}_2\text{O}_2$   
equilibrium constant**

M. von Hobe et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

modified. The difference of this fit to JPL 2002 ranges from a factor 2.5 at 225 K to a factor 20 at 190 K.

#### 4. Implications

Figure 9 shows how changing  $K_{EQ}$  from the JPL 2002 recommendation to the new value greatly increases predicted night-time ClO concentrations. However, the effect on ozone loss rates is expected to be small, because during sunlit hours, when ozone depleting catalytic cycles are effective, the ClO concentration is controlled almost entirely by the balance between the dimer formation Reaction (R1) and its photolysis (R2). This is confirmed by chemistry calculations using the CLaMS model (McKenna et al., 2002) along an example trajectory from 12 December 2002 to 15 March 2003 that remained in the vortex for the whole simulation period and exhibited particularly strong ozone depletion. The model was initialised from a 3-D CLaMS simulation performed for the winter, i.e. 3.2 ppb  $Cl_y$  and 22 ppt  $Br_y$  (Grooß et al., in preparation, 2004<sup>2</sup>). As Fig. 10 shows, using  $K_{EQ}$  from fit 2 compared to JPL 2002 significantly alters the ClO<sub>x</sub> partitioning only at night. However, accumulated ozone loss over this period, also depicted in Fig. 10, is virtually unaffected.

A borderline case occurs under twilight conditions at large solar zenith angles, when there is still enough light for chemical ozone loss to occur but ClO is already appreciably affected by the  $K_{EQ}$  re-evaluation. Under these conditions, the elevated ClO concentrations cause the rate of another strong ozone destroying catalytic cycle, the ClO-BrO cycle (McElroy et al., 1986),



<sup>2</sup>Grooß, J. U., Günther, G., Müller, R., Konopka, P., Bausch, S., Schlager, H., Volk, C. M., and Toon, G. C.: Simulation of denitrification and ozone loss for the Arctic winter 2002/03, in preparation, 2004.

### A re-evaluation of the ClO/Cl<sub>2</sub>O<sub>2</sub> equilibrium constant

M. von Hobe et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion



5 to increase by promoting Reaction (5). The ClO-BrO cycle is the second most important catalytic cycle under polar conditions (Salawitch et al., 1993), and becomes unproportionally more important at large zenith angles because BrCl is photolysed at longer wavelength compared to Cl<sub>2</sub>O<sub>2</sub>. To study the diurnal dependence of the partitioning between ClO and its dimer and the resulting ozone depletion due to both catalytic cycles, a 2-day simulation (1–3 February) for an air parcel at a constant location and temperature was performed. It was initialised with 22 ppt Br<sub>y</sub> and 3.1 ppb Cl<sub>y</sub> and an almost complete chlorine activation of 88% as in the trajectory simulation explained above. For this case the ozone depletion rate and its contribution from the ClO-BrO cycle (R5–R8) and the ClO dimer cycle (R1–R4) has been evaluated both for the equilibrium constants from fit 2 suggested here and from JPL 2002. Figure 11 shows the results for 60° N and 195 K temperature on the 500 K potential temperature level. At zenith angles between about 85° and 95°, particularly just after sunrise when ClO is determined almost entirely by the thermal equilibrium, a significant change in ozone loss rates due to the choice of  $K_{EQ}$  is observed (Fig. 12). At zenith angles greater than 90°, enhanced ozone loss is observed which can be attributed to a faster rate of the ClO-BrO catalytic cycle caused by the elevated ClO concentrations. At solar zenith angles <90°, the dimer cycle dominates ozone loss and the reduced concentration of ClO dimer caused by the equilibrium shift causes this cycle to proceed slower, resulting in less ozone loss (positive difference in dO<sub>3</sub>/dt in Fig. 12).

25 While we find here that the overall ozone loss is not strongly affected by the magnitude of  $K_{EQ}$ , a temperature dependent branching ratio of the ClO association reaction into different isomers could have a large impact. While the ClOOCl photolysis proceeds

## A re-evaluation of the ClO/Cl<sub>2</sub>O<sub>2</sub> equilibrium constant

M. von Hobe et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

mainly according to Reaction (2) with only a minor proportion going back to two ClO radicals, the other two stable isomers, ClClO<sub>2</sub> and ClOClO, could photolyse to different products, including Cl+OCIO, where OCIO in turn photolyses to ClO and an oxygen atom. As the removal of one odd oxygen by the Cl radical is matched by the production of an oxygen radical, this results in a null cycle that does not destroy ozone. This means that if the presence of different isomers of Cl<sub>2</sub>O<sub>2</sub> is indeed the correct explanation for the behaviour of the equilibrium constant, the consequence would be a reduced ozone loss due to the ClO dimer cycle, especially at low temperatures.

## 5. Conclusions

We have presented simultaneous observations of ClO and its dimer (Cl<sub>2</sub>O<sub>2</sub>). Based on these measurements we deduce the thermal equilibrium constant  $K_{EQ}$  for the equilibrium between ClO and Cl<sub>2</sub>O<sub>2</sub>. Different parameterisations are given (Table 1) using the standard format used by the JPL evaluation panel (Sander et al., 2003) as well as a modified format that attempts to reconcile the field observations with available laboratory studies. All parameterisations predict much lower values for  $K_{EQ}$  than recommended by JPL 2002. Using the lower  $K_{EQ}$  value in the CLaMS chemistry model leads to enhanced ozone loss due to the ClO-BrO catalytic cycle at zenith angles between 90° and 95° and reduced ozone loss between 85° and 90° due to a decrease in the rate of the ClO dimer cycle. However, these changes are not significant in the context of the overall ozone loss over time periods of several days or longer.

To further reduce the uncertainty of the estimate given for  $K_{EQ}$ , more simultaneous measurements of ClO and Cl<sub>2</sub>O<sub>2</sub> are desirable, especially just before sunrise, when ClO/Cl<sub>2</sub>O<sub>2</sub> equilibrium is well established. The formation of different isomers of Cl<sub>2</sub>O<sub>2</sub> as one possible explanation for the observed behaviour and the potential impact on ozone loss warrants further laboratory studies of this issue.

*Acknowledgements.* The authors are grateful to MDB and the crew of the M-55 Geophysica for their support during the campaigns, to H. Schlager from DLR Oberpfaffenhofen, T. Peter and

## A re-evaluation of the ClO/Cl<sub>2</sub>O<sub>2</sub> equilibrium constant

M. von Hobe et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

G. Koch from ETH Zürich and R. Salawitch from JPL for their assistance in flight planning, and to ECMWF for meteorologic analyses. VINTERSOL-EUPLEX is funded through the EC grant EUK2-CT-2001-00119. We acknowledge the HGF Vernetzungsfond, the Bundesministerium für Bildung und Forschung (BMBF) and ESA for funding of the ENVISAT-Validation flights and instrument integration costs.

## References

- Avallone, L. M. and Toohey, D. W.: Tests of halogen photochemistry using in situ measurements of ClO and BrO in the lower polar stratosphere, *J. Geophys. Res.-A*, 106 (D10), 10411–10421, 2001.
- 10 Brune, W. H., Anderson, J. G., and Chan, K. R.: Insitu Observations of ClO in the Antarctic – Er-2 Aircraft Results From 54-Degrees-S to 72-Degrees-S Latitude, *J. Geophys. Res.-A*, 94 (D14), 16649–16663, 1989.
- Cox, R. A. and Hayman, G. D.: The Stability and Photochemistry of Dimers of the ClO Radical and Implications For Antarctic Ozone Depletion, *Nature*, 332 (6167), 796–800, 1988.
- 15 Fangstrom, T., Edvardsson, D., Ericsson, M., Lunell, S., and Enkvist, C.: Density functional study of chlorine-oxygen compounds related to the ClO self-reaction, *Int. J. Quantum Chem.*, 66 (3), 203–217, 1998.
- Glatthor, N., von Clarmann, T., Fischer, H., Funke, B., Grabowski, U., Höpfner, M., Kellmann, S., Kiefer, M., Linden, A., Milz, M., Steck, T., Stiller, G. P., Mengistu Tsidu, G., and Wang, D.-Y.: Spaceborne ClO observations by the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) before and during the Antarctic major warming in September/October 2002, *J. Geophys. Res.*, 109 (D11), doi:10.1029/2003JD004440, 2004.
- 20 Golden, D. M.: Reaction  $\text{ClO} + \text{ClO} \rightarrow \text{products}$ : Modeling and parameterization for use in atmospheric models, *Int. J. Chem. Kinet.*, 35 (5), 206–211, 2003.
- 25 Han, Y. K., Kim, K. H., Lee, Y. S., and Baeck, K. K.: Energies and structures of isomers of  $\text{Cl}_2\text{O}_2$  calculated by density functional methods, *Theochem-J. Mol. Struct.*, 431 (1–2), 185–189, 1998.
- Horowitz, A., Crowley, J. N., and Moortgat, G. K.: Temperature-Dependence of the Product Branching Ratios of the ClO Self-Reaction in Oxygen, *J. Phys. Chem.*, 98 (46), 11924–11930, 1994.
- 30

## A re-evaluation of the $\text{ClO}/\text{Cl}_2\text{O}_2$ equilibrium constant

M. von Hobe et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

- Jacobs, J., Kronberg, M., Muller, H. S. P., and Willner, H.: An Experimental-Study On the Photochemistry and Vibrational Spectroscopy of 3 Isomers of Cl<sub>2</sub>O<sub>2</sub> Isolated in Cryogenic Matrices, *J. Am. Chem. Soc.*, 116 (3), 1106–1114, 1994.
- Lee, T. J., Rohlffing, C. M., and Rice, J. E.: An Extensive Abinitio Study of the Structures, Vibrational-Spectra, Quadratic Force-Fields, and Relative Energetics of 3 Isomers of Cl<sub>2</sub>O<sub>2</sub>, *J. Chem. Phys.*, 97 (9), 6593–6605, 1992.
- Li, W. K. and Ng, C. Y.: Gaussian-2 ab initio study of isomeric Cl<sub>2</sub>O<sub>2</sub> and Cl<sub>2</sub>O<sub>2</sub><sup>+</sup> and their dissociation reactions, *J. Phys. Chem. A*, 101 (2), 113–115, 1997.
- McElroy, M. B., Salawitch, R. J., Wofsy, S. C., and Logan, J. A.: Reductions of Antarctic Ozone Due to Synergistic Interactions of Chlorine and Bromine, *Nature*, 321 (6072), 759–762, 1986.
- McGrath, M. P., Clemitshaw, K. C., Rowland, F. S., and Hehre, W. J.: Structures, Relative Stabilities, and Vibrational-Spectra of Isomers of Cl<sub>2</sub>O<sub>2</sub> – the Role of the Chlorine Oxide Dimer in Antarctic Ozone Depleting Mechanisms, *J. Phys. Chem.*, 94 (15), 6126–6132, 1990.
- McKenna, D. S., Grooß, J. U., Günther, G., Konopka, P., Müller, R., Carver, G., and Sasano, Y.: A new Chemical Lagrangian Model of the Stratosphere (CLaMS) – 2. Formulation of chemistry scheme and initialization, *J. Geophys. Res.*, 107, doi:10.1029/2000JD000113, 2002.
- Molina, L. T. and Molina, M. J.: Production of Cl<sub>2</sub>O<sub>2</sub> From the Self-Reaction of the ClO Radical, *J. Phys. Chem.*, 91 (2), 433–436, 1987.
- Muller, H. S. P. and Willner, H.: Synthesis and Properties of Chloryl Chloride, ClClO<sub>2</sub>, *Inorg. Chem.*, 31 (12), 2527–2534, 1992.
- Nickolaissen, S. L., Friedl, R. R., and Sander, S. P.: Kinetics and Mechanism of the ClO+ClO Reaction – Pressure and Temperature Dependences of the Bimolecular and Termolecular Channels and Thermal-Decomposition of Chlorine Peroxide, *J. Phys. Chem.*, 98 (1), 155–169, 1994.
- Pierson, J. M., McKinney, K. A., Toohey, D. W., Margitan, J., Schmidt, U., Engel, A., and Newman, P. A.: An investigation of ClO photochemistry in the chemically perturbed arctic vortex, *J. Atmos. Chem.*, 32 (1), 61–81, 1999.
- Plenge, J., Flesch, R., Köhl, S., Vogel, B., Müller, R., Stroh, F., and Rühl, E.: Ultraviolet Photolysis of the ClO Dimer, *J. Phys. Chem.*, 108, 4859–4863, 2004a.
- Ricaud, P., Lefèvre, F., Berthet, G., et al.: Chlorine activation studies from the ODIN satellite measurements: the arctic and antarctic cases, in Quadrennial Ozone Symposium, edited by Zerefos, C. S., 1032, Kos, Greece, 2004.

## A re-evaluation of the ClO/Cl<sub>2</sub>O<sub>2</sub> equilibrium constant

M. von Hobe et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

Salawitch, R. J., Wofsy, S. C., Gottlieb, E. W., Lait, L. R., Newman, P. A., Schoeberl, M. R., Loewenstein, M., Podolske, J. R., Strahan, S. E., Proffitt, M. H., Webster, C. R., May, R. D., Fahey, D. W., Baumgardner, D., Dye, J. E., Wilson, J. C., Kelly, K. K., Elkins, J. W., Chan, K. R., and Anderson, J. G.: Chemical Loss of Ozone in the Arctic Polar Vortex in the Winter of 1991–1992, *Science*, 261 (5125), 1146–1149, 1993.

Sander, S. P., Friedl, R. R., Golden, M. M., Kurylo, M. J., Huie, R. E., Orkin, V. L., Moortgat, G. K., Ravishankara, A. R., Kolb, C. E., Molina, M. J., and Finlayson-Pitts, B. J.: Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, in Evaluation Number 14, Jet Propulsion Laboratory, Pasadena, 2003.

Schwell, M., Jochims, H. W., Wassermann, B., Rockland, U., Flesch, R., and Rühl, E.: Ionization energies of ClO and Cl<sub>2</sub>O<sub>2</sub>, *J. Phys. Chem.*, 100 (24), 10 070–10 075, 1996.

Slanina, Z.: Dimerization Equilibrium-Constant For the ClO Radical – State-of-the-Art Wide-Temperature-Interval Thermodynamics of Species Related to Ozone Depleting, *Thermochim. Acta*, 196 (2), 467–475, 1992.

Slanina, Z. and Uhlík, F.: An Estimation of Dimerization Energetics of the ClO Radical, *Chem. Phys. Lett.*, 182 (1), 51–56, 1991a.

Slanina, Z. and Uhlík, F.: Temperature-Dependence of the Gibbs Energy Ordering of Isomers of Cl<sub>2</sub>O<sub>2</sub>, *J. Phys. Chem.*, 95 (14), 5432–5434, 1991b.

Stanton, J. F., Rittby, C. M. L., Bartlett, R. J., and Toohey, D. W.: Low-Lying Isomers of the Chlorine Oxide Dimer – a Theoretical-Study, *J. Phys. Chem.*, 95 (6), 2107–2110, 1991.

Stimpfle, R. M., Wilmouth, D. M., Salawitch, R. J., and Anderson, J. G.: First measurements of ClOOCl in the stratosphere: The coupling of ClOOCl and ClO in the Arctic polar vortex, *J. Geophys. Res.*, 109, doi: 10.1029/2003JD003811, 2004.

von Clarmann, T., Wetzel, G., Oelhaf, H., Friedl, F., Linden, A., Maucher, G., Seefeldner, M., Trieschmann, O., and Lefevre, F.: ClONO<sub>2</sub> vertical profile and estimated mixing ratios of ClO and HOCl in winter arctic stratosphere from Michelson interferometer for passive atmospheric sounding limb emission spectra, *J. Geophys. Res.-A*, 102 (D13), 16 157–16 168, 1997.

Zhu, R. S. and Lin, M. C.: Ab initio studies of ClOx reactions, IV. Kinetics and mechanism for the self-reaction of ClO radicals, *J. Chem. Phys.*, 118 (9), 4094–4106, 2003.

**A re-evaluation of the  
ClO/Cl<sub>2</sub>O<sub>2</sub>  
equilibrium constant**

M. von Hobe et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

**A re-evaluation of the  
ClO/Cl<sub>2</sub>O<sub>2</sub>  
equilibrium constant**

M. von Hobe et al.

**Table 1.** Functions for the  $T$  dependence of  $K_{EQ}$  fitted to observations in Fig. 8.

Fit	$K_{EQ} =$
JPL 2002	$1.27 \times 10^{-27} \exp(8744/T)$
Fit 1: “strict” eq. criterion, Eq. (3)	$5.66 \times 10^{-28} \exp(8511/T)$
Fit 2: “soft” eq. criterion, Eq. (3)	$4.06 \times 10^{-23} \exp(6201/T)$
Fit 3: “soft” eq. criterion, Eq. (4b)	$2.31 \times 10^{-13} (T/300)^{-34.9} \exp(-1118/T)$

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

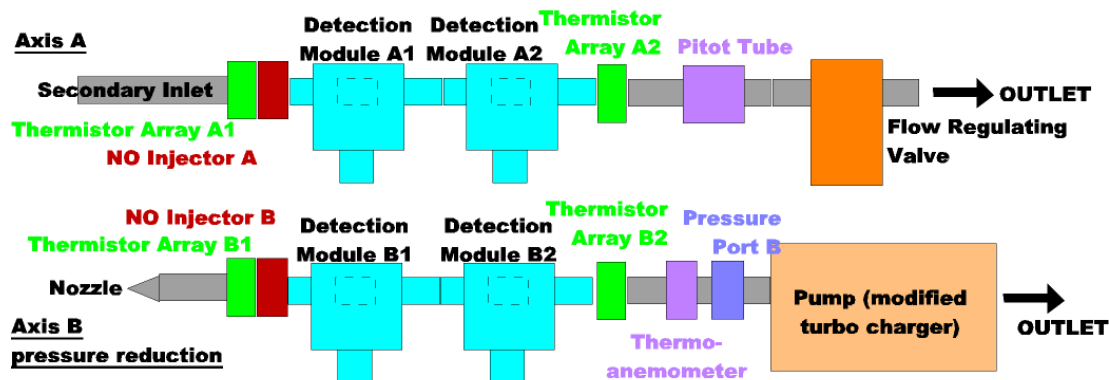
Print Version

Interactive Discussion



## A re-evaluation of the $\text{ClO}/\text{Cl}_2\text{O}_2$ equilibrium constant

M. von Hobe et al.



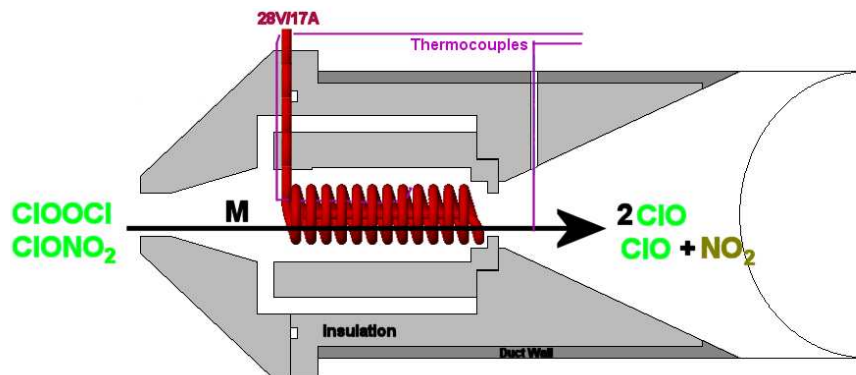
**Fig. 1.** Outline of the HALOX instrument. Modules A1 and B1 detect chlorine, A2 and B2 bromine.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[I◀](#)[▶I](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)

© EGU 2004

**A re-evaluation of the  
 $\text{ClO}/\text{Cl}_2\text{O}_2$   
equilibrium constant**

M. von Hobe et al.

**Fig. 2.** Schematic of the heated inlet.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

I◀

▶I

◀

▶

Back

Close

Full Screen / Esc

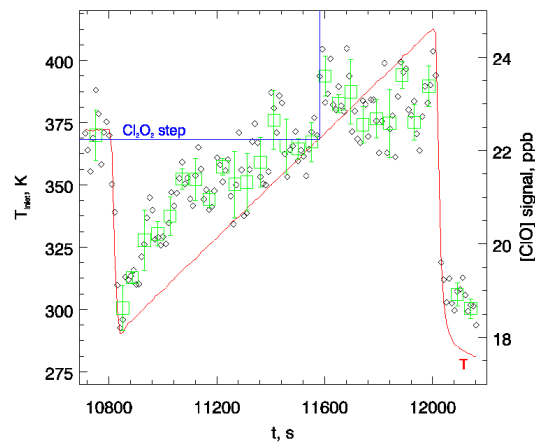
Print Version

Interactive Discussion

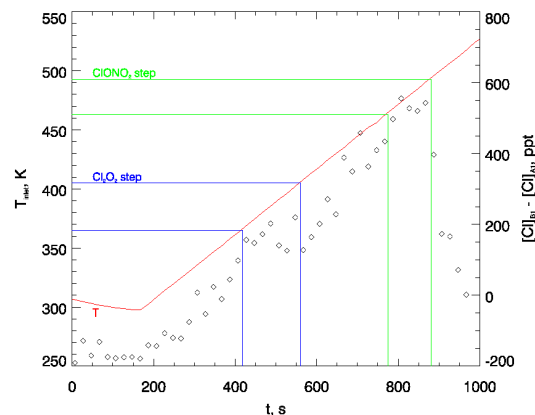
© EGU 2004

**A re-evaluation of the  
ClO/Cl<sub>2</sub>O<sub>2</sub>  
equilibrium constant**

M. von Hobe et al.



(a)



(b)

**Fig. 3.** ClO concentration from resonance fluorescence signal against inlet temperature for a temperature ramp obtained **(a)** under laboratory conditions and **(b)** during a EUPLEX flight on 23 January 2003. Each black diamond represents one individual measurement (i.e. one NO addition cycle); green squares in (a) represent averages over 5 K temperature intervals, error bars representing  $1\sigma$ . Note, that under flight conditions, the natural variability of ClO and Cl<sub>2</sub>O<sub>2</sub> does contribute to the signal.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

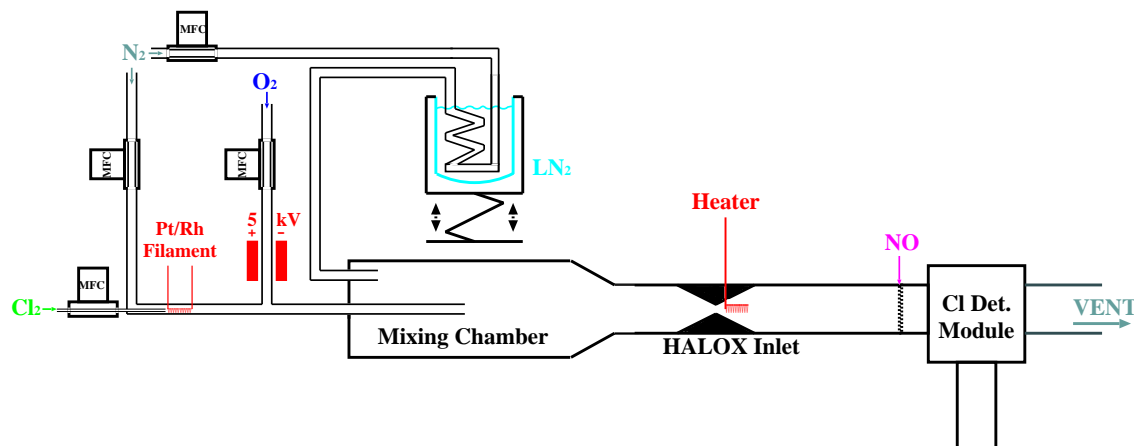
---

**A re-evaluation of the  
ClO/Cl<sub>2</sub>O<sub>2</sub>  
equilibrium constant**

---

M. von Hobe et al.

---



**Fig. 4.** Set up of the ClO-dimer validation/calibration system. All gas flows are regulated by mass flow controllers (MFCs). Temperatures are measured at the inlet heater, at the NO injector and directly behind the chlorine detection module. Pressure and flow velocity are also measured directly behind the detection module. A butterfly valve placed at the HALOX exhaust regulates the flow to maintain a constant pressure inside the measurement duct.

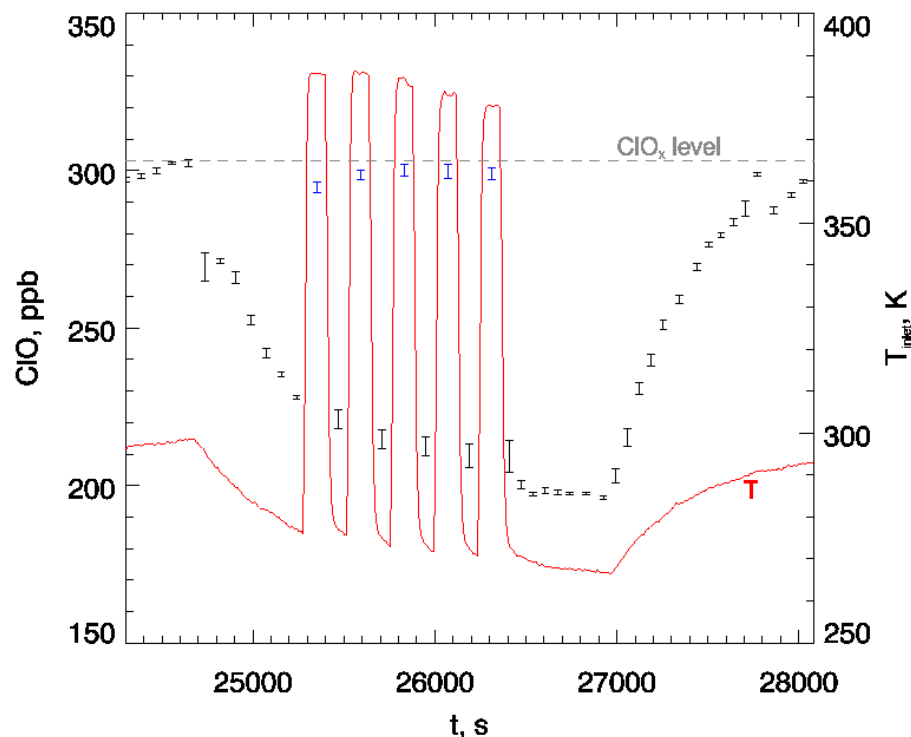
[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)

---

**A re-evaluation of the  
ClO/Cl<sub>2</sub>O<sub>2</sub>  
equilibrium constant**

---

M. von Hobe et al.



**Fig. 5.** Laboratory test ( $P_{duct}=80$  hPa) of dimer conversion efficiency of the heated inlet. Error bars represent the standard error of the mean for one minute averages (equivalent to six NO addition cycles), blue colour indicates that the temperature (red line) of the inlet heater was at the dimer dissociation temperature ( $363\text{ K} < T < 383\text{ K}$ ). The dashed line indicates the reference ClO concentration measured without cooling or heating.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)

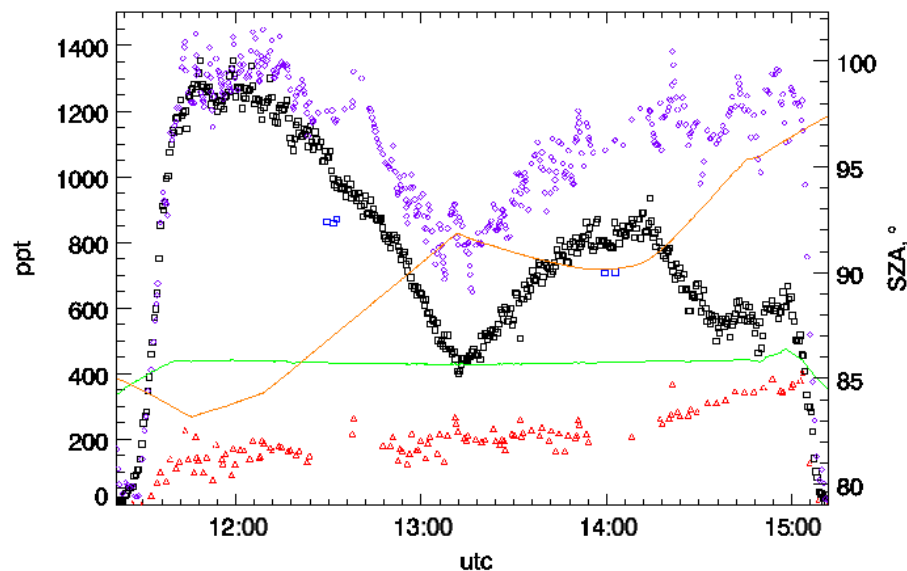
---

**A re-evaluation of the  
 $\text{ClO}/\text{Cl}_2\text{O}_2$   
equilibrium constant**

---

M. von Hobe et al.

---

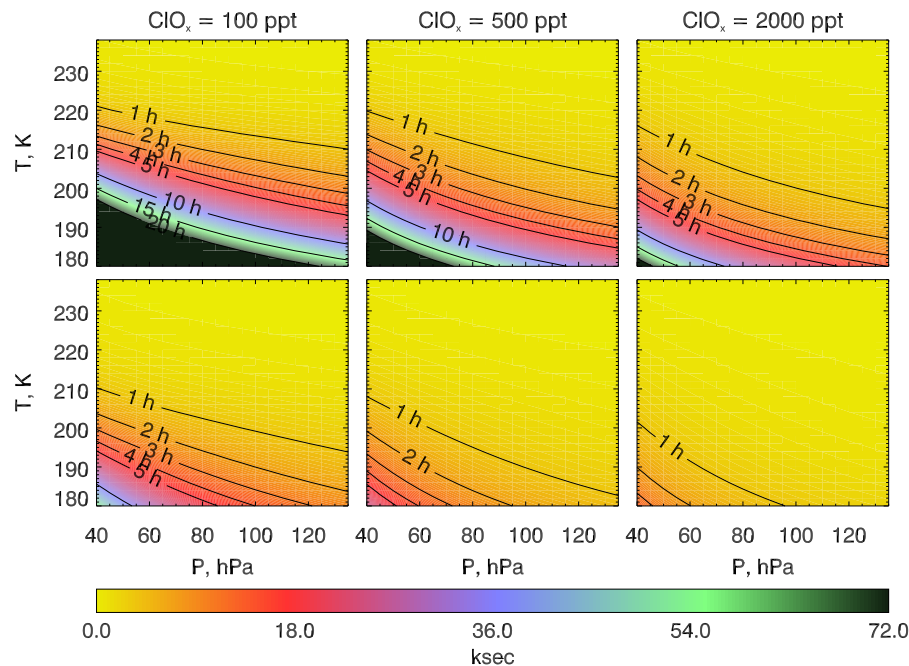


**Fig. 6.** Time series of ClO (black squares: duct A, blue squares: duct B), Cl<sub>2</sub>O<sub>2</sub> (red triangles) and ClO<sub>x</sub> (purple diamonds; from duct B) measured on 30 January 2003. Also shown are potential temperature theta (green line) and solar zenith angle (orange line).

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)

**A re-evaluation of the  
ClO/Cl<sub>2</sub>O<sub>2</sub>  
equilibrium constant**

M. von Hobe et al.



**Fig. 7.** Relaxation time of the ClO/Cl<sub>2</sub>O<sub>2</sub> system into thermal equilibrium ( $[\text{Cl}_2\text{O}_2]/[\text{ClO}]^2 > 0.8 K_{EQ}$ ), as it depends on temperature and pressure for three different ClO<sub>x</sub> concentrations, assuming  $[\text{ClO}] = [\text{ClO}_x]$  and  $[\text{Cl}_2\text{O}_2] = 0$  at  $t = 0$ . Results are shown for both the JPL 2002 equilibrium constant (top panels) and the equilibrium constant inferred from the EUPLEX data (bottom panels).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

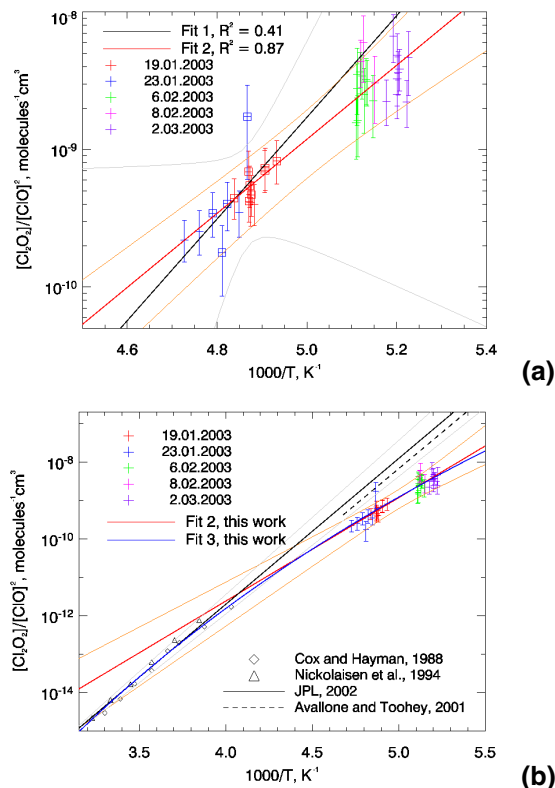
Full Screen / Esc

Print Version

Interactive Discussion

# A re-evaluation of the ClO/Cl<sub>2</sub>O<sub>2</sub> equilibrium constant

M. von Hobe et al.



**Fig. 8. (a)** Van't Hoff plot of EUPLEX data for which thermal equilibrium can be assumed. Data points framed by a square obey the strict equilibrium rule (see text for explanation). Fits 1 and 2 are linear least squares fits of  $\ln([Cl_2O_2]/[ClO]^2)$  against  $1/T$  according to Eq. (3) for the strict equilibrium data and all data points respectively. Uncertainty estimates (grey/orange) take into account error bars on the data and error estimates of the fitting parameters ( $3\sigma$ ). **(b)** Expanded Van't Hoff plot from (a) with laboratory measurements and  $K_{EQ}$  values proposed in the literature for comparison. Fit 2 is the same as in (a), fit 3 employs Eq. (4). Functions and parameters for all fits are summarised in Table 1.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

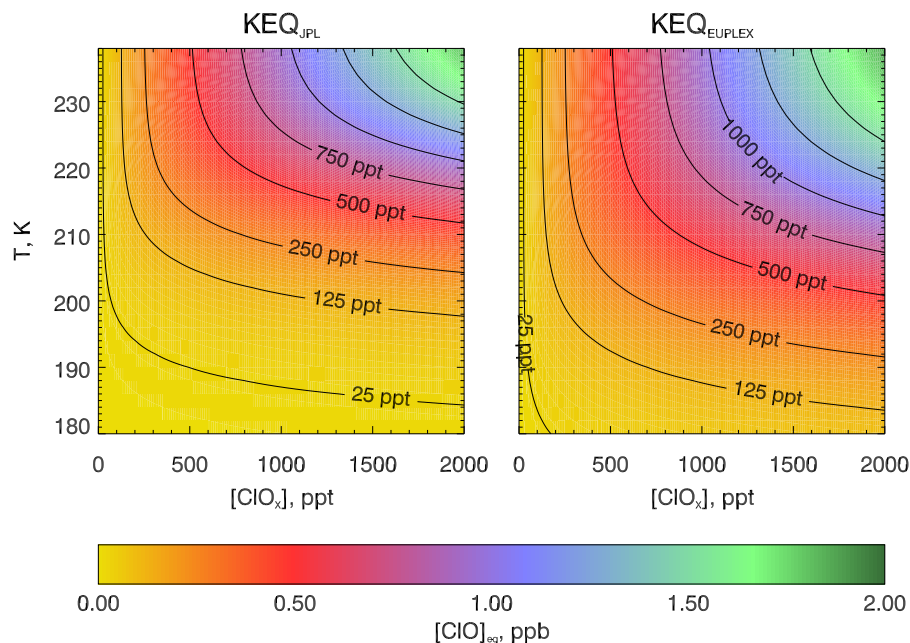
Print Version

Interactive Discussion



**A re-evaluation of the  
ClO/Cl<sub>2</sub>O<sub>2</sub>  
equilibrium constant**

M. von Hobe et al.



**Fig. 9.** Equilibrium ClO concentration as a function of temperature and  $ClO_x$  for the JPL 2002 equilibrium constant (left panel) and the equilibrium constant inferred from fit 2 in this study (right panel).

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)

## A re-evaluation of the ClO/Cl<sub>2</sub>O<sub>2</sub> equilibrium constant

M. von Hobe et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

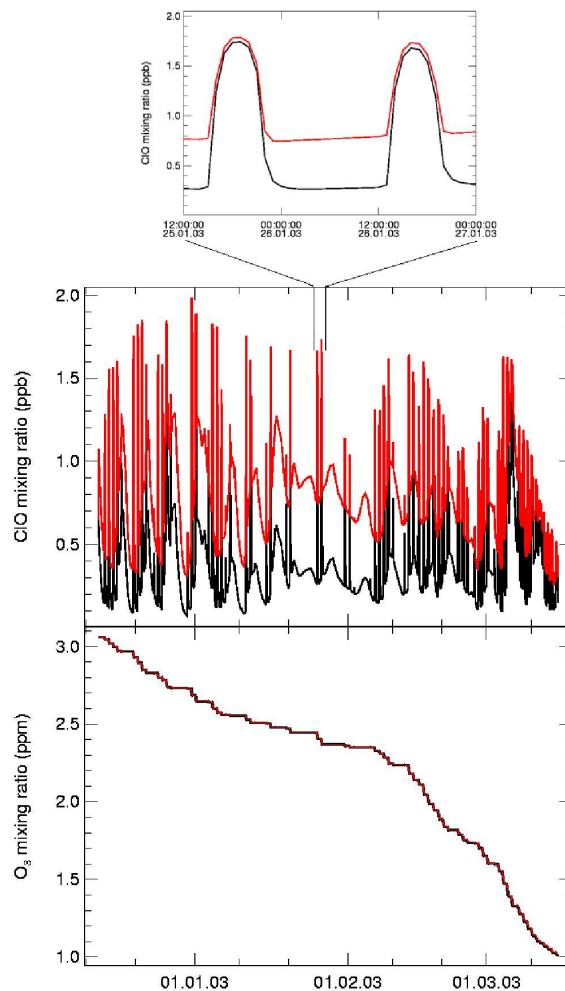
Back

Close

Full Screen / Esc

Print Version

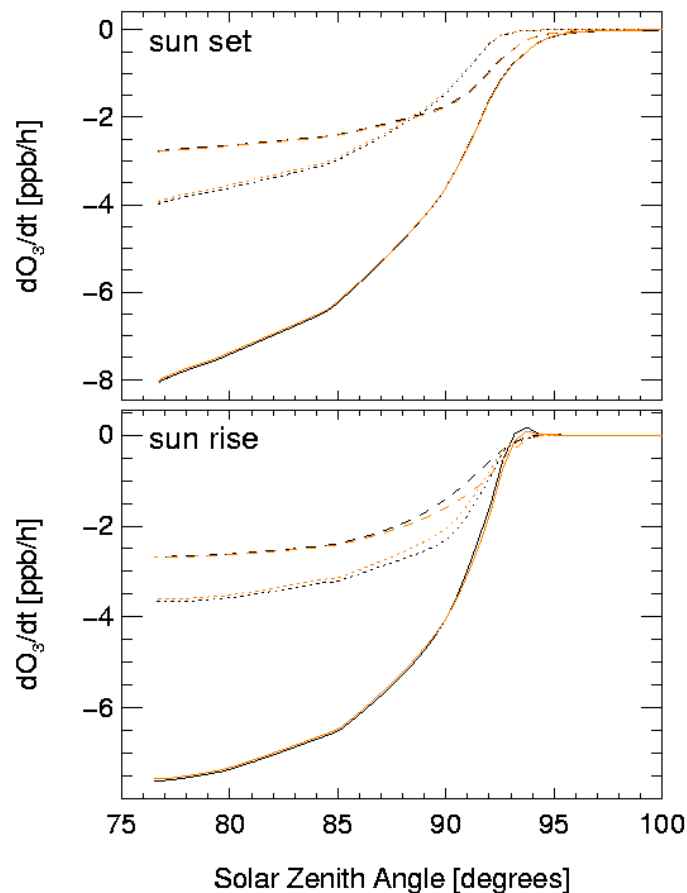
Interactive Discussion



**Fig. 10.** Simulated ClO (top panels) and O<sub>3</sub> (bottom panel) along a sample trajectory using  $K_{EQ}$  values from JPL 2002 (black) and according to Fit 2 (red).

**A re-evaluation of the  
ClO/Cl<sub>2</sub>O<sub>2</sub>  
equilibrium constant**

M. von Hobe et al.



**Fig. 11.** Dependency of the overall ozone loss rate (solid lines) and ozone loss attributed to the ClO-dimer (dotted lines) and ClO-BrO (dashed lines) catalytic cycles on SZA for  $K_{EQ}$  from JPL 2002 (black) and according to Fit 2 (red) at sunrise and sunset for 60° N,  $T = 195$  K on the 500 K potential temperature level.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

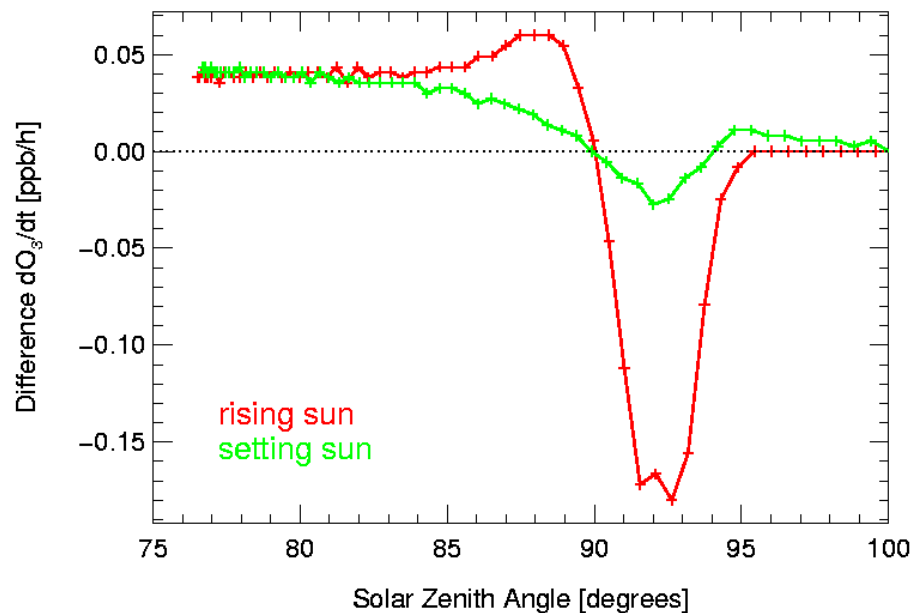
Full Screen / Esc

Print Version

Interactive Discussion

**A re-evaluation of the  
 $\text{ClO}/\text{Cl}_2\text{O}_2$   
equilibrium constant**

M. von Hobe et al.



**Fig. 12.** Change of ozone loss rate induced by using  $K_{EQ}$  according to Fit 2 instead of JPL 2002 recommended  $K_{EQ}$ . Shown is the difference of the solid lines in Fig. 11 (positive values of  $d\text{O}_3/dt$  mean greater ozone loss for the JPL 2002 recommendation).

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)