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A re-evaluation of the ClO/Cl_2O_2 equilibrium constant based on stratospheric in-situ observations

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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 $K_{EQ}=4.06\times10^{-23}\exp(6201/T)$, but to reconcile the observations made at low temperatures with the existing laboratory studies at room temperature, a modified equation, $K_{EQ}=2.31\times10^{-13}(T/300)^{-34.9}\exp(-1118/T)$, is required. This format can be rationalised by a strong temperature dependence of the reaction enthalpy possibly induced by Cl_2O_2 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_2O_2 isomerism are not studied in detail, but the presence of isomers other than ClOOCl would be expected to lead to reduced ozone loss.

1. Introduction

ClO and its dimer (Cl_2O_2) are the key species involved in the most efficient ozone destruction cycle in the cold polar winter stratosphere (Molina and Molina, 1987):

$$ClO + ClO + M \leftrightarrow Cl_2O_2 + M \quad K_{EQ}=k_f/k_b \tag{R1}$$

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with

$$K_{EQ} = [Cl_2O_2]/[ClO] \quad (1)$$

$$Cl_2O_2 + h\nu \rightarrow Cl + ClOO \; J \quad (R2)$$

$$ClOO + M \rightarrow Cl + O_2 + M \quad (R3)$$

$$2(Cl + O_3) \rightarrow 2(ClO + O_2) \quad (R4)$$

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 Cl_2O_2 and the overall rate of the catalytic cycle, the thermal equilibrium (1) of Reaction (R1) controls the ClO/Cl_2O_2 partitioning at night.

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 Cl_2O_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 Cl_2O_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,

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2004b)[1] 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_2O_2. 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_2O_2 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_2O_2 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_2. The chlorine

[1] Plenge, J., Kühl, S., Vogel, B., Müller, R., Stroh, F., Flesch, R., and Rühl, E.: Bond strength of the ClO dimer, Geophys. Res. Lett., submitted, 2004b.

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atoms are detected by resonance fluorescence at 118.9 nm, using low pressure gas discharge lamps containing trace amounts of chlorine in 5hPa 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_3 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^{-1} 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_2O_2 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_2O_2 (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_2O_2+ClO is measured, to extract the Cl_2O_2 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_2O_2 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_2O_2 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

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dissociation of chlorine nitrate, $ClONO_2$ (Fig. 3b). Laboratory tests have shown that less than 1% of any $ClONO_2$ present dissociates at 390 K, so that an overestimation of the Cl_2O_2 concentration due to a possible contribution of $ClONO_2$ can be ruled out. During SOLVE II/VINTERSOL-EUPLEX and the ENVISAT validation campaign, the inlet heater was cycled between the dimer and $ClONO_2$ 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 Cl_2O_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°C, the fluorescence signal returns quantitatively as illustrated in Fig. 5. We ascribe this to formation of Cl_2O_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 $[Cl_2O_2]$ 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.

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Although this flight could not be used for the calculation of K_{EQ} below because the ClO/Cl_2O_2 does not reach thermal equilibrium, the data demonstrate how the 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 [ClO] between two measurements of the same air mass is matched within error limits by the corresponding increase in $2{\cdot}[Cl_2O_2]$.

Temperature measurements were carried out by the Central Aerological Observatory, Russia, employing Rosemount sensors (estimating the maximum error to ±0.6 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 ClO/Cl_2O_2 equilibrium constant

The equilibrium constant of Reaction (R1) can be inferred from observations using Eq. (1). However, this relation is valid only when ClO and Cl_2O_2 are in equilibrium, and the rate of dimer photolysis (R2) is zero. This is usually the case at night when the excess ClO monomer produced photochemically during daytime has relaxed back into thermal equilibrium. The relaxation time needed for the active chlorine species (ClO_x=ClO+$2Cl_2O_2$) to go from the point where practically all ClO_x is in the form of ClO to ClO/Cl_2O_2 equilibrium strongly depends on temperature, pressure and 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, 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

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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:

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

If ΔH^0 is assumed to be independent of T, integration yields:

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

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 ClO_x inferred from measured 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 $[Cl_2O_2]/[ClO]^2$ 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; Nickolaisen et al., 1994). However, if we integrate the Van't Hoff equation under the assumption that ΔH^0 depends linearly on T, we obtain

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

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which can be expressed in the more convenient form

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

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 Cl_2O_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 Cl_2O_2 isomers, namely chlorine peroxide (ClOOCl), chloryl chloride ($ClClO_2$) and chlorine chlorite (ClOClO). Slanina and Uhlík have presented calculations showing that the relative stabilities of the Cl_2O_2 isomers and hence the composition of the equilibrium isomeric mixture depends on temperature (Slanina and Uhlik, 1991b), and that this has direct effects on the temperature dependence of K_{EQ} (Slanina, 1992; Slanina and Uhlik, 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

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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[2]). As Fig. 10 shows, using K_{EQ} from fit 2 compared to JPL 2002 significantly alters the ClO_x 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),

$$ClO + BrO \rightarrow Cl + Br + O_2 \quad \text{(R5a)}$$

$$\rightarrow Br + OClO \quad \text{(R5b)}$$

[2]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.

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$$\rightarrow BrCl + O_2 \quad \text{(R5c)}$$

$$BrCl + h\nu \rightarrow Br + Cl \quad \text{(R6)}$$

$$Br + O_3 \rightarrow BrO + O_2 \quad \text{(R7)}$$

$$Cl + O_3 \rightarrow ClO + O_2 \quad \text{(R8)}$$

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_2O_2. 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_y and 3.1 ppb Cl_y 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_3/dt in Fig. 12).

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

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mainly according to Reaction (2) with only a minor proportion going back to two ClO radicals, the other two stable isomers, $ClClO_2$ and ClOClO, could photolyse to different products, including Cl+OClO, where OClO 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_2O_2 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_2O_2). Based on these measurements we deduce the thermal equilibrium constant K_{EQ} for the equilibrium between ClO and Cl_2O_2. 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_2O_2 are desirable, especially just before sunrise, when ClO/Cl_2O_2 equilibrium is well established. The formation of different isomers of Cl_2O_2 as one possible explanation for the observed behaviour and the potential impact on ozone loss warrants further laboratory studies of this issue.

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

Fit	K_{EQ} =
JPL 2002	$1.27\times10^{-27}\ \exp(8744/T)$
Fit 1: "strict" eq. criterion, Eq. (3)	$5.66\times10^{-28}\ \exp(8511/T)$
Fit 2: "soft" eq. criterion, Eq. (3)	$4.06\times10^{-23}\ \exp(6201/T)$
Fit 3: "soft" eq. criterion, Eq. (4b)	$2.31\times10^{-13}\ (T/300)^{-34.9}\ \exp(-1118/T)$

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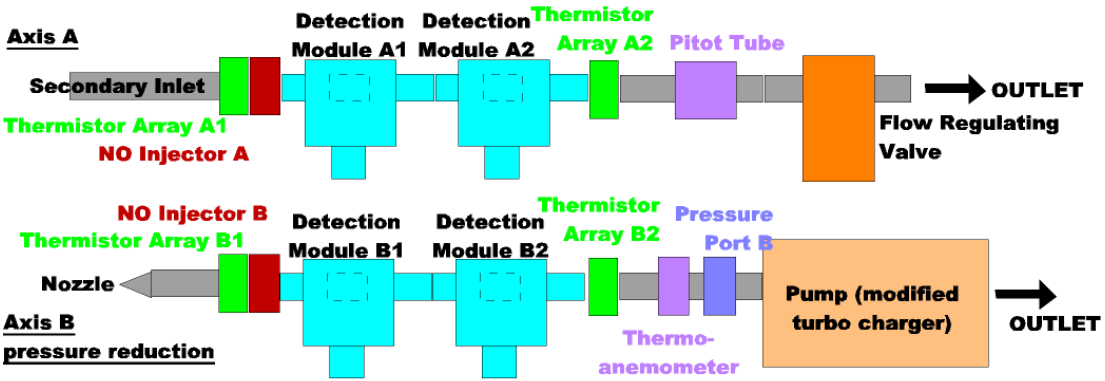

Fig. 1. Outline of the HALOX instrument. Modules A1 and B1 detect chlorine, A2 and B2 bromine.

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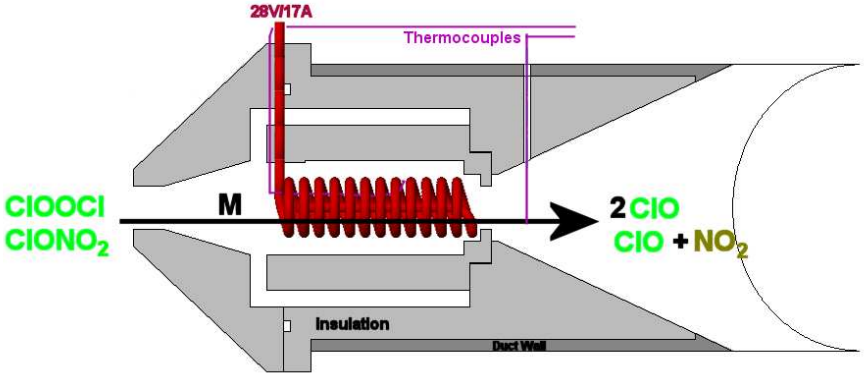

Fig. 2. Schematic of the heated inlet.

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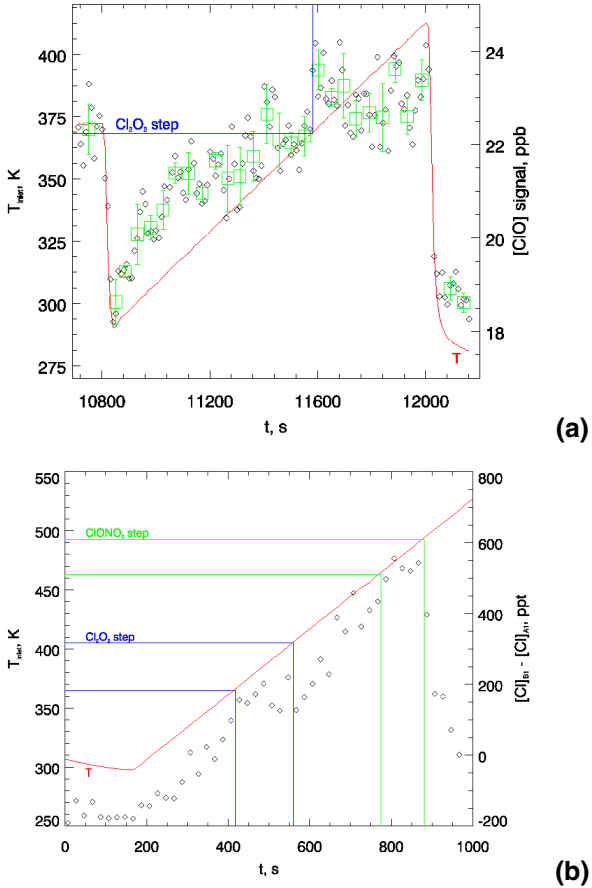

Fig. 3. ClO concentration from resonance fluorescence signal against inlet temperature for a temperature ramp obtained **(a)** under laboratory conditions and **(b)** during a EUPLEX flight on 23 January 2003. Each black diamond represents one individual measurement (i.e. one NO addition cycle); green squares in (a) represent averages over 5 K temperature intervals, error bars representing 1σ. Note, that under flight conditions, the natural variability of ClO and Cl_2O_2 does contribute to the signal.

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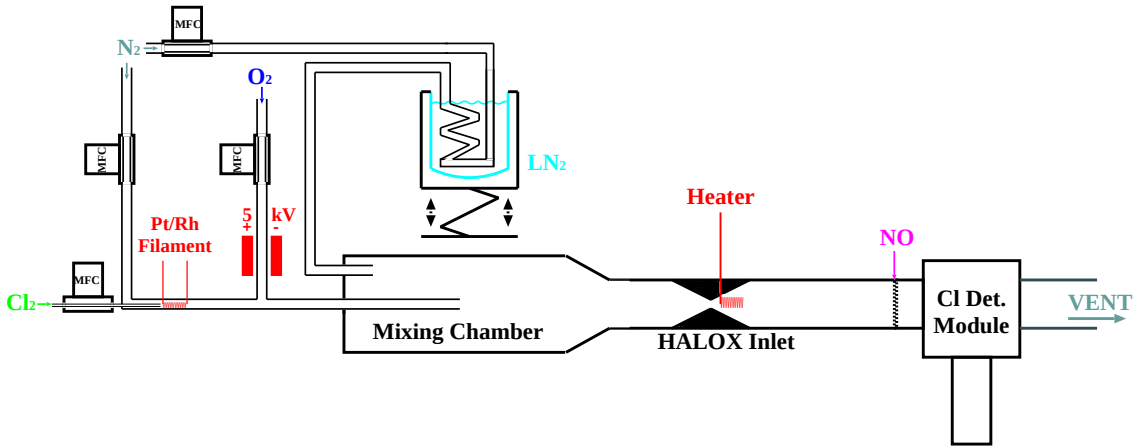

Fig. 4. Set up of the ClO-dimer validation/calibration system. All gas flows are regulated by mass flow controllers (MFCs). Temperatures are measured at the inlet heater, at the NO injector and directly behind the chlorine detection module. Pressure and flow velocity are also measured directly behind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

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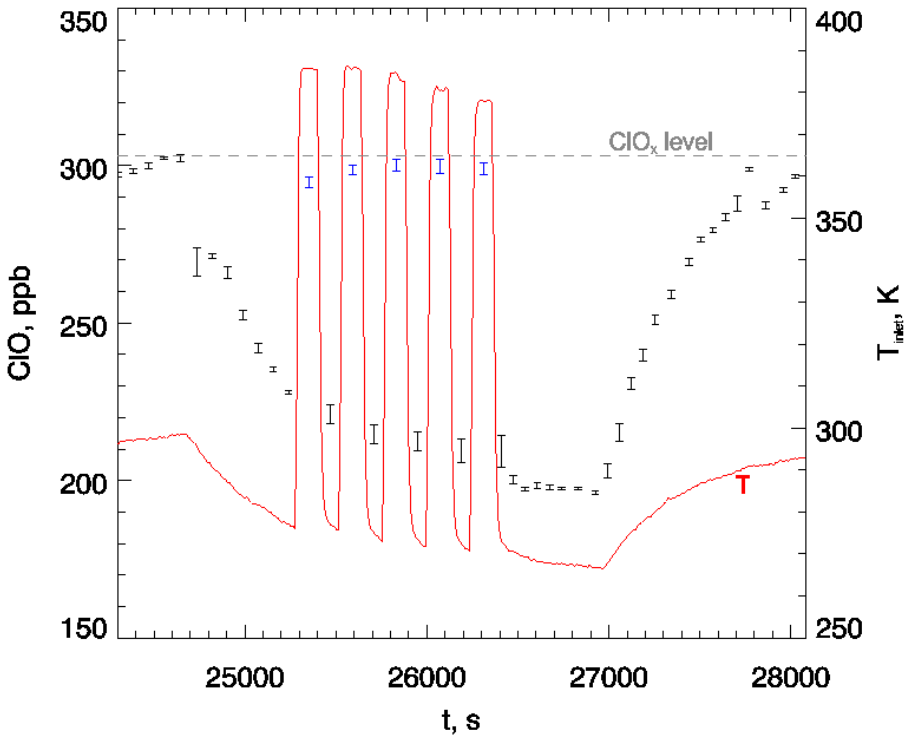

Fig. 5. Laboratory test (P_{duct}=80 hPa) of dimer conversion efficiency of the heated inlet. Error bars represent the standard error of the mean for one minute averages (equivalent to six NO addition cycles), blue colour indicates that the temperature (red line) of the inlet heater was at the dimer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

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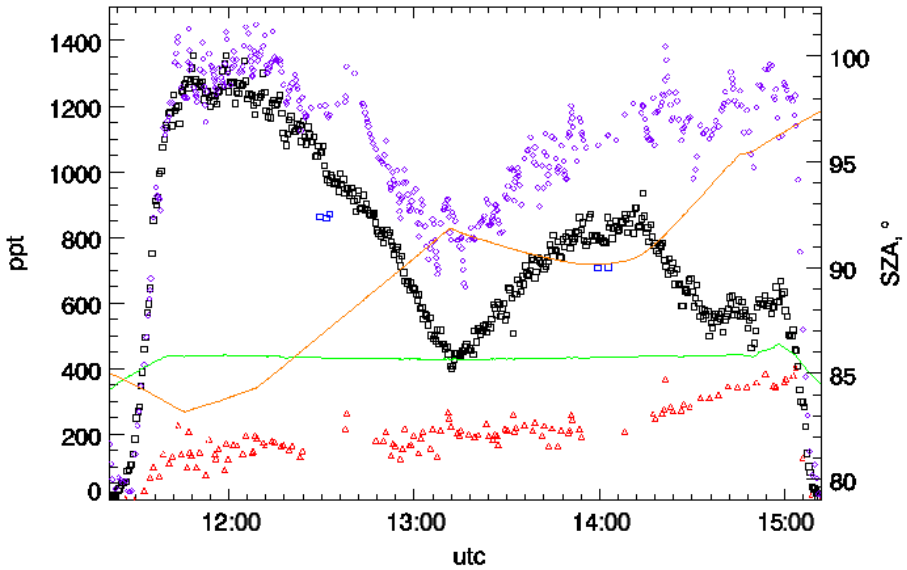

Fig. 6. Time series of ClO (black squares: duct A, blue squares: duct B), Cl_2O_2 (red triangles) and ClO_x (purple diamonds; from duct B) measured on 30 January 2003. Also shown are potential temperature theta (green line) and solar zenith angle (orange line).

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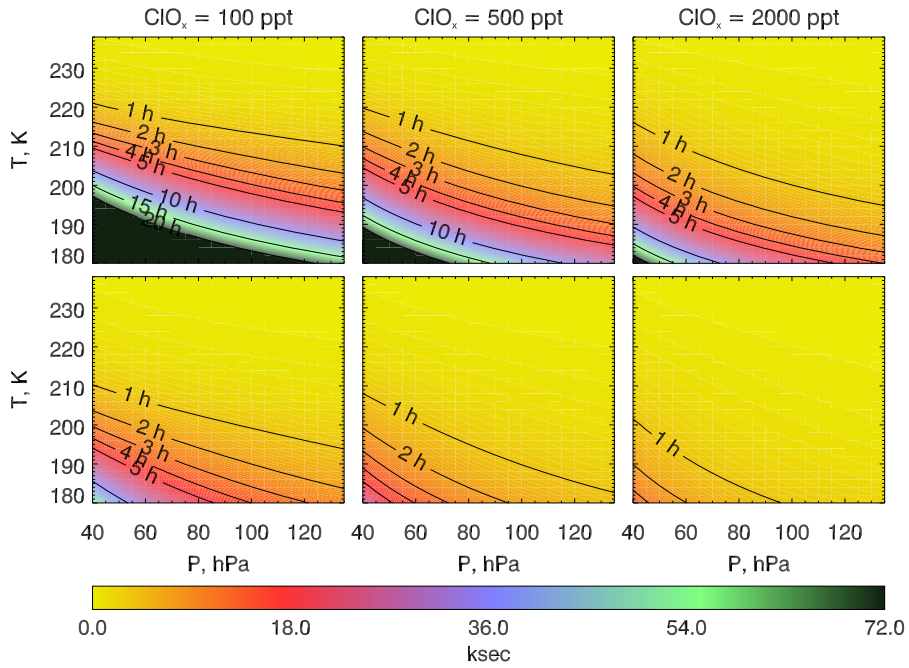

Fig. 7. Relaxation time of the ClO/Cl_2O_2 system into thermal equilibrium ($[Cl_2O_2]/[ClO]^2 > 0.8\,K_{EQ}$), as it depends on temperature and pressure for three different ClO_x concentrations, assuming $[ClO]=[ClO_x]$ and $[Cl_2O_2]=0$ at $t=0$. Results are shown for both the JPL 2002 equilibrium constant (top panels) and the equilibrium constant inferred from the EUPLEX data (bottom panels).

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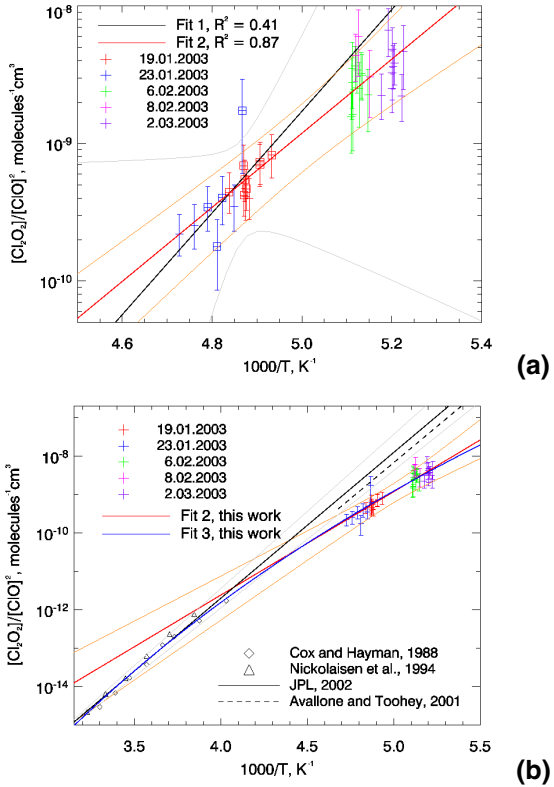

Fig. 8. (a) Van't Hoff plot of EUPLEX data for which thermal equilibrium can be assumed. Data points framed by a square obey the strict equilibrium rule (see text for explanation). Fits 1 and 2 are linear least squares fits of $\ln([Cl_2O_2]/[ClO]^2)$ against $1/T$ according to Eq. (3) for the strict 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 (3σ). **(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.

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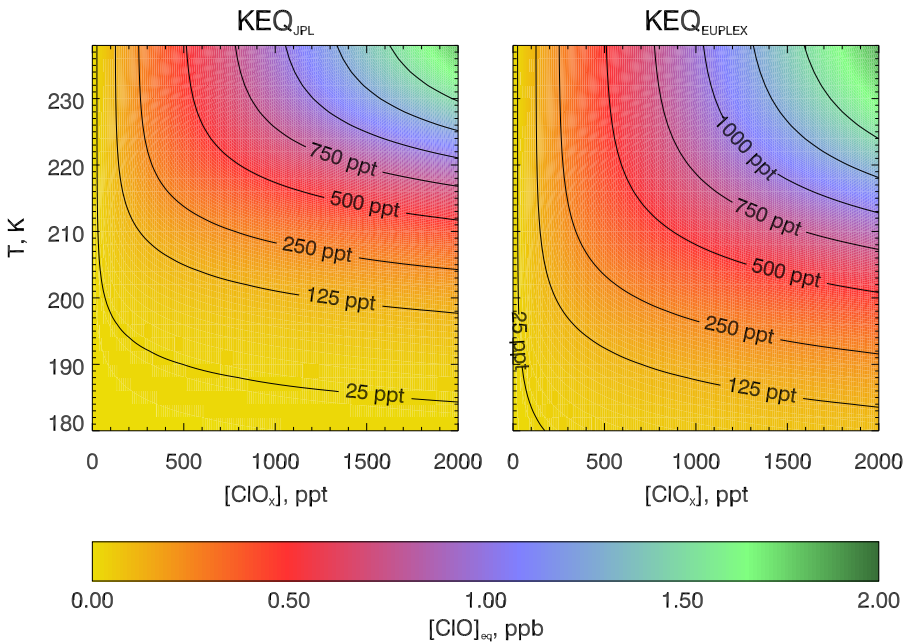

Fig. 9. Equilibrium ClO concentration as a function of temperature and ClO_x for the JPL 2002 equilibrium constant (left panel) and the equilibrium constant inferred from fit 2 in this study (right panel).

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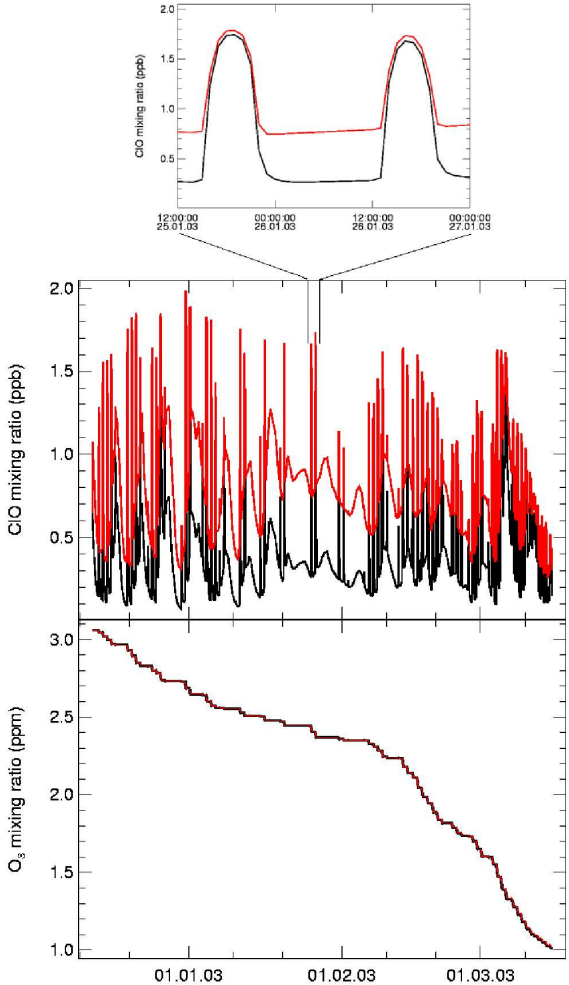

Fig. 10. Simulated ClO (top panels) and O_3 (bottom panel) along a sample trajectory using K_{EQ} values from JPL 2002 (black) and according to Fit 2 (red).

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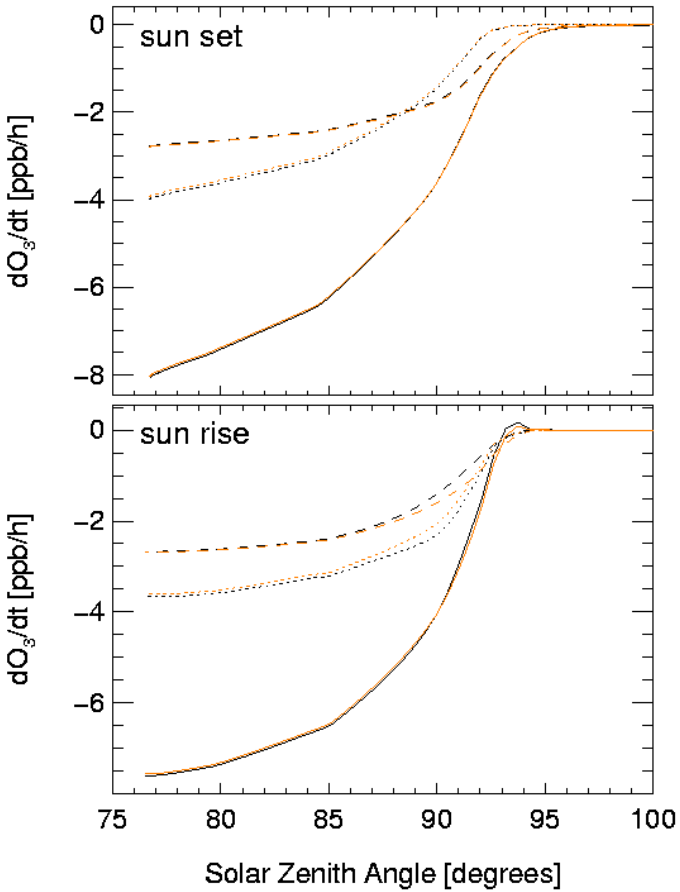

Fig. 11. Dependency of the overall ozone loss rate (solid lines) and ozone loss attributed to the ClO-dimer (dotted lines) and ClO-BrO (dashed lines) catalytic cycles on SZA for K_{EQ} from JPL 2002 (black) and according to Fit 2 (red) at sunrise and sunset for 60° N, $T = 195$ K on the 500 K potential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

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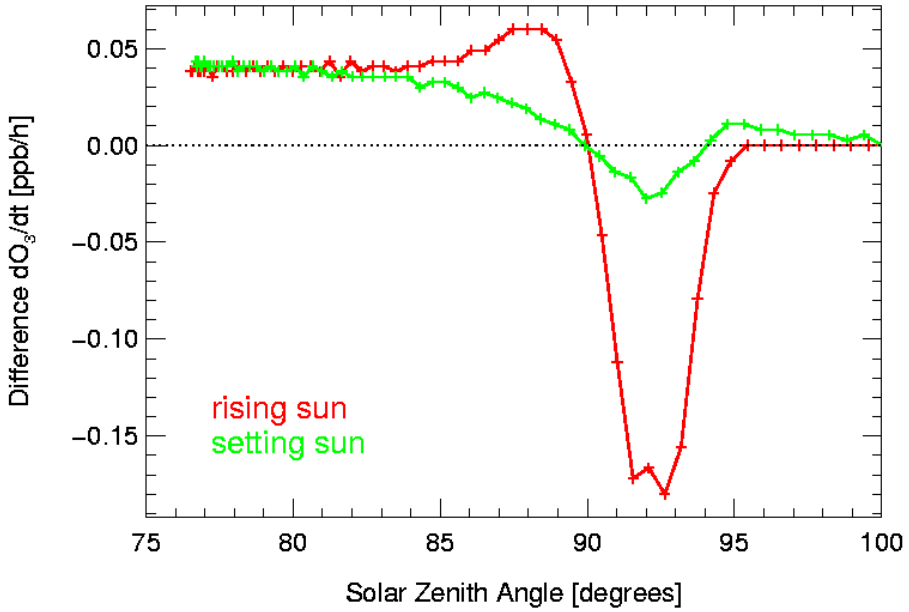

Fig. 12. Change of ozone loss rate induced by using K_{EQ} according to Fit 2 instead of JPL 2002 recommended K_{EQ}. Shown is the difference of the solid lines in Fig. 11 (positive values of dO_3/dt mean greater ozone loss for the JPL 2002 recommendation).

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