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Nighttime chlorine monoxide observations by the Odin satellite and implications for the ClO/Cl_2O_2 equilibrium

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[1] We use measurements of chlorine monoxide (ClO) by the SMR instrument onboard the Odin satellite to study the nighttime thermal equilibrium between ClO and its dimer Cl_2O_2. Observations performed in the polar vortex during the 2002–2003 Arctic winter showed enhanced amounts of nighttime ClO over a wide range of stratospheric temperatures ($185 < T < 225$ K). Odin/SMR measurements are here compared to three-dimensional model calculations using various published estimations of the K_{eq} equilibrium constant between ClO and Cl_2O_2. Our results show that the value of K_{eq} currently recommended by JPL (Sander et al., 2003) leads to a large underestimation of the observed nighttime ClO amounts, and that a realistic estimation of K_{eq} must lie between the values determined by Cox and Hayman (1988) and Von Hobe et al. (2005). **Citation:** Berthet, G., P. Ricaud, F. Lefèvre, E. Le Flochmoën, J. Urban, B. Barret, N. Lautié, E. Dupuy, J. De La Noë, and D. Murtagh (2005), Nighttime chlorine monoxide observations by the Odin satellite and implications for the ClO/Cl_2O_2 equilibrium, *Geophys. Res. Lett.*, *32*, L11812, doi:10.1029/2005GL022649.

1. Introduction

[2] The formation of the chlorine monoxide dimer, Cl_2O_2, is a key process of the polar ozone loss by atmospheric chlorine [e.g., *Molina and Molina*, 1987]:

$$ClO + ClO + M \rightarrow Cl_2O_2 + M \qquad k_1$$

The photolysis of Cl_2O_2 ultimately leads to two chlorine atoms and the destruction of two ozone molecules. However, the efficiency of this process is reduced by the thermal decomposition of Cl_2O_2, which reforms ClO and leads to a null cycle:

$$Cl_2O_2 + M \rightarrow ClO + ClO + M \qquad k_2$$

[3] Because they are not influenced by the photolysis of Cl_2O_2, nighttime measurements of ClO allow to perform a straightforward test of our quantitative understanding of the equilibrium between reactions k_1 and k_2. In darkness, the partitioning between ClO and its dimer is governed by the thermal equilibrium constant defined by $K_{eq} = k_1/k_2 = [Cl_2O_2]/[ClO]^2$, which decreases with temperature. Several studies have employed in-situ observations of ClO alone [e.g., *Avallone and Toohey*, 2001] or simultaneous ClO and Cl_2O_2 measurements [*Stimpfle et al.*, 2004; *Von Hobe et al.*, 2005] to test the kinetic parameters involved in the destruction of polar ozone. The aim of this paper is to extend the previous studies of the Cl_2O_2/ClO equilibrium by using nighttime satellite measurements of ClO in the lower stratosphere by the Sub-Millimetre Radiometer (SMR) instrument onboard the Odin satellite [*Ricaud et al.*, 2005]. Because such measurements from space provide an entire spatial coverage of the polar vortex, they can give access to a wider range of stratospheric temperatures, allowing a better characterization of the value of K_{eq} that should be considered by chemical models. For this purpose, we use here observations performed in the Northern hemisphere from December 2002 to January 2003, when large nighttime concentrations of ClO were detected in regions where temperatures spanned the 185–225K range. These measurements are compared to a series of chemical transport model (CTM) simulations constrained by different values of K_{eq} found in the most recent literature.

2. Instrument and Model Experiment

[4] The Odin mini-satellite, launched on 20 February 2001, is partly dedicated to the observation of chemical species of the stratosphere and mesosphere [*Murtagh et al.*, 2002]. A detailed description of the SMR instrument and/or data reduction methods can be found in *Baron et al.* [2002]. We focus here on the measurements of ClO performed in the 501.18–502.38 GHz frequency domain. Vertical profiles are retrieved from 17 to 50 km with a typical vertical resolution of 2–2.5 km in the lower stratosphere. Upper limits for the systematic errors on ClO mixing ratios are estimated to be about 0.2 ppbv in the lower stratosphere [*Urban et al.*, 2004]. The consistency of ClO measurements is examined by *Ricaud et al.* [2005].

[5] The three-dimensional simulations presented here have been performed with the Reprobus CTM [*Lefèvre et al.*, 1998] driven by the 6-hourly European Centre for Medium-Range Weather Forecast (ECMWF) operational analysis. Except for the thermal decomposition of Cl_2O_2 (reaction k_2), for which different experiments have been conducted, the kinetics of all reactions is taken from the

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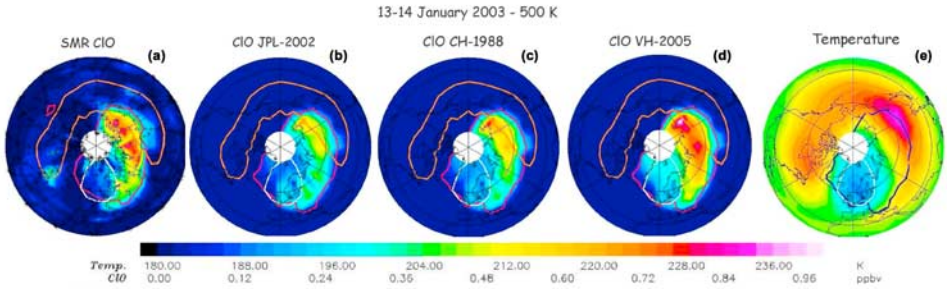

Figure 1. (a) Nighttime ClO field observed by Odin/SMR on 13–14 January 2003, interpolated onto the 500-K surface. Data are corrected from the positive bias discussed in section 3.2. Solar Zenith Angle (SZA) at the location of the observations varies from 96° at 30N to 103° at 80N. Crosses represent orbit tracks over the 24-h period. The 120 ppbv contour of N_2O (red line) has been chosen to represent the vortex edge. The white and orange lines represent the 195 and 220 K temperature contours, respectively. (b) ClO field calculated by Reprobus for the same time and location as Odin/SMR measurements, K_{eq} from the JPL2002. (c) K_{eq} from *Cox and Hayman* [1988]. (d) K_{eq} from *Von Hobe et al.* [2005]. (e) ECMWF temperature analysis.

latest JPL recommendation [*Sander et al.*, 2003, hereinafter referred to as JPL2002]. For this study it is important to note that ClO and Cl_2O_2 are not supposed to be in equilibrium in Reprobus: they are integrated separately in the model. Total inorganic chlorine (Cl_y) is calculated by the model, and approaches 3.7 ppbv in the upper stratosphere, in accordance with the *World Meteorological Organization* (*WMO*) [2002]. At lower altitudes Cl_y depends on the degree of subsidence computed by Reprobus inside the polar vortex, which has been shown to agree favorably with the observed descent rates [*Greenblatt et al.*, 2002]. This is especially true at 500 K and below where we choose to restrict our analysis.

3. Results and Discussion

3.1. Case of 13–14 January 2003

[6] During the Arctic winter 2002–2003 chlorine activation was observed by SMR from the beginning of December [*Urban et al.*, 2004]. Mixing ratios close to 1 ppbv were then measured at night from late December 2002 until mid-January 2003. Figure 1 presents the example of SMR observations of nighttime ClO performed over a wide range of temperatures on the 500 K isentropic level, on 13–14 January 2003. Inside the vortex, ClO is maximum where temperatures are highest. This is consistent with the more efficient Cl_2O_2 thermal decomposition that is expected when temperature increases. Conversely, nighttime ClO on 13–14 January is minimum in the coldest region of the polar vortex, where the low temperatures shift the ClO/Cl_2O_2 equilibrium towards Cl_2O_2.

[7] Odin/SMR observations on 13–14 January have been compared to various Reprobus CTM simulations using different values for the K_{eq} equilibrium constant: experiment "JPL-2002" considers the K_{eq} value recommended by the latest JPL compilation [*Sander et al.*, 2003]; experiment "CH-1988" uses the K_{eq} value determined from *Cox and Hayman* [1988]; experiment "VH-2005" employs the expression of K_{eq} recently evaluated by *Von Hobe et al.* [2005] from in-situ measurements of ClO and Cl_2O_2 in the Arctic.

[8] Figure 1 clearly shows that the maximum ClO mixing ratios calculated by the JPL-2002 simulation are significantly smaller than those observed by SMR: the maximum calculated value is only of 0.5 ppbv whereas a maximum of 0.9 ppbv is observed by the instrument inside the vortex. Better results are obtained with the CH-1988 simulation, which produces larger ClO amounts everywhere in the vortex. A good quantitative agreement is noted in the cold part of the vortex, but the model still underestimates the observed values for higher temperatures. Finally, the ClO amounts computed in the vortex are increased further by the VH-2005 simulation. Mixing ratios are in this case in rather good agreement with SMR for temperatures greater than about 200 K, but appear to overestimate the observations at lower temperatures.

3.2. Extension to the December 2002 to January 2003 Period

[9] We now expand our analysis to the whole period extending from 3 December 2002 to 21 January 2003. Figure 2 compares all the SMR ClO measurements performed at night outside and inside the polar vortex to the coinciding CTM calculations. Outside the vortex, Figure 2 reveals observed nighttime ClO amounts between 0.1 and 0.2 ppbv. Modelled values are mostly close to zero, as expected from the photochemical theory at mid-latitudes and from other measurements performed during the night in these regions [see, e.g., *Stimpfle et al.*, 1994]. We attribute this difference to a systematic positive bias in the SMR observations when ClO amounts fall below the detection limit of the instrument. It is not clear whether this bias is also present in ClO retrievals for which the signal to noise ratio is larger. Nevertheless, we take into account this possibility in our analysis of the measurements performed inside the vortex. In addition to the uncorrected measurements of SMR, Figure 2 also plots the obtained amounts of ClO when reduced by the averaged systematic bias calculated outside the vortex for each level. This shifted curve may be considered as a lower limit for the ClO quantities measured inside the polar vortex by SMR. In the chemically

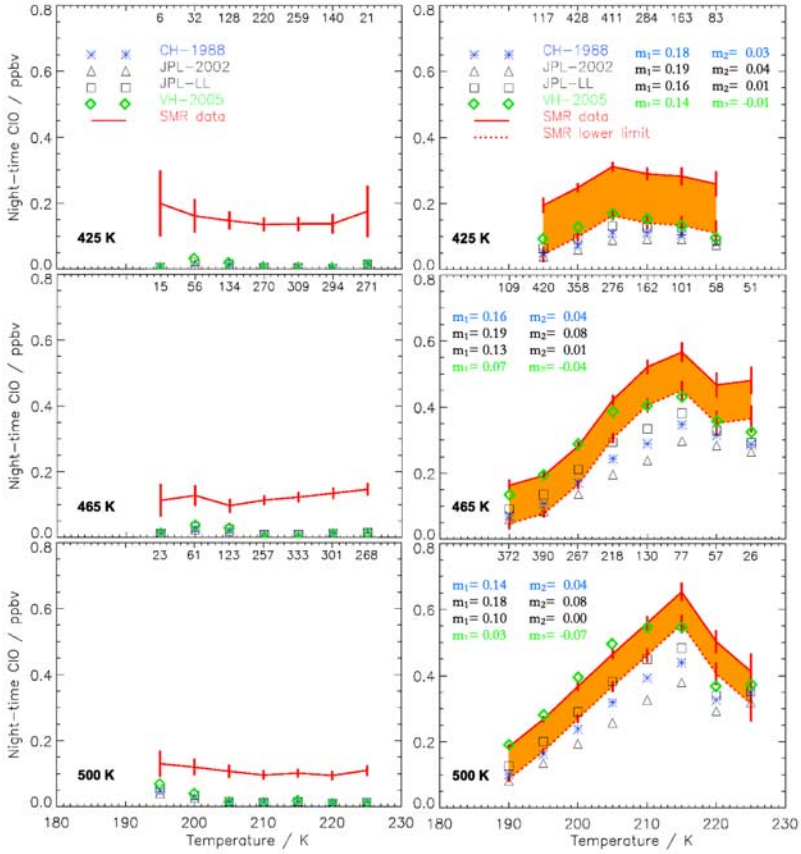

Figure 2. Odin SMR nighttime (100° < SZA < 107°) ClO measurements versus ECMWF temperature (left) outside and (right) inside the polar vortex at 425 K, 465 K and 500 K. Data are averaged over the period 3 December 2002–21 January 2003. Red line: Odin/SMR observations. (left) Dotted red line: Odin/SMR observations shifted by the averaged value calculated outside the vortex. Symbols: Reprobus CTM calculations with K_{eq} from JPL2002 (black triangles), JPL2002 lower limit (black squares), *Cox and Hayman* [1988] (blue stars), and *Von Hobe et al.* [2005] (green diamonds). Data are averaged over 5-K width bins. m_1 and m_2: average of the difference between measurements (SMR data for m_1 and SMR lower limit for m_2) and model results. Also indicated is the number of points used to calculate the averages for each temperature bin. Error bars correspond to a $1 - \sigma$ error on the mean.

perturbed polar vortex, it can be seen from Figure 2 that the observed amount of nighttime ClO tends to increase with temperature up to about 215 K. This results from the displacement of the ClO/Cl_2O_2 equilibrium towards ClO that is expected when temperature increases. A decrease in nighttime ClO is observed above 215 K. This corresponds to data points collected in the warmest regions at the edge of the polar vortex, where the formation of $ClONO_2$ led to partial chlorine deactivation.

[10] The behaviour of the nighttime ClO as a function of temperature is qualitatively similar to the SMR observations for all the Reprobus simulations. However, significantly different results are found in terms of absolute amounts of ClO:

[11] (1) On the three isentropic levels, the ClO amounts computed with the JPL-2002 simulation are underestimated by a significant margin at temperatures between 200 K and 220 K. At 465 K, the model values at these temperatures are lower than the measurements up to a factor of 2. These results are consistent with the analysis of *Avallone and Toohey* [2001] and *Stimpfle et al.* [2004], who also indicate too low calculated quantities of nighttime ClO when using the K_{eq} value currently recommended by *Sander et al.* [2003] ($K_{eq} = 1.27 \times 10^{-27} \exp(8744/T)$). This recommendation is based both on the data of *Cox and Hayman* [1988] and *Nickolaisen et al.* [1994] determined in the 233–303 K and 260–310 K temperature range, respectively. The discrepancy that we observe between the JPL-2002 simulation and the SMR measurements may reflect the large uncertainty associated to the extrapolation of K_{eq} to low stratospheric temperatures. At high stratospheric temperatures, our analysis does not contradict the value of K_{eq} derived from the existing laboratory studies: the disagreement between the JPL-2002 simulation and SMR observations tends to decrease at temperatures above 220 K, at all vertical levels except at 465 K. Note that raising the threshold for polar stratospheric cloud formation by 1.5 K to take into account a possible warm bias in the ECMWF analysis (reported to be less than 1.3 in arctic winter by *Knudsen et al.* [2002]) has a negligible impact on these results at and below 210 K.[1] Above 210 K ClO amounts remain smaller than the SMR lower limit.

[1]Auxiliary material is available at ftp://ftp.agu.org/apend/gl/2005GL022649.

[12] (2) The CH-1988 simulation is based on the laboratory work of *Cox and Hayman* [1988] alone. Their expression of K_{eq} is strongly influenced by a rather uncertain low-temperature point (233 K) which shifts downwards the K_{eq} value compared to *Nickolaisen et al.* [1994]. As a result, between 190 and 200 K, the equilibrium constant derived from *Cox and Hayman* [1988] is about 50% lower than that from JPL2002. At these temperatures, our CH-1988 simulation calculates quantities of ClO that are 20–30% larger than those obtained in the JPL-2002 experiment, and are close to the SMR measurements or within their uncertainty range. This result is consistent with the conclusions of *Stimpfle et al.* [2004] who show that the K_{eq} value of *Cox and Hayman* [1988] gives the best agreement between model calculations and nighttime ClO observations in the 190–200 K temperature range. However, from Figure 2 it is clear that SMR observations remain underestimated at temperatures greater than 200 K.

[13] (3) A lower limit of K_{eq} can be estimated from the temperature-dependent uncertainty factor associated to recommendation of *Sander et al.* [2003]. The use of this lower limit value in our model leads to a significant increase in ClO (Figure 2, JPL-LL simulation). A better agreement with SMR is achieved at the three isentropic levels considered here, in particular at 500 K where the model values are close or within the SMR entire uncertainty range for the whole temperature range sampled by the instrument. The calculated amounts at 210–215 K are still slightly below the ClO lower limit given by SMR on the 465 K and 500 K isentropic levels, but the disagreement is reduced by more than 50% relative to the JPL-2002 experiment. Note that the model nighttime ClO does not change significantly in comparison with the results of the JPL-2002 and CH-1988 experiments at 220 K and above. This is explained by the combination of the reduced uncertainty factor and the decrease in the amount of active chlorine at these temperatures, making the difference with the JPL-2002 less apparent. The difference between both experiments is also less perceptible below 195 K, as the equilibrium between ClO and Cl_2O_2 is displaced towards Cl_2O_2 at low temperatures. The calculated quantities are within the uncertainty range of SMR at these temperatures.

[14] (4) To reconcile the laboratory values of K_{eq} obtained at room temperatures with their new in-situ observations, *Von Hobe et al.* [2005] proposed a function of the form $K_{eq} = 3.61 \times 10^{-27}\ (T/300)^{-2.29}\ \exp(6969/T)$ assuming a strong linear temperature dependence of the reaction enthalpy. This re-evaluation of K_{eq} is lower than the value recommended by *Sander et al.* [2003] at temperatures below 220 K and shifts the thermal equilibrium towards ClO. Thus, the use of this revised K_{eq} value by the VH-2005 simulation leads, below 220 K, to the largest nighttime ClO values in our four experiments. It must be noted that the different form of the K_{eq} expression causes ClO to peak at 210 K, whereas SMR and the other model experiments indicate a maximum at 215 K. However, considering the uncertainty range of the SMR observations, the re-evaluated constant gives the best agreement at the 465 K level. On the 500 K level, for temperatures below 210 K, using the re-evaluated K_{eq} leads to a slight overestimation of nighttime ClO. At all isentropic levels, the VH-2005 simulation gives results that are comparable to the other model experiments at 220 K and above. This is an expected result since the expression for K_{eq} given by *Von Hobe et al.* [2005] is established to fit the same laboratory data as *Sander et al.* [2003] in the 250–310 K temperature range.

4. Conclusion

[15] Our results show that the value of the thermal equilibrium constant K_{eq} currently recommended by the JPL evaluation panel [*Sander et al.*, 2003] is too strong in the 200–220 K range to reproduce the nighttime ClO amounts observed at these temperatures. This result expands the conclusions of previous studies based on observations performed over a more limited temperature domain. The reason for this discrepancy can be related to the large uncertainty that is associated to the extrapolation of laboratory data obtained at room temperature to stratospheric temperatures for which no direct measurements of K_{eq} are available.

[16] The introduction of the recent re-evaluation of K_{eq} given by *Von Hobe et al.* [2005] leads to a large increase in the amounts of nighttime ClO in our model. The agreement with the Odin/SMR observations is particularly improved in the 210K–215K temperature range on the 465 K and 500 K isentropic levels. At lower temperatures, the value of this re-evaluated K_{eq} appears to be too small and the ClO mixing ratios computed by the model are overestimated.

[17] Our model experiments suggest that a realistic estimation of K_{eq} lie somewhere between the value determined in laboratory by *Cox and Hayman* [1988] and the value estimated from in-situ measurements by *Von Hobe et al.* [2005]. An intermediate value of K_{eq} that falls in this range is obtained by taking the lowest possible value allowed by the estimated uncertainty of the *Sander et al.* [2003] recommendation. CTM simulations using this JPL lower limit agree best with the Odin/SMR observations. Additional laboratory studies are necessary to reduce the large uncertainty currently associated to the ClO/Cl_2O_2 equilibrium, especially at low temperatures.

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