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Observational constraints on the kinetics of the ClO-BrO and ClO-ClO ozone loss cycles in the Arctic winter stratosphere

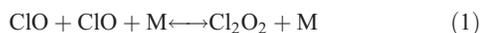
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[1] Observations of the balloon-borne LPMA/DOAS remote sensing instruments performed in the Arctic stratosphere in February 1999 are used to constrain a photochemical model. Measurements of all relevant nitrogen, chlorine, and bromine species indicate that moderate heterogeneous chlorine activation occurred in a filament of the Arctic vortex. Model-measurement comparisons for OCIO serve as an indicator of how well various scenarios of the involved reaction kinetics, in particular of the ClO-BrO and the ClO-ClO cycles, reproduce the observations. Recent suggestions for the photolysis rate of the ClO dimer, the equilibrium constant between ClO dimer and monomer, the rate of the ClO-ClO association reaction, and the branching ratio of the ClO-BrO reaction are consistent with the observations. Formation of an unstable isomer of ClONO₂ cannot be reconciled with the observations. Modeled odd oxygen loss rates can be larger by 10% to 20% for the updated reaction kinetics compared to standard recommendations. **Citation:** Butz, A., H. Bösch, C. Camy-Peyret, M. Dorf, A. Engel, S. Payan, and K. Pfeilsticker (2007), Observational constraints on the kinetics of the ClO-BrO and ClO-ClO ozone loss cycles in the Arctic winter stratosphere, *Geophys. Res. Lett.*, *34*, L05801, doi:10.1029/2006GL028718.

1. Introduction

[2] Several studies indicate that measured ozone loss in the Arctic winter/spring stratosphere is underestimated by current stratospheric chemistry models [e.g., *Rex et al.*, 2003] when using JPL-2002 recommendations for the reaction kinetics [*Sander et al.*, 2003]. Erroneous representation of the known catalytic odd oxygen ($O_x = O + O_3$) loss cycles in the models could explain why modeled ozone loss falls short when compared to observations. Odd oxygen loss in the polar winter/spring stratosphere is dominated by the ClO-ClO and the ClO-BrO catalytic cycles. The former is initiated by



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the latter by



where reaction (5) is bracketed since it leads to no net O_x loss if formation of OCIO is followed by photolysis. Recently, updates of the reaction kinetics of these catalytic cycles were suggested by *Stimpfle et al.* [2004], *Rivière et al.* [2004], *Plenge et al.* [2005], *von Hobe et al.* [2005], and *Canty et al.* [2005].

[3] Here we revisit a case study for the Arctic stratosphere in February 1999 where ozone loss occurred locally in a moderately activated polar vortex. Under such conditions which are often observed in the Arctic winter/spring stratosphere the importance of the ClO-BrO cycle is enhanced compared to typical Antarctic winter/spring conditions where chlorine activation is more substantial. Simultaneous balloon-borne solar occultation observations of HNO₃, NO₂, NO, HCl, ClONO₂, Cl₂, OCIO, and BrO provide an unprecedented opportunity to constrain and to validate a stratospheric chemistry model. In particular, simultaneous measurements of BrO and OCIO can be used to inspect the ClO + BrO reaction, the branching ratio of which has been questioned by *Canty et al.* [2005]. Simultaneous observations of ClONO₂ and NO₂ are particularly useful to investigate deactivation of the short-lived chlorine species and the possible existence of unstable isomers of ClONO₂ as speculated on by *Rivière et al.* [2004]. Our study aims at testing the suggested kinetic updates by constraining the stratospheric chemistry model to all observed species except for OCIO. The latter is used for model-measurement comparisons providing an estimate on how well the ClO-BrO cycle and to a lesser degree the ClO-ClO cycle are represented by the proposed model scenarios. Implications for O_x loss are discussed on the basis of the modeled O_x loss rates.

2. Methods and Observations

[4] During the past decade the LPMA/DOAS (Limb Profile Monitor of the Atmosphere/Differential Optical Absorption Spectrometer) balloon payload conducted solar occultation measurements under various geophysical conditions. On February 10, 1999, LPMA/DOAS was launched from Kiruna (67.9°N, 21.7°E) into a filament of the

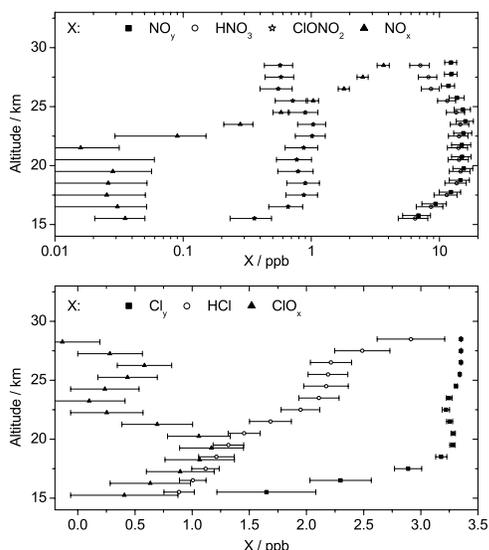


Figure 1. Volume mixing ratios of the (top) nitrogen and (bottom) chlorine species observed during sunset (SZA = 90°) at Kiruna on February 10, 1999. For simplicity ClONO₂ is only shown in the top plot. NO_y is calculated from measured HNO₃, NO₂, NO, ClONO₂ and modeled N₂O₅. Cl_y is inferred as described in the text. The composite ClO_x is calculated from ClO_x = Cl_y - HCl - ClONO₂. For clarity some data points are slightly offset in altitude. Note the logarithmic scale in the top plot.

Arctic vortex and ascended to 28.5 km ceiling altitude. Lines-of-sight during solar occultation crossed intra-vortex air masses below 21 km altitude as illustrated by the potential vorticity map in the auxiliary material¹. Above 21 km extra-vortex air masses contributed to the measured spectra to a significant but variable degree. This interpretation is supported by a kink in the N₂O dynamic tracer profile (see auxiliary material). Although the Arctic winter 1998/1999 was an exceptionally warm stratospheric winter, temperatures were occasionally low enough for formation of PSCs in the beginning of December 1998 and in early February 1999, right before the LPMA/DOAS balloon flight [European Ozone Research Coordinating Unit, 1999].

[5] The LPMA/DOAS payload consists of a Fourier Transform Spectrometer (FT-IR) sensitive to the infrared [Camy-Peyret et al., 1995] and a two-channel DOAS spectrometer sensitive to the UV/visible spectral ranges [Ferlemann et al., 2000]. A sun-tracker points to the center of the solar disk and provides a parallel beam of sunlight to the FT-IR and DOAS spectrometers such that the instruments sample the same air masses. The direct-Sun spectra are analyzed for trace gas concentrations integrated along the lines-of-sight (Slant Column Densities (SCDs)) applying the DOAS spectral retrieval algorithm [Stutz and Platt, 1996] in the UV/visible and a forward modeling approach [Payan et al., 1998] in the IR spectral range. Altitude information of an ensemble of spectra recorded during

balloon ascent or solar occultation is exploited by ray-tracing the path of the light from the Sun to the balloon-borne instruments and by applying a linear *Maximum A Posteriori* optimal estimation technique yielding vertical profiles of the target trace gases [Butz et al., 2006]. Here, LPMA/DOAS spectra are analyzed for the absorption of BrO and OCIO in the UV [e.g., Dorf et al., 2006], O₃ and NO₂ in the visible [e.g. Butz et al. 2006], O₃, HNO₃, NO₂, NO, ClONO₂, HCl, and N₂O in the infrared [e.g., Dufour et al., 2005]. The amount of inorganic chlorine (Cl_y) is determined from N₂O observations with the help of a standard Cl_y-N₂O correlation (see auxiliary material) inferred from measurements of a balloon-borne cryogenic whole air sampler [e.g., Engel et al., 2002] launched from Kiruna four days prior to LPMA/DOAS on February 6, 1999.

[6] Figure 1 shows vertical profiles of the observed nitrogen and chlorine species. Clearly, the nitrogen budget is dominated by HNO₃. NO_x (= NO + NO₂) is an important constituent above 25 km altitude but amounts to less than 1% of total nitrogen (NO_y) below 21 km. The very low amounts of NO_x in the lower stratosphere indicate a denoxified layer where NO_x has been effectively converted to N₂O₅ (and to ClONO₂) and further heterogeneously processed to HNO₃. The denoxified layer between 16 km and 21 km altitude coincides with observations of depleted N₂O and a layer of enhanced ClO_x (= Cl_y - HCl - ClONO₂) with mixing ratios up to 1.2 ppb around 20 km altitude indicating moderate heterogeneous chlorine activation. Above 21 km, the chlorine budget is dominated by HCl. For BrO, SCDs (see auxiliary material) instead of mixing ratio profiles are used for further processing as described below for the treatment of OCIO.

[7] These observations are used to constrain the stratospheric chemistry model. The model is an updated version of the one used, for example, by Butz et al. [2006] and is based on a comprehensive set of the relevant gas-phase and heterogeneous reactions as given by the JPL-2002 report on Chemical Kinetics and Photochemical Data [Sander et al., 2003]. The model is initialized above Kiruna at 0:05 UT on February 10, 1999, by choosing the initial abundances (see auxiliary material) of O₃, NO₂, HNO₃, ClONO₂, HCl, Cl_y and inorganic bromine (Br_y) such that agreement is obtained

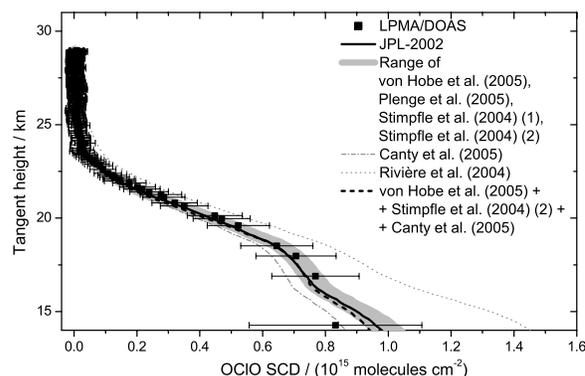


Figure 2. Measured (boxes) and modeled (lines) slant column densities of OCIO as a function of tangent height. Various model runs are shown as indicated in the legend.

¹Auxiliary material data sets are available at <ftp://ftp.agu.org/apend/gl/2006gl028718>. Other auxiliary material files are in the HTML.

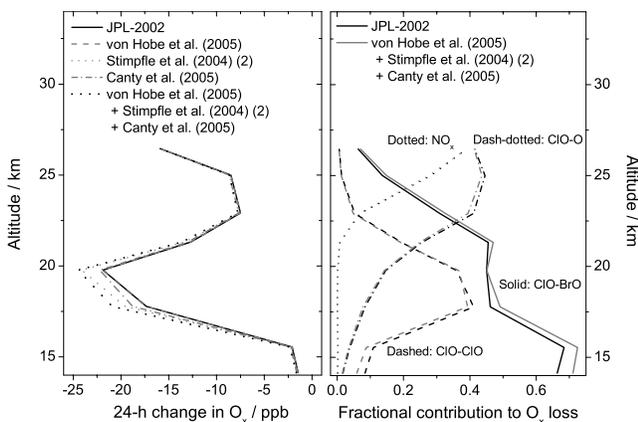


Figure 3. Modeled change of O_x (left panel) and relative contributions to O_x loss (right panel) for February 10, 1999, at Kiruna integrated over 24 hours using various kinetic parameters as indicated in the legend.

between modeled and observed O₃, NO₂, NO, HNO₃, ClONO₂, HCl, Cl₂, ClO_x and BrO in the afternoon of February 10. Constraining BrO is most important for the production of OCIO through reaction channel (5). A model-measurement comparison for BrO-SCDs is illustrated in the auxiliary material. The remaining species and the relative partitioning among the constituents of the composite species ClO_x and Br_y are initialized from output of the 3-D chemical transport model SLIMCAT [Chipperfield, 1999]. Modeled OCIO is not constrained to the observations but used for model-measurement comparison as detailed below. Model runs are performed for air masses stationary above Kiruna for a 1.5 day period. For justification of the stationarity hypothesis see auxiliary material. Modeled 24-h O_x loss is inferred between 10:50 UT on Feb. 10 and 10:50 UT on Feb. 11. The corresponding sunlit fraction of the day is 8 h 50 min. The integration period is chosen sufficiently far from initialization and sunrise, such that the partitioning of short-lived species and the loss of odd oxygen are not impacted by initialization effects.

3. Discussion

[8] Our balloon-borne observations of OCIO can be used as a marker of how well the ClO-BrO and, for our measurement conditions to a lesser degree, how well the ClO-CIO catalytic cycles are implemented in the model. Therefore, Figure 2 compares measured and modeled SCDs of OCIO as a function of tangent height (lowest altitude level crossed by the line-of-sight). SCDs instead of vertical mixing ratio profiles are favored for comparison since OCIO (as well as BrO) is subject to fast photochemical build-up (destruction) during sunset and hence, the derivation of vertical profiles from solar-occultation measurements is not possible without considerable photochemical correction. The inferred odd oxygen loss rates and fractional contributions of the ClO-BrO, ClO-CIO, ClO-O, and NO_x catalytic cycles are illustrated in Figure 3 with the intention to illustrate the impact of the tested model scenarios on O_x loss under the observed conditions.

[9] The JPL-2002 standard model run yields good to excellent model-measurement agreement for OCIO and

peak O_x loss of about 21 ppb/day around 20 km altitude coinciding with the layer of activated chlorine. In the altitude layer of activated chlorine, the major contributions to O_x loss come from the ClO-BrO and ClO-CIO cycles. The former plays the dominant role for the considered case study where chlorine activation is only of moderate degree as is often observed in warm Arctic winters. At altitudes above 21 km, the importance of the coupled inter-halogen cycles decreases and O_x loss due to the ClO-O and NO_x cycles start to dominate.

[10] Apart from JPL-2002 standard kinetics, several recently published updates of the reaction kinetics are tested (for details see auxiliary material). *Plenge et al.* [2005] and *von Hobe et al.* [2005] suggested to decrease the equilibrium constant between ClO and its dimer Cl₂O₂ (reaction (1)) with respect to JPL-2002. The resulting modeled OCIO SCDs are larger than for the standard run, since more ClO is available to react with BrO. The efficiency of the ClO-BrO cycle is enhanced while the ClO-CIO cycle becomes less important. Due to these canceling effects peak odd oxygen loss is only negligibly increased.

[11] *Stimpfle et al.* [2004] concluded from *in situ* airborne observations of ClO and Cl₂O₂ that either the rate coefficient of Cl₂O₂ production (reaction (1)) is to be decreased or that the photolysis rate of Cl₂O₂ (reaction (2)) is to be increased with respect to JPL-2002. The former hypothesis (*Stimpfle et al.* [2004] (1)) is tested by setting the low and high pressure limits of the ClO + ClO association reaction to the values recommended by JPL-2000 [*Sander et al.*, 2000] which results in more available ClO and hence larger modeled OCIO SCDs. The impact on O_x is roughly the same as for the *von Hobe et al.* [2005] scenario.

[12] The alternative possibility (*Stimpfle et al.* [2004] (2)) is an increase of the Cl₂O₂ photolysis rate with respect to JPL-2002 recommendations by using the absorption cross section of *Burkholder et al.* [1990] and extrapolating it from 410 nm to 450 nm. Enhancing Cl₂O₂ photolysis leads to a larger catalytic efficiency of the ClO-CIO cycle and thus enhances available ClO and modeled OCIO. Due to this accelerated cycling and more available ClO for the ClO-BrO cycle, peak O_x loss is increased by as much as 11% compared to JPL-2002 kinetics.

[13] Further, a study by *Canty et al.* [2005] found that night-time observations of OCIO can only be reconciled with modeled abundances if the branching ratio of the ClO + BrO reaction (reactions (3) through (5)) is altered such that 11% instead of the recommended 7% of the reaction processes yield BrCl at the expense of the OCIO yield. This scenario implies slower OCIO production and hence smaller OCIO SCDs than for the standard run but fosters peak O_x loss by up to 5% due to enhanced efficiency of the ClO-BrO cycle.

[14] *Rivière et al.* [2004] suggested to consider highly unstable isomers of ClONO₂ and BrONO₂ to improve model agreement with their night-time measurements of NO₂ and OCIO. They suggested to assume a branching ratio of 1/3 for the formation of ClONO₂ and BrONO₂ and 2/3 for the formation of the unstable isomers. The *Rivière et al.* [2004] scenario is the only model run where the initialization cannot be chosen such that the LPMA/DOAS observations can be reproduced and hence, O_x loss cannot be assessed. The modeled OCIO SCDs plotted in Figure 2 are calculated

for a model run where NO₂ is scaled such that the measurements are reproduced while modeled ClONO₂ is lower than the measurements. Then, the Rivière *et al.* [2004] scenario produces larger OCIO SCDs than all other scenarios.

[15] A composite run using the recommendations of Stimpfle *et al.* [2004] (2), von Hobe *et al.* [2005] and Canty *et al.* [2005] yields modeled OCIO SCDs similar to those inferred from JPL-2002 kinetics. However, O_x loss is larger by 10%–20%. The main contribution comes from the increased efficiency of Cl₂O₂ photolysis, which enhances both the ClO-ClO cycle due to a faster cycling rate and the ClO-BrO cycle due to more available ClO. Fractional contributions to O_x loss are similar to those inferred from JPL-2002 reaction kinetics.

[16] Implications for the recently published JPL-2006 compendium on reaction kinetics [Sander *et al.*, 2006] are fully consistent with JPL-2002 for the reactions considered here. The only update in JPL-2006 affecting our reasoning is a slightly lower equilibrium constant of reaction (1) compared to JPL-2002. At stratospheric temperatures, however, the JPL-2006 equilibrium constant is still larger than the von Hobe *et al.* [2005] recommendation implying that changes to the modeled OCIO SCDs and O_x loss rates are of minor importance with respect to JPL-2002.

[17] The only scenario which cannot be reconciled with the measurements is the hypothesis by Rivière *et al.* [2004]. For the other tested scenarios observational error bars are too large to decide whether model-measurement agreement for OCIO is improved by the new recommendations. This incomplete result could be remedied by a similar future study relying on night-time observations when OCIO abundances are larger than during sunset.

[18] Our findings for O_x loss are similar to those inferred by Frieler *et al.* [2006] who conclude on an up to 20% increased maximum possible ozone loss when using the recommendations of Stimpfle *et al.* [2004] (2), and von Hobe *et al.* [2005] in their modeling study for the Arctic winter 1999/2000. During the stratospheric winter 1998/1999, which is considered here, the polar vortex was heavily perturbed and the absolute amount of chlorine activation and ozone loss inferred from the LPMA/DOAS observations cannot be regarded as typical of this winter. Several studies indicate that total ozone loss during the winter 1998/1999 was on the order of 5% or less and barely significant in the entire lower and middle stratosphere [World Meteorological Organization, 2003]. Hence the inferred O_x loss rate cannot be extrapolated to conclude on average O_x loss during that winter but rather has to be considered as a local, process oriented snapshot of catalytic ozone destruction.

4. Conclusion

[19] Our study tests the reaction kinetics of the ClO-BrO and ClO-ClO catalytic odd oxygen loss cycles in a moderately activated Arctic vortex by constraining and comparing a stratospheric chemistry model to simultaneous observations of all relevant trace gas species, in particular NO₂, ClONO₂, BrO and OCIO. The model-measurement comparisons show that the formation of an unstable isomer of ClONO₂ as suggested by Rivière *et al.* [2004] cannot be reconciled with our observations. The suggestions of

Stimpfle *et al.* [2004], Plenge *et al.* [2005], von Hobe *et al.* [2005], and Canty *et al.* [2005] and combinations of them produce model output consistent with observations of OCIO for a model constrained by measured BrO. However, odd oxygen loss can be enhanced by 10% - 20% compared to JPL-2002 standard kinetics. In the future, similar studies conducted during night-time will allow for testing the various suggested kinetic scenarios even more sensitively.

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