Toward a better quantitative understanding of polar stratospheric ozone loss

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[1]   Previous studies have shown that observed large O_3 loss rates in cold Arctic Januaries cannot be explained with current understanding of the loss processes, recommended reaction kinetics, and standard assumptions about total stratospheric chlorine and bromine. Studies based on data collected during recent field campaigns suggest faster rates of photolysis and thermal decomposition of ClOOCl and higher stratospheric bromine concentrations than previously assumed. We show that a model accounting for these kinetic changes and higher levels of BrO can largely resolve the January Arctic O_3 loss problem and closely reproduces observed Arctic O_3 loss while being consistent with observed levels of ClO and ClOOCl. The model also suggests that bromine catalysed O_3 loss is more important relative to chlorine catalysed loss than previously thought. **Citation:** Frieler, K., M. Rex, R. J. Salawitch, T. Canty, M. Streibel, R. M. Stimpfle, K. Pfeilsticker, M. Dorf, D. K. Weisenstein, and S. Godin-Beekmann (2006), Toward a better quantitative understanding of polar stratospheric ozone loss, *Geophys. Res. Lett.*, *33*, L10812, doi:10.1029/2005GL025466.

1.   Introduction

[2]   Proper quantitative understanding of polar stratospheric O_3 destruction, including the relative contributions of bromine and chlorine species, is a prerequisite for reliable predictions of future polar ozone. The topic has become especially exigent as many independent studies indicate measured O_3 loss is consistently underestimated by current stratospheric chemistry models, particularly during cold Arctic Januaries [e.g., *Hansen et al.*, 1997; *Becker et al.*, 1998; *Deniel et al.*, 1998, *Rex et al.*, 2003, *Rex et al.*, 2004]. The discrepancies lie outside of uncertainties related to heterogeneous chlorine activation [e.g., *Rex et al.*, 2003]. This suggests the possibility of unknown O_3 loss processes, especially under cold mid-winter conditions, or that established catalytic processes are more efficient than currently thought.

2.   Tools

[3]   We use Match results for the cold Arctic winters 1994/95, 1995/96, 1999/00, 2000/01, 2002/03 and the Antarctic winter 2003 to test our quantitative understanding of measured O_3 loss. We have not reprocessed data for the Arctic winter 1991/92, because only a rudimentary Match analysis was carried out and these data are generally less reliable. Following *Rex et al.* [2003], a photochemical box model is run along trajectories identical to those studied within the Match campaigns. To quantify chemical O_3 loss independent from transport effects, the Match technique is based on a regression analysis of pairs of ozonesonde measurements of the same air parcel sampled at different times.

[4]   Here, we use the model system described by *Rex et al.* [2003] to calculate the amount of ClO_x ($ClO + 2 \times$ ClOOCl) ("necessary ClO_x") needed to reproduce the measured O_3 loss rate. The model has two updates. First, by specifying HO_2 concentrations as a function of SZA [*Hanisco et al.*, 2002], the model now accounts for O_3 loss due to cycles limited by $ClO + HO_2$ and $BrO + HO_2$, in addition to loss by the $ClO + ClO$, $BrO + ClO$ and $O + ClO$ cycles. These two new cycles contribute $\sim$2% to total O_3 loss. Second, the integration scheme has changed [e.g., *Canty et al.*, 2005]. While the old model version represented the diurnal variation of all species assuming a zonal flow (balance of 24 hour avg. production and loss), the new model fully integrates the chemical equations along air mass trajectories. The resulting difference in calculated O_3 loss rates is less than 5%. Thus, the updated version of the model is consistent with results given by *Rex et al.* [2003].

[5]   Since *Rex et al.* [2003], a number of atmospheric observations have appeared suggesting an alternative description of ClO-ClOOCl kinetics and increased levels of stratospheric bromine. Here, we quantify the effect of these observations on chemical O_3 loss for the Arctic and Antarctic vortices using four different sets of model parameters. The "reference run" uses JPL 2002 kinetics [*Sander et al.*, 2003] and a BrO_x ($BrO + BrCl$) profile for the Arctic vortex, Feb. 2000, found by the AER 2D model assuming only CH_3Br + halons supply stratospheric bromine. The BrO_x profile ranges from 11 to 13 pptv at the 450 to 525 K potential temperature (Θ) levels, respectively, and is similar to a profile calculated by the 3D CTM Mimosa-CHIM (see auxiliary material[1]).

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[6] The "new kinetics" run uses values of the ClOOCl absorption cross section (σ_{ClOOCl}) and the ClO-ClOOCl equilibrium constant (K_{EQ}) based on recent atmospheric observations of [ClO] and [ClOOCl]. *Stimpfle et al.* [2004], using daytime observations during cold Arctic conditions, showed that dimer photolysis (J_{ClOOCl}) may be occurring significantly faster than calculated using JPL 2002 values of σ_{ClOOCl}. Assuming the JPL 2002 rate constant for formation of ClOOCl, they demonstrated consistency between atmospheric observations and J_{ClOOCl} found using σ_{ClOOCl} from the laboratory study of *Burkholder et al.* [1990]. Nighttime measurements of [ClO] and [ClOOCl] were used to suggest that K_{EQ} is smaller than the JPL 2002 recommendation and is in better agreement with the *Cox and Hayman* [1988] value, leading to a higher [ClO] to [ClOOCl] ratio during darkness. Lower values of K_{EQ} are also supported by stratospheric observations provided by *von Hobe et al.* [2005] and *Berthet et al.* [2005] and a recent laboratory measurement by *Plenge et al.* [2005]. For the "new kinetics" simulation, we use values of σ_{ClOOCl} from *Burkholder et al.* [1990] extrapolated to 450 nm as described by *Stimpfle et al.* [2004] and K_{EQ} from *Cox and Hayman* [1988].

[7] We show results for a BrO_x profile based on a DOAS measurement of BrO over Kiruna, Sweden (68°N) on Feb. 18, 2000 [*Fitzenberger*, 2000; *Dorf*, 2005]. The BrO_x profile ranges from 19 to 21 ppt between 450 and 500 K. This is nearly 50% larger than both model BrO_x profiles that assume supply of Br_y from CH_3Br + halons, likely reflecting a ~6 pptv contribution to stratospheric inorganic bromine (Br_y) from short lived bromocarbons and tropospheric BrO [e.g., *Pfeilsticker et al.*, 2000]. Higher values of BrO, similar to the Arctic DOAS profile used here, have been reported by independent aircraft and balloon observations of BrO [*Salawitch et al.*, 2005]. Further discussion of BrO and details of how we have accounted for small temporal variations in Br_y are given in the auxiliary material. For clarity, results using JPL 2002 kinetics and the DOAS BrO_x profile are not shown, since they differ only slightly from the "new kinetics" run. Results are shown for a "combined run" that uses "new kinetics" and the DOAS BrO_x profile.

3. Improvements with Respect to the "January Ozone Loss Problem"

[8] The "reference run" (Figure 1, black lines) shows that, for January of all presented Arctic winters and July of the Antarctic winter, the amount of "necessary ClO_x" to match observed chemical O₃ loss rates (top half of each box) exceeds ~3.7 ppbv, the maximum amount of total stratospheric chlorine [*World Meteorological Organization* (*WMO*), 2003]. For 3 of the 6 winters, O₃ loss rates calculated on the basis of ClO_x = 3.7 ppbv ("maximum possible ozone loss", shown in lower half of each box only for the time period when nearly complete chlorine activation might be expected) underestimate the observed O₃ loss by more than the 1σ uncertainty of the measurements. This suggests our current representation of known O₃ loss cycles is insufficient to account for observed loss rates.

[9] Figure 1 shows that changes to J_{ClOOCl} and K_{EQ} ("new kinetics") increase "maximum possible ozone loss"
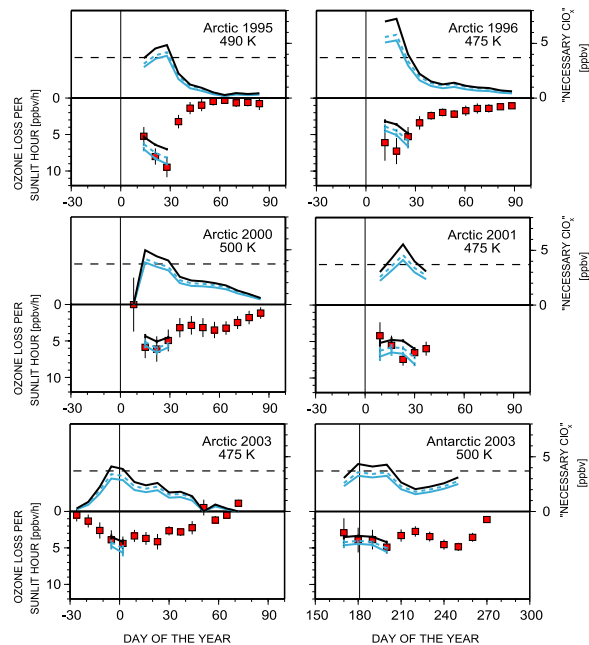
Figure 1. Chemical O₃ loss rate in the polar vortex based on Match (red boxes; error bars are 1σ uncertainty). The abundance of ClO_x necessary to account for the measured O₃ loss ("necessary ClO_x") and the modeled O₃ loss assuming ClO_x = 3.7 ppbv ("maximum possible ozone loss") are shown in the upper and lower parts of each plot, respectively. The dashed line in the upper part of each plot marks the level of 3.7 ppbv ClO_x. Maximum possible ozone loss is shown only for the time periods where nearly complete chlorine activation is likely to occur. Black lines: reference run (JPL 2002 kinetics + AER BrO_x); dashed blue lines: "new kinetics" (J_{ClOOCl} from *Burkholder et al.* [1990] and K_{EQ} from *Cox and Hayman* [1988]) + AER BrO_x; solid blue lines: "new kinetics" + BrO_x derived from DOAS BrO measurements.

by ~20% (blue dashed lines). This effect is due to higher J_{ClOOCl}; the extrapolation of the ClOOCl cross sections longward of 410 nm plays no significant role in this result. The overall effect of the new K_{EQ} is a slight decrease in modeled O₃ loss (~2%). The impact remains small if K_{EQ} is taken from "Fit 2" of *von Hobe et al.* [2005], the lowest reported value of K_{EQ}.

[10] Results from a model run that uses "new kinetics" and DOAS BrO_x ("combined run") are shown by solid blue lines in Figure 1. This simulation leads to a ~30–40% increase in ozone loss relative to the reference run and largely resolves the discrepancy between maximum possible ozone loss and measured loss. Present uncertainties in BrO_x derived from DOAS BrO lead to a ~7% uncertainty in "maximum possible ozone loss".

[11] The selection of different Θ levels for Figure 1 is driven by the availability of reliable Match data between 475 and 500 K. For Arctic 2002/03 and Antarctic 2003 we also modeled the 500 and 475 K levels, respectively. Results are similar to those shown in Figure 1. The "combined run" is not sufficient to fully resolve the discrepancy for 1991/92 reported by *Rex et al.* [2003] (not shown). A discrepancy at the 1σ to 2σ level remains for two points during that year.
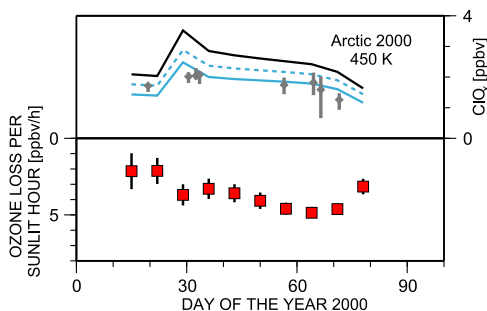
Figure 2. Chemical O_3 loss rate in 1999/2000, 450K, based on Match (red boxes; error bars are 1σ uncertainty). The lines represent the necessary ClO_x to account for measured O_3 loss, where the colors/line types correspond to the same model runs as described in Figure 1. Gray diamonds: mean value of all ClO_x measurements at 450 ± 10 K, for the 8 ER-2 flights that remained entirely inside the vortex, vertical bars represent the maximum and minimum of the considered ClO_x data.

However, the overall picture is that modeled maximum possible ozone loss rates for the "combined run" are within the statistical and systematic uncertainties of the observed rates for nearly all time periods considered.

[12] These results should not be interpreted as evidence for complete, quantitative understanding of polar O_3 loss because the calculations are based on upper limits of ClO_x. A more meaningful comparison of modeled and measured ozone loss rates is described in the following section, which considers measurements of ClO_x at the 450 K level of the Arctic winter 1999/2000. Similar measurements of ClO_x are not available for higher Θ levels considered in Figure 1.

4. Arctic Winter 1999/00, 450 K: "Necessary ClO_x" in Comparison to Measured ClO_x

[13] A stringent test of our quantitative understanding of chemical O_3 loss is provided by comparing measured ClO_x to calculated "necessary ClO_x" needed to account for observed ozone loss rates. Here, we use a time series of ClO_x based on measurements of [ClO] and [ClOOCl] from *Stimpfle et al.* [2004], for Arctic winter 1999/00. We compare measurements near Θ = 450 K (e.g., ClO_x collected between 440 and 460 K) to results from the Match analysis at 450 K. We selected data from 8 flights within the Arctic vortex, during the period Jan. 20 to Mar. 12, 2000. For each individual flight, the average of all ClO_x measurements at 450 ± 10 K is compared to the "necessary ClO_x" derived from measured ozone loss rates. The air masses encountered by the aircraft are representative of vortex conditions sampled by Match (see auxiliary material).

[14] Figure 2 shows that to explain the measured O_3 loss rates, the "reference run" based on JPL 2002 kinetics and BrO_x from CH_3Br + halons needs significantly more ClO_x (black line) than was observed. During late Jan./early Feb., the discrepancies are larger than the 20% uncertainty of the ClO_x measurements [*Stimpfle et al.*, 2004]. The amount of ClO_x needed to account for measured O_3 loss on the basis of the "new kinetics" (dashed blue line) is also higher than the observations, but is just within the uncertainty range. Results using DOAS BrO_x and JPL 2002 kinetics are almost

indistinguishable from the "new kinetics" run. Nearly perfect agreement between measured ClO_x and "necessary ClO_x" is found for the "combined run" (solid blue line). Figure 2 demonstrates that use of a faster photolysis rate for ClOOCl (consistent with atmospheric observations of [ClO] and [ClOOCl]) and higher bromine loading (consistent with a ~6 pptv source of Br_y from species other than CH_3Br + halons) provides an overall good quantitative explanation of Arctic ozone loss rates.

[15] *Rex et al.* [2003] noted the tendency for models to underestimate observed chemical loss of Arctic O_3, particularly during cold Januaries. They speculated that changes to ClO-ClOOCl kinetics and BrO_x, similar to those considered here, could largely resolve the discrepancy. The calculations shown in this paper are given greater credence by numerous studies related to ClO-ClOOCl kinetics [*Stimpfle et al.*, 2004; *Berthet et al.*, 2005; *Plenge et al.*, 2005; *von Hobe et al.*, 2005] and stratospheric Br_y [*WMO*, 2003; *Canty et al.*, 2005; *Dorf*, 2005; *Salawitch et al.*, 2005] that have appeared since *Rex et al.* [2003] was completed. Hence, this work builds upon and advances the speculation of our earlier study.

5. Relative Importance of the BrO + ClO Cycle

[16] To calculate the relative importance of each O_3 loss cycle in the model, we use all Match measurements between Jan. 10 to Feb. 10 (Arctic, all years) and Jul. 10 to Aug. 10 (Antarctic, 2003) to calculate O_3 loss per sunlit hour for these winter periods. The model was run along trajectories, with ClO_x adjusted to reproduce the measured O_3 loss rates for the three combinations of kinetic parameters and BrO_x considered above (Figure 3, top). We calculate O_3 loss per sunlit hour for the 5 catalytic cycles and then derive the relative fraction of each cycle to the total modeled loss rate
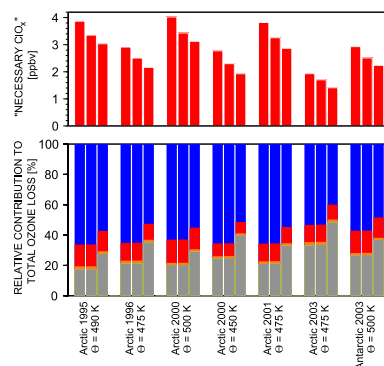
Figure 3. (top) Level of ClO_x needed to account for observed O_3 loss for the "reference run" (JPL 2002 kinetics, AER BrO_x) (1st bar of each grouping), the "new kinetics run" (2nd bar), and the "combined run" (3rd bar). Each grouping of columns represents results of model runs executed along the Match trajectories available between Jan. 10 and Feb. 10 (Arctic) and Jul. 10 and Aug. 10 (Antarctic), respectively. (bottom) Relative importance of the ClO + ClO cycle (blue), the BrO + ClO cycle (gray), the ClO+O cycle (red), and the HOCl cycle (orange) to total O_3 loss. The contribution from the HOBr cycle was calculated but is too small to represent. Groupings are the same as for Figure 3 (top).

(Figure 3, bottom), which by definition equals the measured O_3 loss rate.

[17] The kinetics changes considered here do not alter the relative importance of the BrO + ClO cycle (the increase in J_{ClOOCl}, which dominates the "new kinetics" run, results in faster O_3 loss by all cycles). Even using K_{EQ} of *von Hobe et al.* [2005], the effect on the relative importance of BrO + ClO is negligible. In contrast, use of DOAS BrO_x increases the relative importance of the BrO + ClO cycle by ~10–15%. Hence, the BrO+ClO contribution to total O_3 loss ranges from ~27 to 48% for the "combined run", in comparison to 17 to 33% for the "reference run". The relative importance of the BrO + ClO cycle increases with decreasing ClO_x. This explains the differences between results for winter 2000/01 compared to winter 2002/03, where chlorine activation derived from measured O_3 loss rates is much lower.

6. Concluding Remarks

[18] We show that use of a faster value for J_{ClOOCl} and abundances of BrO_x derived from a measured BrO profile increase calculated polar O_3 loss rates by up to 40%, resulting in overall consistency between observed O_3 loss rates and upper limits for O_3 loss based on an assumption of a completely activated vortex (e.g., $ClO_x \approx 3.7$ ppbv). Levels of ClO_x needed to account for observed O_3 loss rates at $\Theta = 450$ K are shown to be in remarkably good agreement with measurements of ClO_x for the Arctic winter of 999/00. The faster value of J_{ClOOCl} is based on a laboratory study [*Burkholder et al.*, 1990] and is consistent with measured partitioning of ClO and ClOOCl [*Stimpfle et al.*, 2004] and the JPL 2002 rate constant for the ClO self reaction. The DOAS BrO_x profile is ~6 pptv higher than a model profile based on supply of Br_y from only CH_3Br + halons, consistent with other estimates of contributions to Br_y from short lived bromocarbons and tropospheric BrO [*Pfeilsticker et al.*, 2000; *Salawitch et al.*, 2005]. Further laboratory observations of the ClOOCl cross section, extending to 450 nm, are needed to assess the accuracy of J_{ClOOCl}. Also, further atmospheric observations of BrO are needed to better define levels of BrO_x in the polar vortices.

[19] This study suggests that previous discrepancies between measured and modeled polar O_3 loss rates might be resolved by greater efficiency of known catalytic cycles, rather than by the introduction of new chemical loss processes. These results could represent an important "bridge" between analysis of atmospheric observations and computationally expensive 3D model descriptions of climate chemistry interactions used to predict future levels of polar ozone.

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