Toward a better quantitative understanding of polar stratospheric ozone loss


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[1] Previous studies have shown that observed large O3 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 ClOOC1 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 O3 loss problem and closely reproduces observed Arctic O3 loss while being consistent with observed levels of ClO and ClOOC1. The model also suggests that bromine catalysed O3 loss is more important relative to chlorine catalysed loss than previously thought.


1. Introduction

[2] Proper quantitative understanding of polar stratospheric O3 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 O3 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 O3 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 O3 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 O3 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 ClOx (ClO + 2 x ClOOC1) (“necessary ClOx”) needed to reproduce the measured O3 loss rate. The model has two updates. First, by specifying HO2 concentrations as a function of SZA [Hanisco et al., 2002], the model now accounts for O3 loss due to cycles limited by ClO + HO2 and BrO + HO2, in addition to loss by the ClO + ClO, BrO + ClO and O + ClO cycles. These two new cycles contribute ∼2% to total O3 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 O3 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-CIOOC1 kinetics and increased levels of stratospheric bromine. Here, we quantify the effect of these observations on chemical O3 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 BrOx (BrO + BrCl) profile for the Arctic vortex, Feb. 2000, found by the AER 2D model assuming only CH3Br + halons supply stratospheric bromine. The BrOx 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 material1).

The “new kinetics” run uses values of the ClOOCIC absorption cross section ($\sigma_{\text{ClOOCIC}}$) and the ClO-ClOCl equilibrium constant ($K_{\text{EQ}}$) based on recent atmospheric observations of [ClO] and [ClOCl]. Stimpfle et al. [2004], using daytime observations during cold Arctic conditions, showed that dimer photolysis ($J_{\text{ClOOCIC}}$) may be occurring significantly faster than calculated using JPL 2002 values of $\sigma_{\text{ClOOCIC}}$. Assuming the JPL 2002 rate constant for formation of ClOCl, they demonstrated consistency between atmospheric observations and $J_{\text{ClOOCIC}}$ found using $\sigma_{\text{ClOOCIC}}$ from the laboratory study of Burkholder et al. [1990]. Nighttime measurements of [ClO] and [ClOCl] were used to suggest that $K_{\text{EQ}}$ 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 [ClOCl] ratio during darkness. Lower values of $K_{\text{EQ}}$ 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 $\sigma_{\text{ClOOCIC}}$ from Burkholder et al. [1990] extrapolated to 450 nm as described by Stimpfle et al. [2004] and $K_{\text{EQ}}$ from Cox and Hayman [1988].

We show results for a BrO profile based on a DOAS measurement of BrO over Kiruna, Sweden (68°N) on Feb. 18, 2000 [Fitzenberger, 2000; Dorf, 2005]. The BrO profile ranges from 19 to 21 ppt between 450 and 500 K. This profile is nearly 50% larger than both model BrO profiles that assume supply of Br$_3$ from CH$_3$Br + halons, likely reflecting a ~6 pptv contribution to stratospheric inorganic bromine (Br$_3$) 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, are given in the auxiliary material. For clarity, results using JPL 2002 kinetics and the DOAS BrO 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 profile.

3. Improvements with Respect to the “January Ozone Loss Problem”

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$^+$” to match observed chemical O$_3$ 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, O$_3$ loss rates calculated on the basis of ClO$^+$ = 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 O$_3$ loss by more than the 1σ uncertainty of the measurements. This suggests our current representation of known O$_3$ loss cycles is insufficient to account for observed loss rates.

Figure 1 shows that changes to $J_{\text{ClOOCIC}}$ and $K_{\text{EQ}}$ (“new kinetics”) increase “maximum possible ozone loss” by ~20% (blue dashed lines). This effect is due to higher $J_{\text{ClOOCIC}}$; the extrapolation of the ClOCl cross sections longward of 410 nm plays no significant role in this result. The overall effect of the new $K_{\text{EQ}}$ is a slight decrease in modeled O$_3$ loss (~2%). The impact remains small if $K_{\text{EQ}}$ is taken from “Fit 2” of von Hobe et al. [2005], the lowest reported value of $K_{\text{EQ}}$.

Results from a model run that uses “new kinetics” and DOAS BrO (“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 derived from DOAS BrO lead to a ~7% uncertainty in “maximum possible ozone loss”.

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.
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$_x$ from species other than CH$_3$Br + 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-CIOOCl 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 CIO-CIOOCl kinetics [Stimpfle et al., 2004; Berthet et al., 2005; Plenge et al., 2005; von Hobe et al., 2005] and stratospheric Br$_x$ [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, bottom), which by definition equals the measured O₃ loss rate.

[17] The kinetics changes considered here do not alter the relative importance of the BrO + ClO cycle (the increase in \( J_{\text{CIO}} \), which dominates the “new kinetics” run, results in faster O₃ loss by all cycles). Even using \( K_{\text{EO}} \) of von Hobe et al. [2005], the effect on the relative importance of BrO + ClO is negligible. In contrast, use of DOAS BrO increases the relative importance of the BrO + ClO cycle by \( \sim 10–15\% \). Hence, the BrO+ClO contribution to total O₃ loss ranges from \( \sim 27 \) 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. This explains the differences between results for winter 2000/01 compared to winter 2002/03, where chlorine activation derived from measured O₃ loss rates is much lower.

6. Concluding Remarks

[18] We show that use of a faster value for \( J_{\text{CIO}} \) and abundances of BrO, derived from a measured BrO profile increase calculated polar O₃ loss rates by up to 40\%, resulting in overall consistency between observed O₃ loss rates and upper limits for O₃ loss based on an assumption of a completely activated vortex (e.g., ClO \( \approx 3.7\) ppbv). Levels of ClO needed to account for observed O₃ loss rates at \( \Theta = 450\) K are shown to be in remarkably good agreement with measurements of ClO, for the Arctic winter of 1999/00. The faster value of \( J_{\text{CIO}} \) is based on a laboratory study [Burkholder et al., 1990] and is consistent with measured partitioning of ClO and CIO [Stimpfle et al., 2004] and the JPL 2002 rate constant for the ClO self reaction. The DOAS BrO profile is \( \sim 6\) ppbv higher than a model profile based on supply of Br₂ from only CH₂Br₂ + halons, consistent with other estimates of contributions to Br₂ from short lived bromocarbons and tropospheric BrO [Pfeilsticker et al., 2000; Salawitch et al., 2005]. Further laboratory observations of the CIOClCl cross section, extending to 450 nm, are needed to assess the accuracy of \( J_{\text{CIO}} \). Also, further atmospheric observations of BrO are needed to better define levels of BrO, in the polar vortices.

[19] This study suggests that previous discrepancies between measured and modeled polar O₃ loss rates might be resolved by greater efficiency of known catalytic cycles, rather than by the introduction of new chemical 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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