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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Atmospheric test of the $J(BrONO_2)/k_{BrO+NO_2}$ ratio: implications for total stratospheric Br_y and bromine-mediated ozone loss" *by* S. Kreycy et al.

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My apologies on the delay in reviewing this manuscript.

This paper presents observations from 3 instruments measuring NIR, UV-Vis direct-sun and UV-Vis Limb viewing from a balloon platform conducted in Kiruna from the 6-9th September 2009 to examine the kinetics of the BrONO2 mediated ozone loss in the stratosphere. This work represents a unique data-set combined with complex photochemical/radiative transfer/chemical modeling. It is a valuable contribution to our knowledge of stratospheric chemistry, and in particular is important in the discussion concerning the total bromine loading of the stratosphere. I recommend publication,

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Discussion Paper

however there are some areas were the science has confusing arguments that leave the reader unconvinced of the validity of the conclusions. I believe that this can be easily addressed with the measurements that the authors have at hand, and it will significantly strengthen this paper. These are detailed below.

No analysis of the airmasses was performed to assess that indeed the assumption that the same airmass was being sampled (where the justification for the use of a 1D photochemical model is made – page 27826, line 11). Where the photochemical model did not match the observations then the argument that an airmass discrepancy was the cause is made. This may be the underlying cause, but as the discrepancies are being used to argue for different kinetics then the role of sampling different airmasses really needs to be eliminated. As the authors have access to N2O and O3 data (though the viewing geometry of the NIR spectrometer is not provided in the manuscript), this would be useful in assessing the airmass origin, using tracer-tracer correlations. This should be performed to assure the readers that indeed airmasses are unchanging and that discrepancies are only due to kinetic/Bry deficiencies. This will significantly strengthen the conclusions. Sampling different geometries / viewing different airmasses with the direct-sun versus the limb should not be an impediment to determining kinetic deficiencies – if the transport issues (BrONO2/Bry ratios or temperatures) are adequately dealt with in the analyses (i.e. if a large temperature range is sampled then the kinetic parameters should reflect this).

A second area requiring clarity is the selective use of sunrise and sunset data to suit the argument being made. Early in the manuscript the role of BrOH photolysis complicating the sunrise BrO polar sunrise analysis (page 27827, line 8) is made, however later this is ignored and the sunrise data is used to access the BrONO2 kinetics. This will effect both the solar occultation and limb sounding data – why is only the solar occultation data excluded from further analyses? i.e. (page 27827, line 24) where the discussion of dawn limb BrO tending to appear more rapidly that the simulations suggests could very well just be because of BrOH photochemistry inadequacies.

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Interactive Comment

The results section requires reworking to ensure that these apparent contradictions are clarified – both in ensuring that dynamical effects are accounted for, as well as photochemical complications due to BrOH photolysis at dawn.

Minor comments

Abstract:

should contain the date range and location of the measurements

Introduction:

too short, there are many examples of using atmospheric data to test laboratory kinetic data with success (for the ClO dimer cycle) [Shindell and deZafra, 1996; Solomon, 2002; Avallone et al., 2003; Vogel, 2003; Stimpfle, 2004; Hobe et al., 2005; Schofield et al., 2008; Kremser et al., 2011]. It would be valuable to frame this work in this context and talk about the uniqueness of looking at BrO to do this. The first sentence is misleading since bromine has the largest effect on ozone through coupling with the ClOx cycle (which is mentioned later in this page).

How does the heterogeneous hydrolysis of BrONO2 influence conclusions drawn here? There is no discussion about the role of BrONO2 + H2O heterogeneous reaction as an important reaction in the lowermost stratosphere. Any error introduced by misrepresentation of the aerosol size distribution could potentially dramatically change the conclusions made here. Please discuss.

Methods: Perhaps tabulate the instrumental descriptions (with references). i.e. Instrument, wavelength range, viewing geometry, target species, references

Page 27825 line 1 and else where, please use NIR, direct-sun or limb viewing geometries to describe the spectrometers rather than a) b) and c) will stop the readers having to refer back in the manuscript.

Page 27825 line 21 radio-metrically calibrated – is this standard terminology for this

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(absolutely calibrated)?

Page 27829 line 12-17 this should be earlier when 20.3ppt is described.

Conclusion (3) tropospheric conditions are not tested in this current paper, and this is very speculative. Due to the higher temperatures in the troposphere I am not convinced that this argument holds, as the kinetics may be well represented at these higher temperatures (closer to the laboratory tested conditions).

Avallone, L., D. Toohey, T. Fortin, K. McKinney, and J. Fuentes (2003), In situ measurements of bromine oxide at two high-latitude boundary layer sites: Implications of variability, J Geophys Res-Atmos, 108, –, doi:10.1029/2002JD002843. Hobe, von, M., J. Grooss, R. Müller, S. Hrechanyy, U. Winkler, and F. Stroh (2005), A re-evaluation of the ClO/Cl2O2 equilibrium constant based on stratospheric in-situ observations, Atmos. Chem. Phys., 5, 693–702. Kremser, S. et al. (2011), Retrievals of chlorine chemistry kinetic parameters from Antarctic ClO microwave radiometer measurements, Atmos. Chem. Phys., 11(11), 5183–5193, doi:10.5194/acp-11-5183-2011. Schofield, R. et al. (2008), Polar stratospheric chlorine kinetics from a self-match flight during SOLVE-II/EUPLEX, Geophysical Research Letters, 35(1), –, doi:10.1029/2007GL031740. Shindell, D., and R. deZafra (1996), Chlorine monoxide in the Antarctic spring vortex .2. A comparison of measured and modeled diurnal cycling over McMurdo Station, 1993, J Geophys Res-Atmos, 101, 1475–1487. Solomon, P. (2002), Measurements of stratospheric ClO over Antarctica in 1996–2000 and implications for ClO dimer chemistry, Geophysical Research Letters, 29(15), doi:10.1029/2002GL015232. Stimpfle, R. M. (2004), First measurements of ClOOCl in the stratosphere: The coupling of ClOOCl and ClO in the Arctic polar vortex, J. Geophys. Res., 109(D3), doi:10.1029/2003JD003811. Vogel, B. (2003), Vertical profiles of activated ClO and ozone loss in the Arctic vortex in January and March 2000: In situ observations and model simulations, J. Geophys. Res., 108(D22), doi:10.1029/2002JD002564.

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