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Atmospheric Chemistry and Physics Discussions

Interactive comment on "A re-evaluation of the ClO/Cl_2O_2 equilibrium constant based on stratospheric in-situ observations" *by* M. von Hobe et al.

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General Comments

Based on new in situ measurements of ClO and Cl2O2 from the M55-Geophysica aircraft, von Hobe and coworkers find that abundances of these species in darkness in the perturbed arctic vortex can be explained by an equilibrium expression that is significantly different than the one recommended in current rate paramater compilations, in particular the JPL 2002 compendium. First, they find the value for the equilibrium constant to be approximately 5-20% of the value currently recommended by JPL over the temperature range 191-212 K. Second, they find a functional relationship for the van't Hoff plot to have a significantly larger y-intercept (e.g. standard entropy) than

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that expected for the species ClOOCl, implying a potential role for isomers of Cl2O2 in the polar stratosphere. It is important to note that this result is quite different from results reported previously based on in situ measurements from the Arctic [Brune et al., 1991, Kawa et al., 1992, Pierson et al., 1999, Avallone and Toohey, 2001, Voemel et al., 2002, Stimpfle et al., 2004, and Vogel et al., 2004], and remote observations from the Antarctic [Shindell and deZafra, 1996], which found reasonable agreement with the JPL recommendation, with the in situ measurements indicating a somewhat smaller value for Keq (about 50% of the recommended value). What is important in the von Hobe et al. study is that the species Cl2O2 was measured simultaneously with ClO. Of the previous studies, only that of Stimpfle et al. [2004] was based on measurements of both of these species, whereas the others relied on inferred values of Cl2O2.

This is a very careful and thorough study, and one to be taken very seriously. The authors are to be commended on a very difficult measurement. To my knowledge, they are the first to produce Cl2O2 and quantify it in the laboratory with the same instrument that is used to measure it in the atmosphere. What is compelling is that abundances of ClO that are observed in sunlight at ˜20 km are very similar to those reported previously (˜1.2-1.3 parts per billion, or ppb, see Figure 6). Consequently, the difference in this study compared to previous ones is that the Cl2O2 abundances are significantly lower (by a factor of 2-4) than those observed or inferred in the earlier studies. The authors carry out a modeling study to show that the implications for ozone loss are not significant, but what really matters is whether or not our understanding of polar ozone chemistry is sound. If it is based on processes that cannot be corroborated by observations, this might be telling us that we are missing something fundamental.

I believe that this paper should be published solely based on the fact that these measurements are very difficult, and it is important to put them out on the table for discussion, especially if the authors are convinced that they are not undermeasuring the Cl2O2. I have my concerns about this latter point which I will address below.

Specific Comments

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Major points

The main difference between this study and the previous ones referred to above is that von Hobe et al. found considerably less Cl2O2 than was measured by Stimpfle et al. or inferred in the other studies that measured ClO alone. Figure 6 of von Hobe et al. is very interesting. In sunlight on 30 January 2002 they found 1.2-1.3 ppb of ClO, similar to what others have observed at the same altitude and season, and nearly identical to values reported by Stimpfle et al. from ER-2 aircraft measurements on 2 February 2000. In sunlight, thermal decomposition of Cl2O2 is much less important than photolysis, such that one would expect similar amounts of Cl2O2 to be present in these two sets of observations. However, Stimpfle et al. measured 250% or more Cl2O2 under these conditions than did von Hobe et al. This discrepancy is similar in darkness, where Stimpfle et al. observed ˜900 ppt of Cl2O2 in equilibrium with ClO, whereas von Hobe et al. observed only ˜350 ppt. On this basis, I am suspicious that the von Hobe et al. measurements are missing an important fraction of the Cl2O2 that is present. It is no surprise that the different Keq values determined by these two groups would differ by a factor of 6-7.

There are other indications that the instrument employed by von Hobe et al. might be underestimating abundances of Cl2O2. In Figure 6, as the Geophysica flew into darkness, ClOx, the sum of ClO+2Cl2O2, decreases from about 1.4 ppb to 0.85 ppb. It then increases to about 1.2 ppb as the Geophysica turns around and samples the same air as on the outbound leg, but this time when the sun is just dropping below the horizon. In a similar flight track of the ER-2 in 2000, Stimpfle et al. found the ClOx to remain remarkably constant near 2.0 ppb under similar conditions. I must caution here that I don't expect the atmospheres on 30 January 2002 and 2 February 2000 to be identical, but the fact that the two groups measured the same ClO (within 5% or so) in sunlight, but Cl2O2 abundances that differed by 250-300%, concerns me. The demonstration by Stimpfle et al. of conserved ClOx at the day-night terminator is a powerful validation of their methods. It would be nice to see a similar demonstration for

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the von Hobe et al. measurement technique, one that does differ from that of Stimpfle et al. in an important way. The latter group measures at ambient pressure, while von Hobe et al. reduce pressure to reduce the power necessary to heat the air flow.

Von Hobe et al. were justifiably concerned that their method might miss some Cl2O2, so they carried out an elegant laboratory study where they presumably produced Cl2O2 by cooling a flow of ClO, and then proving that the ClOx was conserved following detection using the same hardware as that used to detect Cl2O2 in flight. This is a compelling result, but one that should still be taken with caution. The abundances of ClOx employed in the laboratory study (and necessary for rapid conversion of ClO to Cl2O2) were 200 times larger than those measured in the atmosphere. It is quite possible that at such levels of chlorine the walls of their system behaved differently than in flight. A much more convincing laboratory study would have been one that demonstrated conservation of ClOx over a wide range of abundances, including similar ones to those observed in the atmosphere. Nevertheless, it is important to recognize that these are very difficult experiments, and von Hobe et al. are to be congratulated for having successfully carried out a demonstration that has eluded others.

Another issue I have long been concerned about in thermal decomposition measurements is the possible release of organic compounds (either adsorbed to walls of the instrument or from materials of construction) that react rapidly with chlorine atoms at elevated temperatures. For this reason I find the demonstration of constant ClOx through the terminator by Stimpfle et al. to be a necessary (although not sufficient) result.

There is another potential problem in the analysis performed in this study. The authors note that there were few occasions where the Geophysica sampled air that had been in darkness long enough that equilibrium between ClO and Cl2O2 was assured (what they refer to as the "strict" equilibrium criterion). It is useful to note that this criterion was only met with a few observations at 203 K and higher temperatures. In order to extend their analysis to lower temperatures for a wider dynamic range, the authors resorted to a "soft" equilibrium criterion that includes observations taken near the sunset termina-

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tor. It is unclear from the discussion whether or not the sun is still above the horizon for some of these data points, but what is important to note in this context is that the time to reach equilibrium becomes longer with decreasing temperature (as shown in their Figure 7). This is primarily because the rate for the ClO + ClO reaction is quadratic in the concentration of ClO, and at lower temperatures the equilibrium concentration of ClO is smaller for a fixed abundance of ClOx. What is interesting in the data presented in Figure 8 is that the difference between the von Hobe et al. Keq and that inferred by others is about a factor of 2.5 at 212 K, whereas it is a factor of 10 at 191 K. It seems plausible that the "soft" equilibrium criterion is passing values for which ClO has not yet dropped to equilibrium. The assumption that the ClO abundances have truly reached asymptotic values is something that should be verified with a trajectory model. In this context it is also important to consider the potential compression of time by the westerly polar jet (i.e. the eastward motion of air parcels reduces the true amount of time since air was last in sunlight, and this can be significant at high latitudes in winter with a strong jet stream), as well as the possibility that the airmasses sampled by the Geophysica are adiabatically warming or cooling by vertical motion.

Minor Points

The following points are relatively minor, and can easily be addressed by the authors.

(1) Page 5076, line 23 - BrO + ClO is more efficient in destroying ozone than ClO + ClO, as it can destroy nearly as much ozone with considerably less BrO than ClO. I presume that the authors meant to say "more important cycle" instead.

(2) Page 5077, line 19 - should be "...give a higher estimate of Keq..."

(3) Page 5077, line 24 - It is a bit unfair to say that Simpfle et al. made no effort to derive Keq from their measurements. In fact, their results agreed well with those of Avallone and Toohey, as they noted. In addition, see my comments above regarding obvious differences in Cl2O2 observations under similar conditions in this study compared to theirs. It is not difficult to determine to what the differences are due.

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(4) Page 5078, lines 7-10 - I think this paper would also benefit from a discussion of differences with previous studies that were based on observations. Such a discussion is probably more useful to the readers than a section on implications of the smaller Keq, especially when your results are very different from those previous studies.

(5) Page 5079, line 14 - It would be good to report here the reduced pressure at which the measurements are made (unless I missed it somewhere else).

(6) Page 5080, line 10 - It would be good to report here the abundances of ozone used to produce ClO, and how those might compare to ambient values.

(7) Page 5080, line 19 - What is the residence time of gas upstream of the inlet and after the ClO flow is cooled?

(8) Page 5081, lines 4-6 - I am a bit discouraged by the same observation that the authors use as evidence that the dimer measurement isn't missing an important fraction of the ClOx. I encourage them to consider the possibility that they miss a significant fraction of Cl2O2, and reexamine the notion that the differences at ˜14:35 and ˜12:05 in Figure 6 are within the error limits. For example, if I assume that Cl2O2 is actually 300% of the value they report in Figure 6, I calculate a ClOx value of ˜2.25 ppb at 12:05, and 2.45 ppb at 14:35. These values agree to within 4%, better than the current 10% difference that can be derived by data shown in Figure 6. In either scenario, mine or yours, the agreement of ClOx to within error limits does not constrain the value of Cl2O2, as you can see from this example. And one might use the counter argument that forcing the two ClOx values to agree, as you might expect for the same airmass, requires the Cl2O2 to be considerably larger than you have measured, which is probably a dangerous thing to do.

(9) Page 5082, line 1 - Define "horizon". Is it the visible horizon at the altitude of the airplane? Is it the point where 50% of the sun is eclipsed by the earth or clouds?

(10) Page 5082 - It seems that whatever explanation you have for the discrepancy

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ought to apply to other studies that found a larger Keq, one that is within a factor of two of the JPL recommendation. Is this the case? If not, can you explain why the situation may have been different for those previous studies?

(11) Section 4 - I don't disagree with your analysis of the implications of a smaller Keq, but wonder if it wouldn't be better to put more effort into a discussion of the discrepancies of this study with previous ones mentioned above (especially the results of Stimpfle et al.) rather than into the implications of a result that is clearly at odds with those other studies?

References

Avallone, L.M. and D.W. Toohey, Tests of halogen photochemistry using in situ measurements of ClO and BrO in the lower polar stratosphere, J. Geophys. Res., 106, 10411-10421, 2001.

Brune, W.H., J.G. Anderson, D.W. Toohey, D.W.Fahey, S.R. Kawa, R.L. Jones, D.S. McKenna, and L.R. Poole, The potential for ozone depletion in the arctic polar stratosphere, Science 252, 1260, 1991.

Kawa, S.R., D.W. Fahey, L.E. Heidt, W.H. Pollock, S. Solomon, D.E. Anderson, M. Loewenstein, M.H. Proffitt, J.J. Margitan, and K.R. Chan, Photochemical partitioning of the reactive nitroge and chlorine reservoirs in the high-latitude stratosphere, J. Geophys. Res., 97, 7905-7923, 1992.

Pierson, J.M., K.A. McKinney, D.W. Toohey, U. Schmidt, A.Engel, J. Margitan, and P.A. Newman, An investigation of ClO photochemistry in the chemically perturbed arctic vortex, J. Atmos. Chem., 32, 61-81, 1999.

Shindell, D.T. and R.L. deZafra, Chlorine monoxide in the Antarctic spring vortex 2. A comparison of measured and modeled diurnal cycling over McMurdo Station, 1993, J. Geophys. Res., 101, 1475-1487, 1996.

Stimpfle, R.M., D.M. Wilmouth, R.J. Salawitch,and J.G. Anderson, First measurements

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of ClOOCl in the stratosphere: The coupling of ClOOCl and ClO in the arctic polar vortex, J. Geophys. Res, 109, doi:10.1029/2003JD003811, Art. D03301, 2004.

Voemel, H., D.W. Toohey, T. Deshler and C. Kroger, Sunset observations of ClO in the arctic polar vortex and implications for ozone loss, Geophys. Res. Lett., 28, 4183-4186, 2001.

B. Vogel, R. Muller, T. Deshler, J.-U. Grooss, J. Karhu, D.S. McKenna, M. Muller, D. Toohey, G.C. Toon, and F. Stroh, 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, 10.1029/2002JD002564, Art. 8334, 2003.

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 5075, 2004.