**Atmospheric
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Interactive
Comment

Interactive comment on "A re-evaluation of the ClO/Cl$_2$O$_2$ equilibrium constant based on stratospheric in-situ observations" *by* M. von Hobe et al.

M. von Hobe et al.

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General comments

We would like to thank Darin Toohey for his positive and constructive review.

We share his main concern, i.e. the obvious discrepancy to previous determinations of Keq and to most stratospheric observations, and the question this raises on the possible underestimation of the ClO dimer abundance by our HALOX instrument. Indeed, when we first plotted our data in a van't Hoff plot as the one shown in Figure 8, we were surprised and concerned about how far below the recommended parameterisations for K$_{eq}$ our data fell. Because of these concerns we carefully examined our data analysis routine for potential error sources, and carried out an extensive laboratory validation of our method. As D. Toohey points out in his review, this laboratory study was difficult for

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a number of reasons, and uncertainties remain, which we will refer to in the Specific Comments below. Based on the tests carried out in the laboratory and during flight, we have not found compelling arguments to make corrections to our Cl_2O_2 measurements, and all identified sources of error are represented in the error margins given.

In our opinion, an adjustment of the data based purely on observed discrepancies to previous studies would be rather arbitrary and not help scientific progress, especially as the discrepancies are not necessarily due to erroneous measurements but could be due to scientific reasons such as yet unidentified nighttime ClO_x reservoirs other than ClOOCl, or problems with the assumptions on the amount of inorganic chlorine and the extent of its activiation in some studies (where the ClO dimer was not measured). An exception is of course the study by Stimpfle et al. (cf. Specific Comments below). In any case we will follow D. Toohey's advice and include a discussion on this issue in the revised manuscript, where we will try to quantify (in terms of the existing differences between the K_{eq} values) remaining uncertainties in our evaluation and potential problems with studies where the dimer was not measured.

Specific comments

Major Points:

D. Toohey: *"The main difference between this study and the previous ones referred to above is that von Hobe et al. found considerably less Cl_2O_2 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 Cl_2O_2 is much less important than photolysis, such that one would expect similar amounts of Cl_2O_2 to be present in these two sets of observations. However, Stimpfle et al. measured 250% or more Cl_2O_2 under these conditions than did von Hobe et al. This discrepancy is similar in*

darkness, where Stimpfle et al. observed 900 ppt of Cl_2O_2 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 Cl_2O_2 that is present. It is no surprise that the different K_{eq} values determined by these two groups would differ by a factor of 6-7."

We agree that generally, Stimpfle has observed higher Cl_2O_2 mixing ratios than we did with HALOX; this is obvious from the fact that their nighttime measurements are in line with previous evaluations of K_{eq}. At this stage the discrepancy is impossible to resolve, and the most likely explanation indeed seems an underestimation of Cl_2O_2 on our side or an overestimation by Stimpfle et al. One should be cautious however on trying to compare individual data sets and quantify the possible errors from this: even though the conditions for some flights (e.g. 02-02-2000 and 01-30-2003 to which D. Toohey refers) may look similar from looking at the flight paths, potential temperature profiles, zenith angle traces, etc., a number of factors may resolve a significant fraction of the difference in the dimer measurements. Temperature data need to be checked (between 201 and 210 K for the 01-30-2003 EUPLEX flight) and exact irradiation histories need to be compared. We would like to point out that none of the data points for 01-30-2003 satisfied either the strict or the soft equilibrium criteria described in our manuscript. Also, during the EUPLEX flight, chlorine nitrate was present at a lower limit of 400 ppt (concerning the HALOX $ClONO_2$ measurement, we are still in the process of trying to quantify the conversion efficiency, but we know it is significantly less than unity; cf. below). We also want to mention at this point, that even an error on the order of 300% for our Cl_2O_2 measurements would cause the inferred K_{eq} value to increase by only a factor of 3 (that's assuming that the ClO measurement is correct).

D. Toohey: *"...The latter group measures at ambient pressure, while von Hobe et al. reduce pressure to reduce the power necessary to heat the air flow."*

Actually, the reason for the pressure reduction in duct B was originally to be able to measure BrO at higher ambient pressures. Under typical flight conditions between 200 and 50 hPa ambient pressure, the pressure in B is reduced to about 50 to 70%

ambient pressure and is monitored continuously. When we developed the option to measure ClO dimer and chlorine nitrate, the inlet seemed a good place for the heater, as the air stream is confined to a small volume that is easily isolated against the surroundings. The pressure reduction is taken into account in the data analysis, and the ClO measurements of both ducts agree reasonably well. We are currently not aware of any systematic errors resulting from the pressure reduction.

D. Toohey: *"...The abundances of ClO_x employed in the laboratory study (and necessary for rapid conversion of ClO to Cl_2O_2) 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.*
We can not completely rule out a different behaviour at the ClO_x levels used in our laboratory compared to those found in the atmosphere. However, wall effects seem more likely under the laboratory conditions, and are indeed observed at very low temperatures and if any untreated metal sufaces are present in the calibration system. Tests on the conservation of ClO_x at low concentrations were prevented by the extremely low temperatures required to produce the ClO dimer in significant amounts over the timescale of the laboratory measurement at low initial [ClO]. At these low temperatures, a significant fraction of ClO is frozen out at the walls.

D. Toohey: *"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.*
We have indeed found this to be a great problem for our chlorine nitrate measurement: we believe the sharp signal decrease observed as the HALOX inlet temperature is raised above 500 K (Figure 3b) is due to organics outgassed from one of our inlet insulation materials at these temperatures. Laboratory tests show, that if this material

is removed, the signal falloff at higher temperatures disappears. We have found that at the temperatures of the dimer measurement this outgassing effect is not observed, which is confirmed by the temperature ramps performed during the EUPLEX flights. Experiments carried out in the laboratory where the temperature in the inlet was raised without prior cooling also showed the measured ClO concentration to remain constant with inlet temperature at least up to the upper limit of the chosen dimer dissociation temperature.

D. Toohey: *"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 Cl_2O_2 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 terminator. 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. K_{eq} 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."
In our opinion, this issue is the largest uncertainty associated with the new parameterisation for K_{eq} given in our paper. Although the sun is below the horizon for any data points included in Figure 8 (which will be stated clearly in the revised version of the paper), and the ability of the soft equilibrium criterion to discriminate data points close to the sunset terminator is shown by the fact that no data points from the flight shown in Figure 6 pass this criterion, we do admit potential problems here especially at very cold temperatures and low [ClO$_x$]. To calculate the relaxation time to equilibrium (Figure 7) we have used the ClO recombination rate constant k_f given by JPL 2002, which is at the high end of published values. Even using a moderately lower k_f will cause the relaxation time for the ClO/Cl$_2$O$_2$ system to reach equilibrium to increase. We will look further into this issue and, in the revised manuscript, will give a discussion of the potential errors for the derived K_{eq}.

We will also check the trajectories for the extent of the compression of time by the westerly jet.

Minor Points:

We will take into account the recommendations made by D. Toohey and make corrections/changes to the revised manuscript accordingly.

(5) about 60% of ambient P
(6) [O$_3$] at the point of ClO production was several ppm, [O$_3$] after dilution (i.e. the value relevant at the conversion of ClO to Cl with NO was about 1 ppm.
(7) The residence time of gas between the point where ClO is mixed into the cold N$_2$ and the heated inlet was about 0.5 to 1 s. It varied to some extent as experiments were carried out at different pressures, temperatures and flow velocities.
(8) We have to admit that our argument to constrain the Cl$_2$O$_2$ value was not very well chosen, as the magnitude of the change in Cl$_2$O$_2$ concentration inferred from the ClO measurements allows for a rather large range of Cl$_2$O$_2$ measurements to fall within error limits.

(9) We mean the visible horizon at flight altitude, and the $5°$ is also as seen from the plane.

(10) cf. General Comments

(11) We will include a discussion of the discrepancies.

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