**Atmospheric
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Discussions**

Interactive comment on "Understanding the kinetics of the ClO dimer cycle" *by* M. von Hobe et al.

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Following submission of a revised manuscript, further reviews were obtained. In combination with the previously published reviews, the anonymous comments listed below were considered in the decision not to publish this manuscript in ACP.

Review of the paper "Understanding the kinetics of the ClO dimer cycle" by M. von Hobe et al.

This paper attempts to reconcile the body of laboratory and field data that pertain to the partitioning between ClO and Cl_2O_2 in the polar stratosphere. The following comments should be considered in connection with this manuscript:

One goal of this paper is to compare field measurements of Cl_2O_2 and ClO with calcu-

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lations that make use of the steady-state approximation, i.e. $[Cl2O2]/[ClO]2 = 2krec/J$ The paper compares expressions for krec derived from direct kinetics studies with one derived from Keq*kdiss. In turn, Keq and kdiss are derived from comparisons between direct lab measurements and values derived from thermochemistry.

In the case of kdiss, the paper essentially repeats the calculation presented in Golden's 2003 paper on ClO + ClO, which forms the basis for the recommendation in the JPL06 data evaluation. Golden's paper pointed out that the measured rate coefficients for krec are higher than krec values calculated using Troe's expression, even for values of the weak collision parameter close to unity. This is where Golden and this paper follow different reasoning. Golden (2003) and JPL06 accept the measured values of krec from Bloss et al. (2001) while the present paper rejects the Bloss et al. (and the subsequent Boakes et al. paper, which obtains even larger rate constants at the lowest temperatures) on the grounds that the values from the latter two studies are inconsistent with theory. For their comparisons with field measurements, the present authors use the results of Nickolaisen et al. (1994) for krec,0, which are smaller than those obtained by Bloss et al. and Boakes et al. This is an unsatisfactory choice because a careful reading of the Bloss et al. paper would have shown that the latter study supersedes the study of Nickolaisen et al. The Bloss et al. paper points out that the Nickolaisen et al. study assumed that the ClO cross sections in the UV were temperature independent below 220 K, when in fact both Bloss et al. and Boakes et al. showed that the cross sections have a significant negative temperature dependence.

Another element in this discussion is that the present paper puts too much faith in the predictive capability of Troe's equation for kdiss,0. As pointed out by Troe, the correction factors in this equation are based on fits to RRKM calculations, which are themselves based on thermochemical parameters, such as the O-O bond dissociation in ClOOCl, which have significant uncertainties. The NASA data evaluations and possibly the IUPAC evaluations use the comparisons with Troe's equation as a general guide to assess the reasonableness of experimental determinations of kdiss,0. In

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cases where the inferred values of the weak collision parameter differ significantly with expectations, a flag is raised in the note for the reaction, and the uncertainties for the recommended rate constants are evaluated accordingly. However, the recommendations are never derived from Troe's equation when credible experimental are available. This is contrary to the approach used in this paper.

p. 3: The rationale given in support of the "preferred" values of the ClOOCl enthalpy of formation is very weak. The paper says that Cox and Hayman and Basco and Hunt actually establish the equilibrium between ClO and Cl2O2 while Nickolaisen uses only the information from the temporal dependence of ClO to determine the equilibrium constant. Basco and Hunt (1979) was a weak study for many reasons, mainly because the cross sections they derived for ClOOCl are in very poor agreement with all other studies near the ClOOCl peak at 245 nm, indicating the presence of impurities and secondary reactions. Also, Basco and Hunt measured Keq only at 298 K. Their estimate of deltaHf from ClOOCl was derived from a highly inaccurate estimation of the ClOOCl entropy by analogy with other molecules, in combination with their single measurement of Keq. This is mainly because Basco and Hunt wrote their paper before the microwave and IR spectroscopy studies that established the structure of ClOOCl. It is therefore extremely surprising that the current paper gives this paper any credence. Ellermann et al. (1995) also measured Keq only at 295 K using a time-resolved method which is basically the same as that used by Nickolaisen et al. The present paper seems to be deriving deltaHf by the same method used by Basco and Hunt, i.e. from the calculated ClOOCl entropy in combination with Keq from the measurement 295 K only. This will give a highly uncertain result. As for the measurement of Cox and Hayman (1988), the determination of Keq is far more robust than that of Basco and Hunt and Ellermann et al because the data are acquired over a wide range of temperature.

Another point is that there is really very little disagreement in the Third Law deltaHf values summarized in Table 2, and the paper makes far too much of the small differences between the values in the Table. The values listed in the table have uncertainties of +-

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0.2 kJ/mol, but these are incorrect. Nickolaisen et al. and Cox and Hayman's values all have uncertainties around 3 kJ/mol, and Plenge's result derived from appearance potentials has a similar uncertainty. As mentioned above, the results derived from Ellermann et al. and Basco and Hunt are actually much more uncertain than the other results, but Table 2 still quotes the uncertainties as 0.2 kJ/mol. It should be noted that the differences in the extrapolated values of Keq between the studies of Nickolaisen et al. and Cox and Hayman are biased strongly by the two lowest-temperature points of Cox and Hayman. These points have the largest uncertainties because the time constant for establishment of equilibrium in their cell is fairly long (several seconds at the lowest temperature). Tony Cox has stated on several occasions that these two points may not be reliable because of this problem (wall losses of ClO and ClOOCl).

Finally, the comparisons between Keq from lab measurements and the value inferred from field measurements are very weak - the atmosphere is not a laboratory for the measurement of rate coefficients because too many factors cannot be controlled. The value of the comparisons between model predictions based on laboratory data, and field data is only useful if the two are independent of one another. If rate parameters are selected on the basis of field measurements, the comparisons become circular. This is particularly true in this case because the paper assumes that there are no uncertainties associated with field measurements of ClOOCl and ClO. In fact, both molecules are measured by indirect methods (especially ClOOCl), and the ClOOCl technique has never actually been calibrated in the laboratory using ClOOCl. The use of field data to lend confidence to one or another lab measurement of a rate parameter, as is done in this paper on p.3, is therefore highly suspect.

With respect to the calculation of J values for photolysis of ClOOCl, the paper derives an entirely new set of cross sections called "MPIC" which are larger than the values recommended in JPL02 and JPL06. The rationale for the use of this spectrum is not clearly spelled out. The MPIC cross sections appear to be influenced strongly by the old study of DeMore and Tschuikow-Roux, which was superseded by the study

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of Huder and DeMore. Therefore, the DT cross sections should not be used in any assessment of cross sections (DeMore has said as much in several talks he has given in the past). The Burkholder et al. cross sections appear to be contaminated by impurities such as Cl2O3, which is probably responsible for the peak they observed around 270 nm. The presence of Cl2O3 and residual Cl2 would have made it very difficult for Burkholder et al. to obtain the correct cross sections for Cl2O2 beyond 300 nm. This is why the IUPAC Panel has recently recommended the Huder and DeMore spectrum, which has cross sections considerably smaller than the MPIC spectrum. Introducing a new set of ClOOCl cross sections is a bad idea, especially when their only merit is that they give marginally better agreement with the flight data. There is no theoretical basis for the log-linear extrapolation used in generating Table 6. If Table 6 is published, people will be quoting the numbers for decades to come, to three significant figures! Table 6 and the use of the MPIC cross sections should be eliminated. Note, if we are to believe the error bars on the lower two plots of Figure 9, all of the experimental cross sections agree fairly well with the observations.

One needs a microscope to read the subscripts on Figures 6, 8 and 9 and to identify the points or symbols on Figures 7 and 8. Parentheses would be better than subscripts; e.g. J(Burkholder et al.). Also using a line or printing in light gray is barely legible; darker colors are needed.

In summary, this paper does little to clarify the issues concerning ClOx chemistry in the polar stratosphere. The main problems are: 1. The discussion of krec largely repeats the analysis in Golden (2003) and the NASA/JPL data evaluations. 2. There are key points in several laboratory papers that are missed in the discussion, causing incorrect conclusions to be drawn about the results. 3. The paper lacks a clear analysis of the propagation of uncertainties from the laboratory parameters and their impact on model calculations of ClOOCl and ClO in the atmosphere. There is also no discussion of uncertainties in the atmospheric measurements of ClOOCl and ClO, and how these compare with uncertainties propagated through the model calculations to answer the

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question of whether there are indeed missing steps in the assumed mechanism of polar stratospheric ozone depletion. The paper has a strong bias in its recommendations toward those lab measurements which result in agreement with the field measurements, which is not the way the problem should be analyzed.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 7905, 2006.

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