Atmos. Chem. Phys. Discuss., 6, S2790–S2792, 2006
www.atmos-chem-phys-discuss.net/6/S2790/2006/

Atmospheric Chemistry and Physics Discussions

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

M. von Hobe et al.

Received and published: 30 August 2006

A significant proportion of our paper presents a review of previous studies, and indeed our evaluation of the various parameters follows similar lines as JPL and IUPAC. However, the format of a scientific paper allows us to do this in a much more detailed manner than can be done in the JPL and IUPAC reports. Given the large number of publications and the obvious discrepancies that exist between them (see response to D. Golden's comment), together with the importance of the ClO/Cl_2O_2 kinetics in the context of polar ozone loss, we felt that an extensive and critical review that goes beyond the type of assessment that can be done by JPL and IUPAC would be helpful. This was, in fact, one motivation for writing this paper.

But clearly, "Understanding the kinetics of the ClO dimer cycle" is not merely a review paper. We feel that it contains a substantial amount of new science, which has been

Full Screen / Esc
Printer-friendly Version
Interactive Discussion
Discussion Paper

listed in our response to D. Golden's comment. As both reviewers acknowledge, a key point (but not the only one) is the comparison of model calculations with field measurements. Although a similar analysis has been presented before (Stimpfle et al., 2004), we feel that the analysis of atmospheric observations in our paper still makes a significant contribution towards improving our understanding of the ClO dimer chemistry. Our study not only increases the confidence in the conclusions made by Stimpfle et al., but also presents novel aspects such as detailed discussion of AM/PM differences with a data set spanning a broad range of solar zenith angles, examination of nighttime data for a much larger range of temperature than has been conducted in any prior study, and the use of two independent modeling approaches (i.e. steady state "constrained" data analysis and time dependent box model studies).

The MPIC cross sections were not found in an arbitrary manner. The rational behind these cross sections is explained on Page 7917 and in Table 5. Due to their construction by averaging a different choice of laboratory studies in different wavelength regions, these cross sections necessarily involve possibly subjective judgement, but the same is true for the constructions made for example for the JPL assessment. The MPIC cross sections were formed prior to the start of modeling portion of our study, and have been unaffected by our results (i.e., we did not alter the cross sections to obtain any particular result). The fact that the MPIC cross sections, based on an assessment of available data by laboratory scientists, appears to be consistent with the atmospheric observations of ClO and ClOOCl, is an important scientific finding that we have chosen to highlight.

The question of the reliability of Cl_2O_2 field measurements is of course critical for our conclusions. This question has been adressed for the Geophysica HALOX measurements in this paper and in von Hobe et al. (2005), and for the ER-2 measurements by Stimpfle et al. (2004). We also discuss briefly (Page 7924, line 2) that an unknown problem with the measurement technique used would invalidate our analysis. As with essentially all field and laboratory measurements, this possiblility cannot be completely

ACPD
6, S2790–S2792, 2006

EGU

ruled out. But without substantial evidence suggesting otherwise and after careful quality check we choose to consider the data reliable, within the error limits determined by careful analysis. Confidence in the Cl_2O_2 observations is increased by the fact that they typically fall into the range of values expected for the given ClO and Cl_y.

As noted by D. Golden, the results of the latest laboratory study on the Cl_2O_2 photolysis cross section by Pope et al. pose a serious challenge to the conclusions drawn from our steady state and box model analyses. Thus, we felt a strong need to discuss the implications in our conclusions (Page 7923, line 18-22). To our knowledge, a paper on this laboratory study is in preparation, and we have some hope that we may be able to replace the reference to the poster in the final version. However, at this stage we felt it would be scientifically improper to ignore the Pope et al. results, especially as they come from an experienced group with a strong reputation for laboratory studies on chemical kinetics and spectral properties. Therefore we chose to reference the poster (an AGU fall meeting conference contribution, which is appropriate to cite) in a qualitative manner, i.e. not using any numbers from this study or including it in any of our graphs.

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