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

M. von Hobe et al.

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Before addressing the specific points of the review, we want to discuss the question raised by Dr. Golden "does the paper itself advance this understanding (i.e. the understanding of the ClO/Cl_2O_2 kinetics)?". Clearly, the paper does not present any new laboratory, field or theoretical data. But that was never the intention. A large number of papers on the various aspects of the ClO/Cl_2O_2 kinetic system have been published over the past two decades, but the appearance of ever new studies has not always led to a better understanding, at least quantitatively. With the latest studies by Boakes et al. and Pope et al., the uncertainties for the dimer formation and photolysis rates seems larger than ever. It is one of the main purposes of our paper to clearly point out this lack of understanding. Looking at laboratory, field and theoretical studies together, we show that either some of the results published have to be erroneous, or there must

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be more complex atmospheric chemistry governing the ClO/Cl_2O_2 system than currently believed. We have also tried to identify a consistent combination of parameters that is consistent with our theoretical understanding. This has been done previously by various authors, including for example D. Golden and R. Stimpfle, but not nearly in as comprehensive manner as done in our paper. Thus, while we are not claiming to have fully understood the kinetics of the ClO dimer cycle, we feel our paper makes a solid contribution by clearly naming the problems associated with understanding these kinetics, and by raising some key questions that need to be answered in this context.

As Dr. Golden points out, the evaluation of the rate and equilibrium constants has been extensively discussed in the literature. But our paper not only attempts to create constraints through the use of atmospheric data, although in our opinion that alone would justify publication. Our paper critically makes use of all available information (including studies not yet represented in the JPL evaluation) from laboratory studies, atmospheric data and theoretical calculations in an - in our opinion - unprecedented fashion. Of course some of the methods used to reevaluate the rate and equilibrium constants have been used by others. Trying to guide the reader through our line of argument as comprehensively as possible, we describe some of these studies in detail rather than simply including the references (which are of course also given). And sometimes we do go somewhat further in our analysis compared to others. We go into much more detail constraining the dimer formation rate constant using the Troe unimolecular rate theory than for example Bloss et al. (2001), who find agreement of their measured rate constant with theory using β_c close to 1, or Golden (2003), who finds that comparison of the parameters in the current NASA/JPL format with RRKM/master equation modelling suggests an "inordinately high energy transfer efficiency".

Concerning our use of unimolecular rate theory as described in the Troe (1977a,b, 1979) and Patrick and Golden (1983) references, we are well aware of the limitations of this approach and the possible large errors that can arise when estimating some of the parameters in Eq. (4), including F_{anh} and F_{rot}. It should be noted that we do not use or recommend using a rate constant from this theoretical calculation. Absolute values resulting from rate theory calculations are only included in the plots for comparison. To put some constraints on kdiss and krec, we do use the temperature dependence of these quantities resulting from Troe theory. As can mostly be shown by simple calculus, the uncertainty in the temperature dependence of the parameters in Eq. (4) is less than the uncertainty in their absolute values. We use this temperature dependence to: 1) extrapolate the Bröske and Zabel (2006) measurements that were made in a rather limited temperature range (Page 7913, lines 10 - 24), and 2) constrain the temperature dependence of krec. β_c is then used to tune the magnitude of the theoretical rate constants, so the resulting β_c values are naturally empirical and may be influenced by uncertainties in the various correction factors used in Eq. (4). The large range of β_c values obtained when comparing theoretical strong collision rate constants to weak collision rate constants measured in the laboratory has been demonstrated by Patrick and Golden (1983): β_c values in their tables range from 3.9 x 10^{-7} to 1.81. In that respect, the β_c value of 0.6 needed to rationalise Bröske and Zabel (2006) seems fairly close to the expected 0.3 at 300 K, certainly closer than the 0.8 - 1.0 reported by Bloss et al. (2001) to rationalise their laboratory results (cf. above). We discuss on page 7915, lines 14 - 17, that by definition $\beta_c < 1$. Certainly, in none of our calculations or results do we apply a non-physical $\beta_c > 1$!

Interestingly, K_{eq} at temperatures below 300 K has been revised upwards (!) in the new JPL 2006 with A = 9.3 x 10^{-28} and B = 8835, which at 200 K is a factor of 2 higher than Cox and Hayman (1988).

The intercept at low pressures seen in some laboratory studies on k_{rec} has been discussed extensively in the literature. We did not repeat this discussion as we felt it was not that important for our arguments. However, following Dr. Golden's advice, we will include a short paragraph on this issue in Sect. (4) of a revised version.

Concerning the last paragraph of Dr. Golden's review, we believe the statement "this paper says that the data can be reconciled with atmospheric measurements within

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uncertainties" does not adequately reflect the conclusions of our paper. We clearly identify which data (or combinations thereof) can be reconciled with atmospheric measurements and which can not. The implications of the Pope et al. (2005) values are also discussed (Page 7923, lines 22 - 22). We agree with the view that this study will "throw a monkey wrench into everything", but does this mean all papers on this topic should stop, until this work is published? Indeed, we feel analyses such as this will be needed more than ever once the Pope et al. findings are finalized, and submitted for publication. So while we would be the first to say our paper is not the "last word" on this subject, we feel it provides an important synthesis of present knowledge, and possibly an appropriate starting point for approaching the problem once the Pope et al. results are available for quantitative use.

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

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