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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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Review of “Understanding the kinetics of the ClO dimer cycle” by von Hobe et al.

The purpose of this paper is perfectly reflected in its title, so the question is does the paper itself advance this understanding. My quick bottom line is that it does, but not a lot.

There are three elementary processes involved in this cycle. The first two are the reaction to form the dimer and its reverse. These are of course connected via the equilibrium constant. The third is the photolysis cross section. The rate constants for the reactions krec and kdiss are pressure (and nature of the colliding gas) and temperature dependent, although their ratio, the equilibrium constant is only temperature dependent.

In principle these should be measurable independently in the laboratory, with the ratio of krec to kdiss as a check on an independent measurement of the equilibrium constant or some other combination of the redundancy represented by the relationship among these three quantities. Attempts at these measurements and comparisons among them are well-described in the paper.

As pointed out, the relationship among the three quantities might be used to model certain atmospheric observations. In fact, since the laboratory determinations are subject to uncertainties, the atmospheric observations should offer some constraints on the values, providing that uncertainties in the atmospheric observations are not too large. Since the evaluation of the rate constants and equilibrium constant has been well-discussed in the literature and the cross-section data has also been discussed, this paper contributes by attempting to create the constraints mentioned above through the use of atmospheric data. (There is a new JPL evaluation JPL-2006. Unfortunately this was formulated before the publications by Plenge and Bröske and Zabel.)

In the course of their evaluation the authors re-evaluate the rate constant and equilibrium data in a manner used by others. I think one of the disadvantages of this approach is that none of these authors has a substantial background in chemical kinetics and they have not understood the limitations to the approach used in the Troe references and Patrick and Golden. The calculations of the quantity Frot is certainly fuzzy at best. The value of Fanh does not, because we don't know how to do it, take into account stretch-bend interactions. The value of c is simply empirical given our lack of real understanding of the details of energy transfer. It does seem that this value is usually close to 0.3 in air at 300K, so 0.6 as applied to rationalize the Bröske and Zabel data does raise a red flag.

The authors choose to evaluate the equilibrium constant using the Cox data and the Plenge heat of formation. This is perfectly ok. However, Cox has stated that he didn't feel comfortable with the lowest temperature two points, and I don’t see how Cox differs from JPL. See graph below, which also includes the JPL-2006 recommendation. (The system didn’t accept the graph!)

In the laboratory measurements of ClO+ClO, some studies find an intercept at low pressures and others do not. This has not been explained.

The box model calculations are somewhat helpful, but given the not yet published work of Pope et al from JPL on the cross-section and the Boakes higher value for the rate constant krec, I just don’t find that this paper helps that much.

So fundamentally this paper says that the data can be reconciled with atmospheric measurements within uncertainties, but the uncertainties seem large and some are non-physical (i.e. c>1.), and the Pope values will throw a monkey wrench into everything.

I don’t feel the need for this paper to be published.

Sorry for being so negative!

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