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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "UV spectroscopic determination of the chlorine monoxide (ClO) / chlorine peroxide (ClOOCl) thermal equilibrium constant" *by* J. Eric Klobas and David M. Wilmouth

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General Comments

Early observations under perturbed ozone hole conditions found that ClO was non-zero in polar darkness, a result that was explained by the equilibrium with a weakly-bound adduct of ClO. A body of subsequent work showed that this species was chlorine peroxide, ClOOCl. Photolysis of ClOOCl to liberate chlorine atoms, while preserving the O-O bond, is the rate-determining step in the catalytic scheme proposed explain sudden and rapid loss of ozone over Antarctica. It is now known that similar chemistry occurs in the Arctic and in exhaust plumes of rockets fueled by ammonium perchlorate. The research group at Harvard has proposed that this chemistry may be important over the continental United States in summertime. The competition between ozone-destroying photolysis of ClOOCl and harmless thermal decomposition of ClOOCl is a strong function of temperature, largely determined by the magnitude of the equilibrium constant for exchange between ClO and ClOOCl. Roughly speaking, when the temperature in the stratosphere is greater than about 230 K, thermal decomposition of ClOOCl begins to dominate over photolysis, and the effectiveness of catalytic destruction of ozone by chlorine is rapidly diminished. Therefore, in order to account for ozone destruction by chlorine quantitatively, especially above 220 K, one needs a value for Keq that is very accurate.

There are additional reasons why careful laboratory measurements of Keq are important, in particular the key role in linking observations of ClO to the budget of reactive chlorine, the difficulty of measuring ClOOCl in the atmosphere with sufficient accuracy to constrain ozone loss calculations, and demonstration of the fundamental chemical mechanism for ozone destruction under chlorine-activated conditions.

This paper describes a careful and thorough measurement of the ClO/ClOOCl equilibrium over the temperature range ∼230 K to 300 K using a newly designed, moderate-pressure discharge flow reactor coupled to an absorption cell for direct measurements of ClO and ClOOCl using well-characterized UV spectroscopy. This was no easy task, and the authors are to be commended for their high level of preparation, care, and execution of the experiment that is evidenced by the high precision of the results (i.e., near-linear van't Hoff relationship) and closeness to previous results. A key takeaway message is that combined with another recent study (by Hume et al., 2015 - see reference in paper), recommendations of Keq values for use in atmospheric modeling can be improved; in particular, uncertainties in those recommendations at temperatures relevant for stratospheric ozone loss can be reduced. I agree, for the most part, with this conclusion, but because this is the main conclusion of this paper the authors have a little more work to do to make a solid case. My specific comments follow.

Specific Comments

I find the overall presentation of experimental methods, schematic of the apparatus, and figures supporting the conclusions to be clear, adequate, and (for the most part) necessary. However, there were several points where I was craving additional detail in order to convince myself that the uncertainties have been evaluated adequately.

The authors need to present more details of their data and error analysis, clearly addressing precision (statistical errors), accuracy, and possible systematic errors. It is possible that they have adequately addressed all these in their final assessment, but because the main point of the paper is that this study can reduce the current errors assigned to Keq by the JPL assessment panel, they need to spend more time and focus on this aspect of the study. I highly recommend adding a few elements to the paper:

1. Please show an enlargement of residual spectra (e.g., as in Figure 2) with examples calculated at the 1-sigma ranges of the uncertainties. This is especially important for the results at lowest temperatures where ClO absorbances are smallest relative to total absorbance due to the [ClO]-squared nature of Keq.

2. I think it would be very useful to plot the results of the Keq calculations versus inverse temperature of individual replicates prior to temperature averaging. This will help illustrate the reproducibility of the runs (i.e., precision) and give a better sense for the density of replicates at specific temperatures. Note, also, that it is more appropriate to average log(Keq) values from individual replicates than to average Keq values (as described on Page 5, line 25) to avoid a systematic bias of a few percent due to the exponential nature of Keq.

3. Because of the strong dependence of Keq on temperature, a more detailed description of temperature variations and accuracy is essential. Please show (or describe)

how temperature varies axially and radially within the measurement cell during a given replicate. Also, it would be useful to know how much temperature varies with time over the course of a particular replicate. I am a little concerned that a single-point measurement of temperature in the center of a measurement cell may not be adequate for a quantitative assessment of uncertainties (e.g., note that a 1.0 degree variation in temperature translates into a 15% variance in Keq). Presumably the uniformity of temperature has been carefully measured and documented at various temperatures. If so, presentation of such evidence will greatly strengthen the case that this new measurement can be used to reduce uncertainties in the JPL assessment.

4. I appreciate the rationale for co-varying pressure and temperature; however, given the possibility of systematic biases due to pressure (e.g. secondary reactions), it would be useful to know if any detailed measurements with varying pressure were carried out for a fixed temperature. On Page 6, starting on Line 10, the authors state “The precision of repeated measurements conducted at the same temperature but varied flow rates and pressures did not statistically deviate from the precision from temperature-dependence alone.” Over what range (or percentage) were flow rates and pressures varied for a fixed temperature? Or does this refer to unintended variations that may have occurred over the course of a particular replicate?

5. The authors need to show a more detailed error analysis that traces the various sources of error (e.g., from spectral fitting, temperature, and errors in rate parameters for interfering secondary reactions, if relevant). They should also include an assessment of potential systematic errors (such as those described above). They could expand Table 1 to include these errors. I am not sure that the standard deviation values listed in Table 1 are uniformly illustrative - for example, there is no way that a 0.3% standard deviation from two independent measurements at 285.1 K is representative of the true precision when the standard deviation is 10% for the 8 replicates at 253.3 K.

Minor comments

6. Abstract/conclusions. The authors should report the value of Keq over the temperature range 230 to 299 K, reflecting the range over which they have calculated their experimental averages. Alternatively, if they want to claim significance for a measurement at 288 K then they should report a value that is measured over the range 285.5 to 290.5 K (assuming a similar 5 degree average).

7. Page 2, line 28. Please elaborate on "…optimization of target chemistry." What, specifically, was optimized?

8. Page 2, lines 30-31. Discuss whether or not you expect discharge of oxygen to produce O2(singlet delta), and if so, how you might expect reactions of this specie to impact your results.

9. Page 3, line 30. Please list your carrier gas flow rates and residence times in each of the cells.

10. Page 7, lines 31-33. It might be helpful to include a representative 1 sigma uncertainty bar on the results from the February 3, 2000, SOLVE/THESEO ER-2 flight in Figure 5. Please note whether "measurement uncertainties" for those data points refer to uncertainties (or variability) in measured concentrations of ClO and ClOOCl, uncertainties (or variability) of measured temperature, or both. This could also be illustrated with the use of vertical (for concentrations) and horizontal (for temperature) error bars.

11. Page 9, line 8. You might elaborate on how, specifically, the uncertainties in JPL recommended Keq can be reduced. Should results of previous experiments be discounted by the JPL panel? Or should results of various experiments over the years be averaged and weighted according to errors reported at the time?

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