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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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We would like to thank the referee for his detailed and constructive comments and have revised the manuscript accordingly. The reviewer's comments are presented below in **bold** text and our responses to the reviewer appear in plain text.

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 K_{eq}.

The figure requested is shown below (Figure 1) for two independent experiments in which the calculated K_{eq} approximates the 1-sigma uncertainties. Note that the Y axes are different between the two panels. Again, as in Figure 2 of the manuscript, OClO and Cl_2O_3 are included in the fit, but excluded from the visualization as their formation is suppressed by the operation of the reaction cell at 200 K and would appear as flat lines at the 0 A.U. line of each panel.

2. I think it would be very useful to plot the results of the K_{eq} 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(K_{eq}) values from individual replicates than to average K_{eq} values (as described on Page 5, line 25) to avoid a systematic bias of a few percent due to the exponential nature of K_{eq}.

In this case the difference is minimal, but we agree that it is more appropriate to fit the K_{eq} values from individual replicates rather than the binned data. A third law fit of all independent measurements produces a B parameter value of 8528 K, which represents a change of 0.059% from the value of 8533 K reported in the original manuscript. We have revised the manuscript throughout to reflect this value.

A new Figure 3 now appears in the manuscript and is replicated below as Figure 2 of this response. In this figure, the independent experimental results are indicated as small orange circles and are used to determine the black fit line. Note that the density of orange points is obscured for some temperatures where the scatter is small, and thus the updated Table 1 should be referenced.

3. Because of the strong dependence of K_{eq} 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 K_{eq}). 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.

As shown in Figure 1 of the original manuscript, the temperature measurements were conducted at several key points (including immediately prior to the entrance of the gas mixture to the absorption cell and at the halfway point of the absorption cell). For all results reported in this work, the temperature difference between these points was less than 1 K. Radial measurements of the temperature gradient were also performed. Temperature differences of less than 0.5 K were observed between the wall region and the center of flow. We note that, to optimize lamp signal (i.e., to avoid clipping the light), the thermistor junction in the absorption cell was maintained at an intermediate position between the wall and the center of flow for all experimental results reported in this work.

Absorbance and equilibrium cell temperatures can be maintained at a near-constant temperature for an indefinite period of time and are well-insulated from any interference from the surrounding environment. The insulating material used here, cryogel-Z, is an extremely high-quality insulating material. There was never any condensation of water on the experiment, even when operating at 203 K (the lowest attainable temperature of the experiment) for several hours. Gas temperature was observed to remain static (variation within the noise levels of the thermistor ADC) over the course of a single sample acquisition (3 minutes time).

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?

Experiments were performed at a selection of pressures in order to verify asymptotic equilibrium behavior at a fixed temperature. It was typical to scan pressures by ± 20% of the target pressure when evaluating conditions prescribed by the kinetic model. Pressure and flow rates were maintained at a constant value during sample acquisition.

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.

Page 6 of the original manuscript contains a detailed assessment of error from spectral fitting, temperature-dependence, and other obvious potential systematic errors. As for secondary reactions such as the formation of OClO and higher oxides of chlorine, these are highly suppressed in our system due to the operation of the reaction cell at cold temperatures. The Figure 2 caption states that OClO and Cl_2O_3 concentrations were small (and even if present, they would not compromise the experiment, because they are included in the spectral fits). We also point out that we essentially quench the Cl + ClOOCl reaction pathway by operating the experiment with an excess of ozone.

We have revised the method by which we calculate K_{eq}, now evaluating each independent measurement separately in an ordinary least squares fit. Because of this, metrics required for the reproduction of the weighted-least squares fit of the binned data, such as standard deviations of similar-temperature replicates, have been removed from Table 1.

Minor comments

6. Abstract/conclusions. The authors should report the value of K_{eq} 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).

We now calculate K_{eq} using every independent replicate, spanning the temperature range of 228 –301 K.

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

The various flow sections shown in Figure 1 are operated at the optimal conditions for achieving thermal equilibrium. This sentence is simply an introduction to the flow section descriptions that follow.

8. Page 2, lines 30-31. Discuss whether or not you expect discharge of oxygen to produce $O_2(^1\Delta)$, and if so, how you might expect reactions of this specie to impact your results.

$N_2/O_2/O_3$ addition is performed downstream of the microwave discharge, which maintained a constant salmon color when chlorine was not injected and a constant deep

purple color when Cl_2 was injected. The color of the discharge did not change when O_2/O_3 flows were turned on. When pressure was scanned above 533 mbar, the discharge was observed to turn white, indicating backflow of nitrogen from the injector port. All reported experiments were conducted below 333 mbar.

The exact placement of the microwave cavity relative to the O_3 addition port varied for some experiments, as did the size of the discharge depending on flow conditions, but during operating conditions as reported in this work (100 – 333 mbar), we observed no interfering absorbers in the UV spectra (e.g., residual traces were homoskedastic). We observed no evidence of interference from excited oxygen or nitrogen species produced in the microwave discharge.

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

Flow rates for the carrier gases ranged between ~1.0 –1.8 L/min and residence times in the absorption cell ranged between ~1 –11 seconds, depending on pressure and temperature. These values have been added to the manuscript on page 3 line 30 and page 4 line 2.

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.

Including the 2σ uncertainties, all of the SOLVE/THESEO data points overlap the 2σ uncertainty range of our fit. This fact is now stated in the manuscript on page 8 lines 3 –5.

11. Page 9, line 8. You might elaborate on how, specifically, the uncertainties in JPL recommended K_{eq} 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?

The current uncertainty envelope is derived from the minimum uncertainty required to envelop the independent results of Cox and Hayman (1988), Nickolaisen et al. (1994), and Hume et al. (2015). Our results exhibit significantly less scatter than the two earlier studies. Though we do not presume to tell the JPL panel how to evaluate the uncertainty of the ClO/ClOOCl equilibrium constant, a similar approach to the one conducted to determine prescribed uncertainty for the 2015 data evaluation using our work instead of the older studies would produce a significantly smaller uncertainty.

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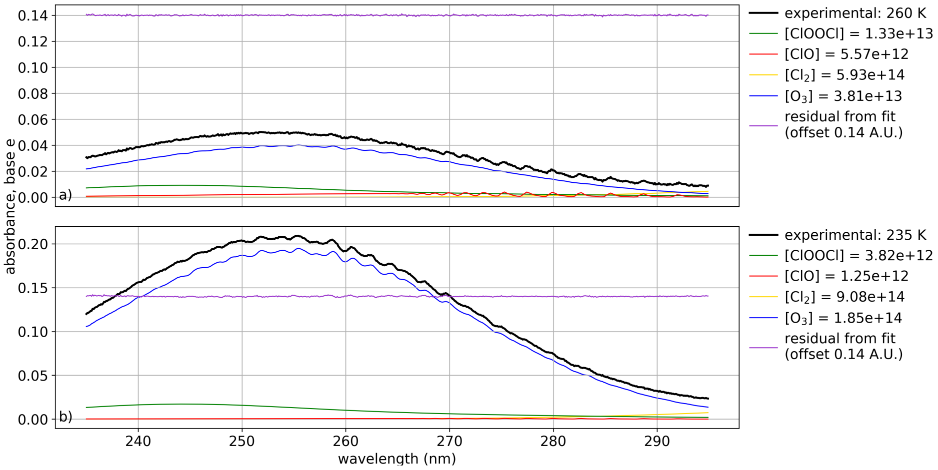

Fig. 1. deconvolution of raw absorbance spectra into individual gas components.

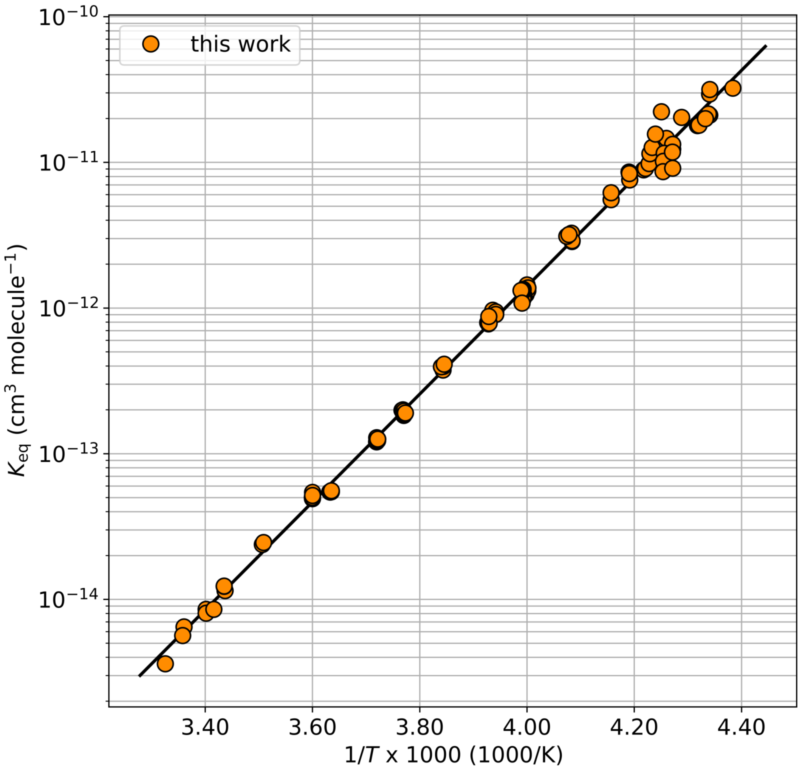

Fig. 2. All independent experimental values of the thermal equilibrium as a function of 1000/T