

## ***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***

**J. Eric Klobas and David M. Wilmouth**

klobas@huarp.harvard.edu

Received and published: 31 January 2019

We would like to thank the referee for his or her 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.

**The microwave discharge that generates atomic chlorine will also be a strong source of VUV radiation due to the strong Cl resonance lines. Since the ozone is introduced only 2.5 cm downstream, one would expect significant photolysis of**

C1

**the ozone, generating  $O(^1D)$ ,  $O(^3P)$ ,  $O_2(a^1\Delta)$ , etc. Also the discharge that generates ozone will also form copious amounts of the singlet states of  $O_2$ . Does the chemical modeling of this system show that none of these reactive species are causing trouble downstream?**

There was no evidence that secondary reactions interfered with our measurements.  $O_3$  was transported 3 m subsequent to generation prior to injection into the experiment.  $O_2(^1\Delta)$  would certainly be quenched prior to injection over this length scale. We observed no evidence of interfering species in the absorbance spectra after fitting for known species (e.g., residual was homoskedastic).

During initial setup and calibration of the apparatus, experiments were performed in which the microwave cavity was placed at varying distances from the ozone injection port and ClO absorbances were quantified. The selected position of the cavity, ~2.5 cm upstream of the ozone injector, was found to be the optimal position for production of ClO (competing with the recombination of Cl). Please our response to Referee 3 for additional details on this topic.

**Typical gas flow rates or the velocities of the flows at the different pressures should be given.**

We have revised page 3 line 30 and page 4 line 2 of the manuscript to provide this information.

**Page 4, line 5: What is the resolution (FWHM) for this slit width?**

The grating and slit width combination produce a resolution of ~0.3 nm. Page 4, line 5 of the revised manuscript now includes this information.

**Page 4, line 10: What are “dark spectra” and how are they used in subsequent spectra?**

Prior to any day of experiments, a spectrum is collected in which the UV lamp is off. This spectrum is subsequently subtracted from all subsequent spectra to provide a

C2

correction for dark current in the photodetector.

**The two runs shown in Fig. 2 can be used to calculate two equilibrium constants: for 230K,  $K = 1.84\text{E}(-11)$  which is 34% lower than Equation 3 predicts; for 300K,  $K = 6.52\text{E}(-15)$  which is 34% higher than Eq.3. Are these typical deviations?**

The spectra presented in Figure 2 were selected because they both featured very similar concentrations of  $\text{O}_3$ , allowing for comparison of the fit residual on the same scale. While these spectra are both members of the experimental ensemble reported, they are far from the best examples we could have chosen here to produce a  $K_{eq}$  in close agreement with the mean reported value. A full list of independent experiments is now presented in Table 1.

**The treatment of the experimental data by “binning” is not the best use of the experimental data. If I understand this manuscript correctly, all values of  $K$  measured within a 5 K range of temperatures are averaged (average of  $K$ , or  $\ln(K)$ ?) and then listed in Table 1 along with the averaged temperature (average  $T$  or  $1/T$ ?). For example, if measurements were done at 250 and 255 K, one should get, according to Equation 3,  $K(250) = 1.438\text{E}(-12)$  and  $K(255) = 7.364\text{E}(-13)$ . The average of  $\ln(K)$  of these two  $K$ 's gives -27.602 or  $K_{(ave)} = 1.029\text{E}(-12)$ , which is close to the value predicted by Eq. 3 for  $T = 252.5$  K. But then using the deviations of these two values of  $K$  from the average  $K$  to get an estimate of the standard deviation of the measurements is not valid. There is no information about the random measurement errors in these two numbers. They are different because they were measured at two different temperatures. Supposed one has only two measurements in one bin that were at different temperatures but, due to random errors, gave almost the same value for  $K$ . The calculated “standard deviation” would now be very small and the weighting factor very large. That is not right. The numbers in the last column in Table 1 should be eliminated. It would be better to do the least squares fitting using all 114 experimental measurements with equal weighting. Then the deviations of the experimental  $K$  val-**

C3

**ues from the least squares fit would give information about the precision of the measurements.**

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 plot of these 114 deviations vs.  $1/T$  would be useful. As mentioned, this will probably show increasing deviations at both the upper and lower limits of temperature.**

The reviewer is correct that there are increasing deviations at the upper and lower limits of temperature. A new Figure 3 of all independent results is now included in the manuscript.

**Certainly the experimental values of the 114 measurements should be preserved, either in a table in the manuscript or as supplemental material.**

These independent measurements are now included in Table 1.

---

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2018-1120>, 2018.