Poster A43A–0870

The Ozone Hole – a Mystery probably not reborn

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The history of the Ozone Hole

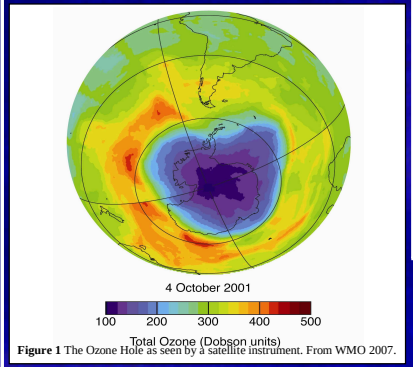

Figure 1 The Ozone Hole as seen by a satellite instrument. From WMO 2007.

In 1985, *Farman et al.* discovered a substantial thinning of the stratospheric ozone layer over Antarctica in spring (Figure 1). Key to understanding this "ozone hole" were the heterogeneous activation of chlorine on polar stratospheric clouds *(Solomon et al., 1986)* and the ClO–dimer (*Molina and Molina, 1987*) and ClO–BrO *(McElroy et al., 1986)* catalytic cycles that rapidly destroy ozone at cold temperatures and high solar zenith angles (Figure 2).

Subsequent work describing the kinetics of these catalytic cycles and observations of chlorine and bromine compounds in the polar stratosphere supported and corroborated the theory.

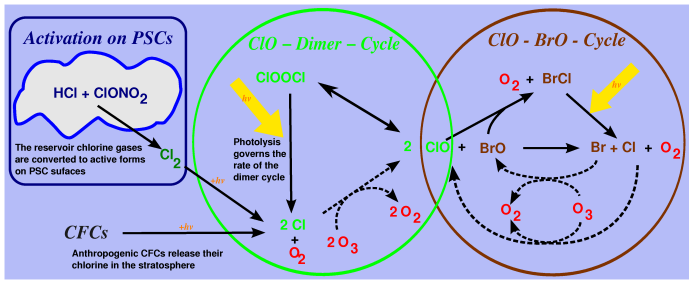

Figure 2 "Polar" catalytic ozone destruction cycles. O_3 loss rates are governed by ClOOCl photolysis: it is usually the rate limiting step in the ClO–dimer–cycle and influences the ClO–BrO–cycle by governing ClO. Dashed arrows denote "instantaneous" processes.

More than 20 years after the discovery of the ozone hole, a new laboratory experiment by *Pope et al.* suggesting much smaller absorption cross sections of ClOOCl (Figure 3) calls into question our understanding of polar ozone depletion.

With the new cross sections, both the ClO–dimer–cycle and the ClO–BrO–cycle run much slower, and atmospheric observations of neither ClO and ClOOCl (Figure 4) nor ozone loss are reproduced by model simulations (Figure 5):

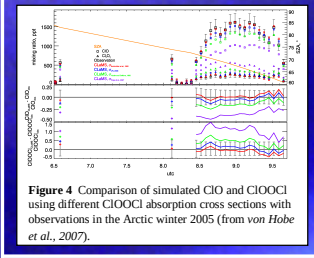

Figure 4 Comparison of simulated ClO and ClOOCl using different ClOOCl absorption cross sections with observations in the Arctic winter 2005 (from *von Hobe et al., 2007*).

the known catalytic cycles would not cause an ozone hole!

This could have severe implications for our ability to predict future polar ozone depletion. It may even raise questions about the recently prognosticated recovery date.

But do we trust a new study that is so clearly at odds with atmospheric observations?

A challenge to the theory

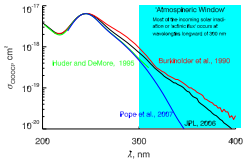

Figure 3 Selected ClOOCl absorption cross sections. The "new" cross sections are much smaller in the atmospherically relevant region > 300 nm, resulting in reduced ClOOCl photolysis rates

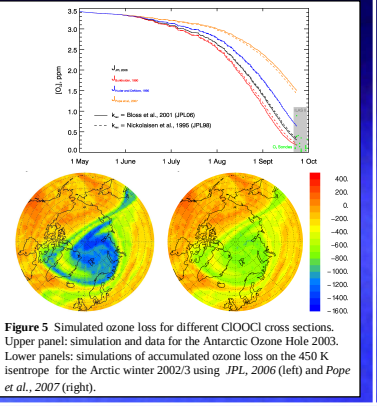

Figure 5 Simulated ozone loss for different ClOOCl cross sections. Upper panel: simulation and data for the Antarctic Ozone Hole 2003. Lower panels: simulations of accumulated ozone loss on the 450 K isentrope for the Arctic winter 2002/3 using *JPL, 2006* (left) and *Pope et al., 2007* (right).

Evidence for larger cross sections – Matrix isolation spectroscopy of ClOOCl

ClOOCl was prepared and trapped as described by *Pope et al.*. A Cl_2/O_3 mixture was photolysed at –70°C and trapped at –128°C (Figure 6). Then the trap was pumped at the same temperature to remove any co-trapped Cl_2.

The sealed trap was moved to a matrix-isolation apparatus (Figure 7, *Müller and Willner, 1992*), where the contents were slowly evaporated into a Ne-Matrix.

IR spectra were used to identify ClOOCl (Figure 8). The only impurity identified was a small amount of OClO.

A UV spectrum (SUV1 in Figure 9) of the ClOOCl containing matrix was recorded, followed by irradiation at 255 ± 23 nm (using an interference filter) to convert the ClOOCl to Cl_2 and O_2. A further IR spectrum was used to check for complete ClOOCl removal and possible products other than Cl_2 (Figure 8). Finally, a second UV spectrum (SUV2 in Figure 9) was recorded.

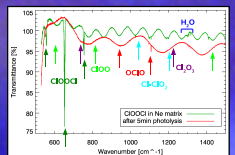

Figure 8 IR spectra of the matrix before and after photolysis

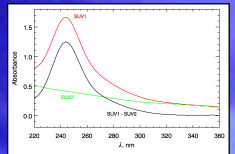

Figure 9 UV spectra of the matrix before (SUV1) and after (SUV2) photolysis

THIS MATERIAL IS *VERY PRELIMINARY*: THE EXPERIMENT WAS COMPLETED < 2 WEEKS AGO !

Unfortunately, there was a non-zero background due to matrix scatter and refraction effects that depends on the amount of material (i.e. mainly Ne) in the matrix. However, SUV2 contains only matrix isolated Cl_2 and O_2 and should scatter in exactly the same way as SUV1. We therefore used SUV2 as background, i.e. we subtracted SUV2 from SUV1. While this leads to negative absorbances in the region of Cl_2 absorbtion, the result should represent the spectrum of pure ClOOCl below 290 nm. This is scaled to the peak absorption cross section at 245 nm to compare with Pope *et al.* and the earlier study by Burkholder *et al.* (Figure 10).

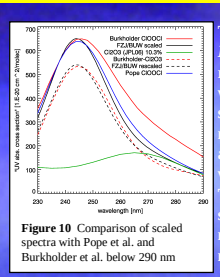

Figure 10 Comparison of scaled spectra with Pope et al. and Burkholder et al. below 290 nm

The agreement with the *Pope et al.* spectrum is rather good in this wavelength region, showing that their method of preparing and purifying ClOOCl was indeed successful. The reason for our spectrum being slightly narrower could be a matrix effect.

Obviously, the agreement with *Burkholder et al.* is not as good. However, the *Burkholder et al.* spectrum is reasonably well reproduced by a scaled combination of our ClOOCl spectrum and the Cl_2O_3 spectrum (as taken from *JPL, 2006*).

Assuming that the contribution of Cl_2O_3 would also affect the mass balance applied by *Burkholder et al.* to calculate absolute cross sections, we scaled our spectrum by a factor of 0.93 when converting it to cross sections. *This depends very much on which Cl_2O_3 cross sections are used and may not be entirely correct at this stage!*

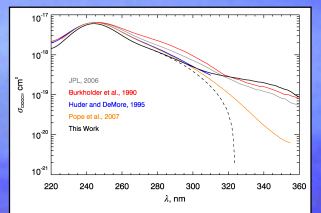

Figure 11 Comparison with previous ClOOCl photolysis cross section measurements

***Pope et al.* analyze their results by fitting the ClOOCl spectrum with two Gaussian expressions and a variable contribution of the known Cl_2 spectrum. Our results suggest that they overestimated the contribution from Cl_2 and that there exists a ClOOCl transition giving rise to an absorption band in this spectral region.**

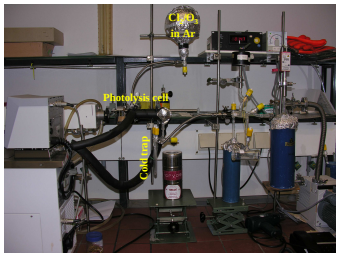

Figure 6 Preparation and isolation of ClOOCl

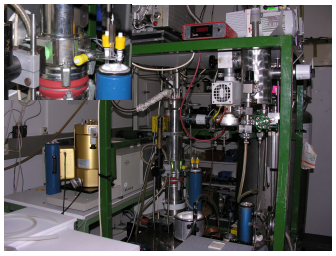

Figure 7 Matrix-isolation apparatus

Preliminary Conclusions:

- ***Pope et al.* was a good experiment! they managed to synthesize ClOOCl in unprecedented yields and purity**
- **However, their Cl_2 correction by "Gaussian fitting" seems to underestimate the ClOOCl absorption in the atmospherically important long wavelength tail of the spectrum.**
- **If we can confirm our new experiment then *there is no new mystery*: the traditional polar ozone loss cycles are sufficient to explain the ozone hole.**

What lies ahead:

- **Verify our results, quantify matrix effects, and attempt to obtain "absolute" (background corrected) spectra to 450 nm**
- **Compare results to *all* previous studies and try to *understand* and *unambiguously identify* the reasons for discrepancies.**

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