Recent laboratory and theoretical studies on the ClOOCl photolysis and other halogen reactions

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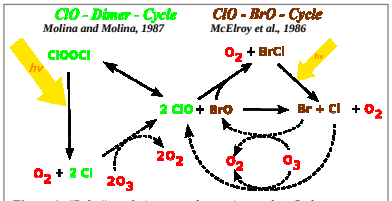

Figure 1 "Polar" catalytic ozone destruction cycles. O_3 loss rates are governed by ClOOCl photolysis: it is usually the rate limiting step in the ClO–dimer–cycle and influences the ClO–BrO–cycle by governing ClO. Dashed arrows denote "instantaneous" processes.

Introduction

In the polar vortices in spring, the following chemical processes lead to ozone depletion:

1. **The chlorine reservoir species HCl and $ClONO_2$ are activated on polar stratospheric clouds**
2. **The activated species – mainly ClO and ClOOCl – participate in the ClO-dimer and ClO-BrO catalytic cycles that rapidly destroy ozone at cold temperatures and high solar zenith angles (Figure 1). The photolysis of ClOOCl effectively determines the rate of ozone depletion.**

To understand these processes quantitatively, information is needed on the chemical and photochemical rate constants. This information is usually obtained in laboratory experiments, with theoretical calculations providing additional, independent information.

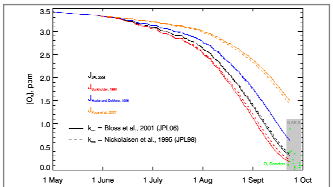

Figure 2 Simulated ozone loss in the Antarctic winter 2003 along a typical trajectory for different ClOOCl cross sections. O_3 sonde data (Tripathi et al., 2006) and the range of ILAS-II O_3 observations within the Antarctic Vortex at 450K pot. Temp. (Tilmes et al., 2006) are shown for comparison. Figure adopted from von Hobe et al. (2007).

Pope et al. (2007) reported that the photolysis of ClOOCl is much slower than previously thought. The new result is incompatible with atmospheric observations and implies that known chemistry could no longer explain the formation of the ozone hole (Figure 2). Obviously this has severe implications for our ability to predict future polar ozone depletion.

Previous studies on ClOOCl UV/Vis absorption cross sections

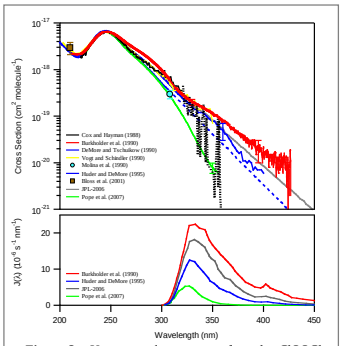

Figure 3 *Upper panel*: summary of results ClOOCl absorption cross section studies currently available. The current NASA-JPL recommendation is also shown while the IUPAC panel recommends the results from the Huder and DeMore (1995) study. *Lower panel*: wavelength dependence of the atmospheric photolysis rate constant *J* at 20 km and a solar zenith angle of 86° obtained using various ClOOCl cross section values. This illustrates the critical importance of the region between 310 and 400 nm and highlights the present level of uncertainty. (Figure courtesy of J. Burkholder, NOAA-ESRL. Lower panel adapted from Pope et al., 2007.)

Existing discrepancies in the ClOOCl absorption cross section data at λ >300 nm (Figure 3) provided motivation for Pope et al. (2007) to revisit this issue.

Rather than resolve the issues, Pope et al. reported ClOOCl absorption cross sections significantly lower than all previous measurements.

Two points are readily apparent from Figure 3:

1. **The disagreement in the published cross-sections is large - a factor of ~4.5 at 330nm, 14 at 350nm and 100 at 380 nm**
2. **The most important region for atmospheric photolysis is 310-400 nm → largest disagreement where it is atmospherically most important!**

It is worth noting that the agreement at the absorption maximum at 245 nm (±15%) is based on four absolute measurements. Other studies make relative measurements, i.e. normalised to the peak value.

Why are the uncertainties in a critical atmospheric parameter so large?

1. **It is hard to prepare pure ClOOCl in the laboratory**
2. **Its UV absorption spectrum lacks any significant features**
3. **Potential interferences from other Cl_xO_y species (e.g. Cl_2 and Cl_2O_2) whose presence in laboratory studies is almost unavoidable and hard to quantify. *Cl_2 seems to be particularly critical (Figure 4).***
4. **The cross-sections in the region of atmospheric interest are low**

Theoretical calculations can provide additional information to compare with the outcome of laboratory studies as well as atmospheric observations.

Theoretical calculations of the energies and oscillator strengths of ClOOCl electronic transitions leading to UV absorption predict 6 or more transitions between 200 and 350 nm. The calculated energy of the transitions with the highest oscillator strengths is in fair agreement with the observed peak absorption at 245 nm. Transitions above 300 nm are predicted to be present but weaker (Figure 5).

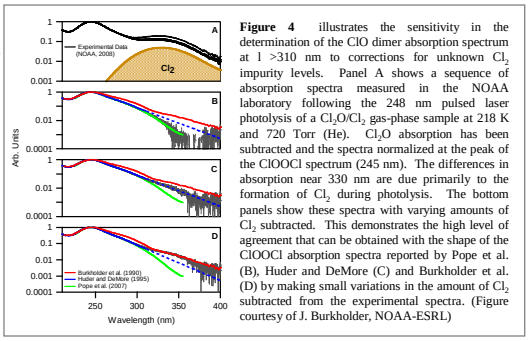

Figure 4 illustrates the sensitivity in the determination of the ClO dimer absorption spectrum at l >310 nm to corrections for unknown Cl_2 impurity levels. Panel A shows a sequence of absorption spectra measured in the NOAA laboratory following the 248 nm pulsed laser photolysis of a Cl_2O/Cl_2 gas-phase sample at 218 K and 720 Torr (He). Cl_2O absorption has been subtracted and the spectra normalized at the peak of the ClOOCl spectrum (245 nm). The differences in absorption near 330 nm are due primarily to the formation of Cl_2 during photolysis. The bottom panels show these spectra with varying amounts of Cl_2 subtracted. This demonstrates the high level of agreement that can be obtained with the shape of the ClOOCl absorption spectra reported by Pope et al. (B), Huder and DeMore (C) and Burkholder et al. (D) by making small variations in the amount of Cl_2 subtracted from the experimental spectra. (Figure courtesy of J. Burkholder, NOAA-ESRL)

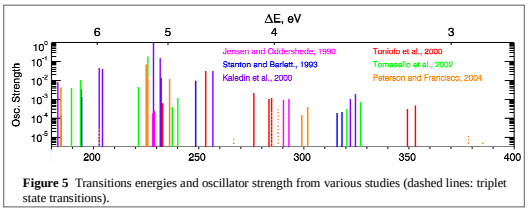

Figure 5 Transitions energies and oscillator strength from various studies (dashed lines: triplet state transitions).

New studies in progress

Four new laboratory studies on ClOOCl UV/Vis absorption cross sections based on independent experimental approaches:

Forschungszentrum Jülich/University of Wuppertal

- **UV spectra of ClOOCl isolated in a neon matrix over the wavelength range 220 – 430 nm**
- **Advantages of matrix isolation:**
  - **no decomposition**
  - **amount and purity of ClOOCl simultaneously tracked by IR and UV spectroscopy**
  - **Cl_2 impurity in the ClOOCl sample removed by low T high vacuum sublimation (confirmed by Raman spectroscopy).**
- **Disadvantages:**
  - **correction for matrix scatter**
  - **possible distortion of UV/Vis spectrum compared to gas phase**
- **Preliminary results (von Hobe et al., *submitted*):**
  - **efficacy of ClOOCl purification by cold trapping by Pope et al. (2007) is confirmed**
  - **weak ClOOCl absorption band centered at ~ 330 nm leads to significant absorption in the long wavelength tail**

NOAA Earth System Research Laboratory in Boulder, Colorado

- **Preparation of ClO radicals and subsequently ClOOCl in the gas-phase by pulsed laser photolysis of static Cl_2O/Cl_2 gas mixtures at temperatures in the range 200 – 235 K at 700 torr total pressure.**
- **Investigation of ClOOCl absorption spectrum by diode array absorption spectroscopy over the wavelength range 210 – 450 nm.**
- **The stoicheometry and mass balance of the reaction system will be used in the determination of the absolute ClOOCl cross sections .**

Harvard University

First experiment to determine ClOOCl cross sections not using absorption spectroscopy!

- **Photodissociation of ClOOCl at 248 nm, 308 nm, and 351 nm using excimer lasers**
- **Detection of Cl atoms produced with atomic resonance fluorescence:**
  - **high signal to noise**
  - **lower concentration of ClOOCl due to high sensitivity of resonance fluorescence detection**
  - **determines product of the ClOOCl absorption cross-section and the quantum yield of Cl atom production**
- **The study is also providing a direct measure of Cl_2, the primary contaminant**

University of Cambridge

- **Generate and measure the UV spectrum of ClOOCl and any Cl_2 impurity present in the same manner as detailed in Pope et al. (2007)**
- **In addition: simultaneous measurement of the Cl_2 concentration in the same absorption cell using cavity enhanced absorption spectroscopy of structured Cl_2 absorption features in the green region of the spectrum (~530 nm) → will allow unambiguous subtraction of the Cl_2 peak**

New calculations:

Univ. of Alabama

- **$ClClO_2$ thermodynamically most stable isomer of Cl_2O_2.**
- **further analysis needed to produce the potential energy surfaces for Cl_2O_2 system → insight into the kinetic barriers to formation and dissociation**
- **presence of low-lying excited states will be important in this regard, but their calculation might be tricky in this system**
- **new information about the electronic transitions and possible absorption features is becoming available.**

Alternative reaction mechanisms and other issues

What reactions involving the ClO dimer are thermodynamically and kinetically possible? → theoretical calculations!

What additional reactions with other species might be important?

ClOOCl + X → → 2 Cl + O_2 could compete with the photolytic destruction

Requirements:
- **k [X] comparable to J_{ClOOCl}**
- **reaction products need to cause O_3 destruction**
- **reaction should have a diurnal variation**
- **→ Test in laboratory experiments!**

A first survey of molecules known to be present in the stratosphere does not reveal any good candidates!

Possibility of an additional ClOOCl absorption at wavelengths greater than 450 nm (photo-dissociation limit ~ 1 µm)?

→ not thought to be likely, but theoretical calculations should provide a good indication if it is likely.

Other reaction whose uncertainty leads to significant uncertainty in the ozone loss calculation: ClO + BrO and its branching ratios into the three reaction channels

→ Recent results support the current NASA-JPL recommendation, but do not reduce the uncertainties significantly.