

Measured and Modeled HOCl Profiles in the Mid-Latitude Stratosphere: Implication for Ozone Loss

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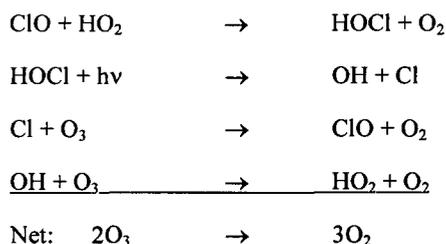
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Abstract. The HOCl catalytic cycle is an efficient ozone loss mechanism in the lower mid-latitude stratosphere. We use a diurnal steady-state photochemical model to calculate profiles of HOCl for conditions encountered by a number of high-altitude balloon flights. To assess how well this model represents ozone loss by the HOCl cycle, we compare our calculations of HOCl and its precursors ClO and HO₂ with measurements obtained by an FTIR solar absorption spectrometer (MkIV), a far-infrared emission spectrometer (FIRS-2), and a submillimeterwave limb sounder (SLS). We then evaluate these comparisons in light of a number of recent laboratory studies of the main formation mechanism of HOCl, the reaction of ClO + HO₂. Those studies measured both the reaction rate constant and the quantum yield for a second product pathway, formation of HCl.

The HOCl catalytic cycle,



is one of the main contributors to ozone loss in the lower midlatitude stratosphere.

To quantify this contribution, we need to know the rate constant, *k*, for the rate-limiting step, reaction of ClO with HO₂ to form HOCl and O₂. This reaction is also the main HOCl production mechanism. Three recent laboratory studies (Knight et al., 2000; Nickolaisen et al., 2000; Laszlo et al., unpublished) caused the JPL 2002 data evaluation panel to effectively halve their previous recommendation for this rate constant for temperatures relevant to the lower stratosphere. These new studies also resulted in an increase in the uncertainty of the value of the rate constant.

In light of the disagreement among the various laboratory measurements of *k*, as well as the importance of *k* to ozone loss in the lower stratosphere, we use a photochemical model to calculate HOCl vertical profiles and then compare these profiles to remote sensing measurements of HOCl obtained with two instruments. We explore how the choice

of rate constant affects the agreement between measured and modeled HOCl. We also compare measured and modeled results for the HOCl precursors, HO₂ and ClO, measured with FIRS-2 and a submillimeterwave limb sounder (SLS), respectively. We then consider the contribution of the HOCl cycle to ozone loss and its sensitivity to the choice of rate constant.

We use a 24-hour steady-state box model consisting of about 200 photochemical reactions (Osterman et al., 1997; Sen et al., 1998), which assumes that production and loss rates for each species are equal when integrated over a 24-hour period. Thus each species is allowed its full diurnal variation. Model inputs consist of profiles of temperature, pressure, ozone, methane, water, carbon monoxide, NO_y, Cl_y, Br_y, and aerosol surface area. Depending on the particular balloon flight, these model inputs are either directly measured or inferred from measurements by well established tracer relations.

For our model runs, we consider three specific HOCl formation rate constants:

- 1) JPL 2002 (slowest *k*),
- 2) JPL 2000 (intermediate *k*),
- 3) Stimpfle et al. 1979 (fastest *k*).

MkIV measures solar occultation in the region 1.8 to 15.4 micron. Spectra are collected for a series of regularly spaced tangent heights below the height of the balloon during either sunrise or sunset. These spectra are then used to simultaneously retrieve vertical profiles of many species, including HOCl.

FIRS-2 measures atmospheric thermal emission in the region 14 to 125 micron. Similarly to MkIV, spectra are collected for a series of regularly spaced tangent heights below the height of the balloon. However, rather than being restricted to sunrise and sunset, the spectra can be taken at any time of the day or night.

We find that although we can use our photochemical model to fit both sets of HOCl data, we can do so only by using different values for the rate constant for HOCl formation. MkIV measurements agree best with model runs that use the slowest rate constant, JPL 2002, while FIRS-2 measurements agree best with model runs that use the fastest rate constant (Stimpfle et al. 1979).

We explore the validity of the measured HOCl profiles by each instrument. Although the HOCl spectral region that FIRS-2 detects is stronger than that detected by MkIV, MkIV compensates by having a much brighter light source, the sun, as compared with the thermal emission measured by FIRS-2. And although FIRS-2 can measure HOCl at times of day when HOCl is at its diurnal maximum, while MkIV is restricted to sunrise or sunset when HOCl is at a minimum, MkIV compensates by measuring absorption along a much longer path length.

Our present state of knowledge is that the FIRS-2 observations of HOCl are most consistent with the fastest rate constant (Stimpfle et al., 1979) while the MkIV observations of HOCl are most consistent with the considerably slower recommendation for k given by JPL 2002. This discrepancy even occurs for data collected by the two instruments when they flew on the same balloon, and is therefore most likely not explained by either atmospheric variability or details of the modeling approach. It is therefore unclear which value of the rate constant for HOCl formation is most consistent with atmospheric observations of HOCl. Owing to the importance of this rate constant to our overall understanding of stratospheric ozone, this issue requires further study, both in the laboratory and with additional measurements of HOCl profiles.

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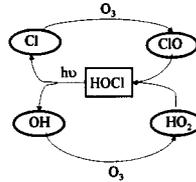
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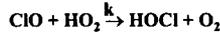
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Background

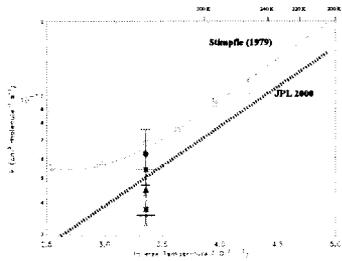
- HOCl cycle is one of the primary halogen mechanisms for ozone loss in the lower midlatitude stratosphere



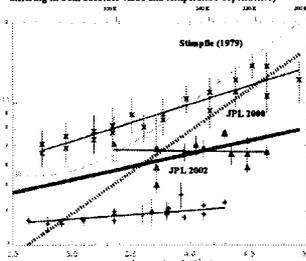
- Problem: Large discrepancy in laboratory measurements of rate-limiting step



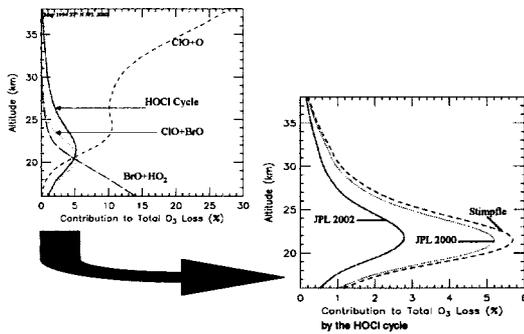
JPL 2000 recommendation (based on 3 studies)



JPL 2002 revision (based on 3 additional studies greatly differing in both absolute value and temperature dependence)



- This revision causes a large decrease in k for stratospheric temperatures
- We find that it halves model calculations of ozone loss by the HOCl cycle:



Purpose of our work

- To test agreement between model and measured HOCl for different values of k
 - JPL 2002 (slowest)¹
 - JPL 2000 (fast)²
 - Stimpfle et al. (fastest)³
- Our approach: use constrained photochemical box model to calculate HOCl for conditions of balloon-borne observations by two instruments, FIRS-2 and MkIV

¹ Sander, S.P. et al., Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Ecol. No. 14, JPL, Pub. 2002-25
² Sander, S.P. et al., Chemical Kinetics and Photochemical Data for Use in Atmospheric Modeling, Ecol. No. 13, JPL, Pub. 2000-2
³ Stimpfle, R.M., R.A. Perry, C.J. Howard, J. Chem. Phys. 71, 5183 (1979)

Method

Photochemical Model

24-hour steady-state box model consisting of about 200 reactions^{1,2}
• Two-km altitude grid, 15-minute time resolution

Input parameters:
• T, P, O₃, N₂O, CH₄, H₂O, NO_x, Cl_x measured by each balloon-borne instrument
• Br_x determined by correlation with measured N₂O
• Aerosol surface area from SAGE II zonal monthly mean profiles

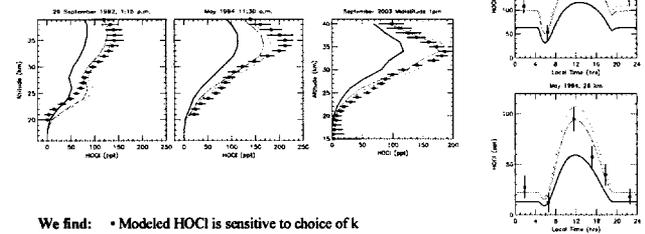
¹ Osterman, G.B. et al., GRL 24, 1107 (1997)
² Sen, B. et al., JGR 102, 3571 (1998)

Balloon-borne Instruments

	Measures	Method	Solar Zenith Angle
MkIV (FIR Solar Absorption Spectrometer)	HOCl and many others	Solar occultation Measures solar absorption from 1.8 to 15.4 μm using Fourier transform spectroscopy	90° at tangent points
FIRS-2 (Far Infrared Emission Spectrometer)	HOCl, HO ₂ , and many others	Measures thermal emission from 14 to 125 μm using Fourier transform spectroscopy	varies
SLS (Submillimeter-wave Limb Sounder)	ClO, HO ₂ , and a few others	Measures thermal emission near 640 GHz using heterodyne spectroscopy	varies

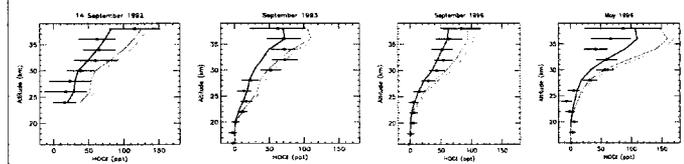
Observed and Modeled HOCl Profiles

FIRS-2 Observations:



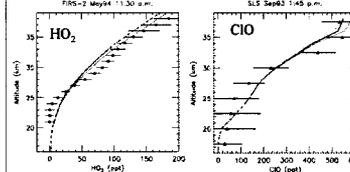
- We find:
- Modeled HOCl is sensitive to choice of k
 - FIRS-2 observations: show poor agreement with current JPL 2002 (slow k) show best agreement with JPL 2000 and Stimpfle (fast k)

MkIV Observations:



- We find:
- Again, modeled HOCl is sensitive to choice of k
 - MkIV observations: show best agreement with current JPL 2002 (slow k) however, display larger error bars than FIRS-2

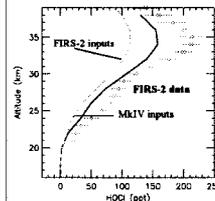
Measured and Modeled Precursor Profiles



- We find:
- Modeled ClO and HO₂ are not sensitive to k (unlike HOCl)
 - ClO and HO₂ observations agree well with model

Can poor agreement between FIRS-2 HOCl and JPL 2002 model be accounted for by model sensitivity to input parameters?

JPL 2002 k:

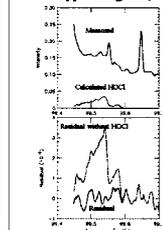


- We find:
- FIRS-2 values for model input parameters always result in lower calculated HOCl than calculated with MkIV input values
 - The 4 most important input parameters are: Ozone, Methane, NO_x, and Cl_x
 - These 4 contribute about equally

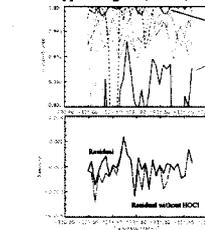
Conclusion: Model sensitivity to measured input parameters accounts for some but not all of the poor agreement of FIRS-2 data with JPL 2002 model results

Signal-to-noise ratio: FIRS-2 vs. MkIV

FIRS-2 typical signal (25 km):



MkIV typical signal (25 km):



Important point:
FIRS-2 data has higher signal-to-noise ratio than MkIV

Conclusions

JPL 2002 revised the rate constant for formation of HOCl, resulting in a factor of 2 decrease for stratospheric temperatures.

We find that this change results in:

- a factor of 2 decrease in model calculations of ozone depletion by the HOCl cycle in the low stratosphere
- a factor of 2 decrease in model calculations of the HOCl profile
- significant discrepancy between modeled and measured HOCl for FIRS-2 field measurements – though less of a discrepancy for MkIV field measurements

Given the stronger signal-to-noise ratio and smaller error bars of FIRS-2 measurements, we suspect the JPL 2000 recommendation may be more accurate than the JPL 2002.