Estimating the abundance of ClO from simultaneous remote sensing measurements of HO_2, OH, and HOCl

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Abstract

Using a simple photochemical model we derive the mixing ratio profile of ClO in the altitude range 20–38 km from simultaneous measurements of HO_2, OH, HOCl, temperature, pressure, and ozone. The measurements were made with the FIRS-2 far-infrared spectrometer during a balloon flight on September 29, 1992. We compare the derived ClO with the ClO profile obtained by the SLS instrument while flying on the same gondola. The good agreement between the two profiles validates our simple model and confirms the relevant rate constants and photolysis cross sections.

Introduction

In the daytime stratosphere the relative abundance of hypochlorous acid (HOCl) and chlorine monoxide (ClO) is determined by the reactions

$$ClO + HO_2 \rightarrow HOCl + O_2 \quad (1)$$

$$HOCl + OH \rightarrow H_2O + ClO \quad (2)$$

$$HOCl + h\nu \rightarrow OH + Cl \quad (3)$$

with rate constants k_1, k_2, and j_3 respectively. Of the other gas phase reactions listed in JPL92-20 [*DeMore et al.*, 1992], the next most important source and loss reactions are slower by factors of 4000 and 6 than reactions 1 and 2, respectively.

Under some conditions, the reaction of $ClONO_2$ and H_2O on aerosol surfaces may provide another significant source of HOCl:

$$ClONO_2 + H_2O(l) \rightarrow HOCl + HNO_3 \ . \quad (4)$$

The probability of reaction 4 on sulphate aerosols decreases rapidly with increasing temperature, changing from 3×10^{-3} at 215 K to 3×10^{-4} at 295 K [*DeMore et al.*, 1992]. For aerosol surface area densities of $5\mu m^2/cm^3$, typical of observations made in the lower stratosphere during 1993 [*Salawitch et al.*, 1994], reaction 4 is 10^2 to 10^3 times slower than reaction 1. At very low temperatures, in the presence of polar stratospheric clouds, or under extreme aerosol conditions, the heterogeneous reaction will have a significant effect on the HOCl abundance. However, for conditions typical of the mid-latitude stratosphere, reaction 4 can be ignored.

Recent work indicates that the rate constant for the reaction of HOCl with O-atoms at room temperature is 20 times higher than the value adopted in JPL92-20 [*Vogt and Schindler*, 1992], making it comparable in importance to the reaction with OH. However, since the reaction with atomic oxygen is believed to have a very large activation energy compared to reaction 2, this reaction will be less significant at cold stratospheric temperatures. Furthermore, since the rate of reaction 2 is already less than 1% of the photolysis rate at solar noon in the mid-latitudes, the small additional loss due to the O-atom reaction is negligible, and will not be considered in the present analysis.

By balancing the creation and destruction rates of HOCl we derive the following expression for ClO:

$$[ClO] = [HOCl]\frac{j_3 + k_2[OH]}{k_1[HO_2]}. \quad (5)$$

We justify the assumption of steady-state by noting that, at a solar zenith angle of 55°, the estimated photolysis rate (see below) implies an HOCl half-life of 22–36 minutes in the middle stratosphere; this is sufficiently short that we can assume ClO and HOCl to be constant equilibrium with each other during the day.

We use equation (5), together with FIRS-2 measurements of HOCl, OH, HO_2, temperature, pressure, and ozone, to estimate the abundance of ClO in the lower to middle stratosphere. We calculate the rate constants k_1 and k_2 using the measured temperature profile and data from JPL92-20. We use the atmospheric radiance program LOWTRAN7 [*Kneizys et al.*, 1988] to estimate the solar flux as a function of wavelength and altitude, using our measured temperature, pressure, and ozone profiles, extended to an altitude of 100 km with the standard profiles provided with the LOWTRAN7 code. Finally, the cross section data from JPL92-20 is used to calculate j_3.

Measurements

The mixing ratios are measured from spectra obtained with the FIRS-2 spectrometer. The instrument and data analysis methods are described in detail elsewhere [*Johnson et al.*, 1995]. The FIRS-2 is a balloon-borne infrared Fourier transform spectrometer which measures stratospheric emission spectra over the wavelength range 14–125 μm. The spectrometer views the sky through an off-axis reflecting telescope with a 0.2° field of view. The telescope elevation angle is measured with respect to a stabilized horizontal reference, with an absolute accuracy of 0.02° under calm conditions.

The data set used here is from a balloon flight launched from Ft. Sumner, New Mexico, on September 29, 1992 at 0750 MDT. The balloon reached a float altitude of 37 km at 1020 MDT, and was cut down 8 hours later. During the flight we recorded spectra at elevation angles ranging from $+30°$ to $-4.62°$, corresponding to a minimum tangent altitude of 16.6 km. For this analysis we have selected a 2.6 hour subset of the data, centered at 1530 MDT, having a mean solar zenith angle of 55°.

Initial temperature and pressure profiles used in the analysis are derived from radiosonde data reported by stations near the flight track. The temperatures are corrected using FIRS-2 measurements of the 15μm band of CO_2. Once the temperature profile has been measured, the pointing angles are corrected using a different portion of the CO_2 spectrum. The rms corrections to temperature and pointing angle are 3.4 K and 0.06° elevation, respectively.

We select a number of spectral windows for each molecule to be analyzed. Each window contains one or several emission lines which are relatively isolated from the lines of other species. We use a non-linear least-squares program to fit the mixing ratio profile to the set of spectra in onion-peeling fashion. We derive independent mixing ratio profiles for each spectral window, and then average the results together to produce the final profile.

In order to evaluate equation (5) we need profiles for HOCl, HO_2, and OH, as well as the temperature, pressure, and ozone profiles which are used to calculate k_1, k_2, and j_3. Descriptions of our HOCl and HO_2 measurements for other balloon flights have appeared elsewhere [*Chance et al.*, 1989; *Traub et al.*, 1990], and retrievals for OH and O_3 are similar. A detailed comparison of our measurements with previous work is described by *Chance et al.* [1995]. We average together results from 24 spectral windows for the final O_3 profile, 21 windows for HOCl, 27 windows for HO_2, and 8 windows for OH.

Results and Discussion

We present the measured profiles and estimated error (1σ) in Table 1. The error includes the statistical fitting error as well as

systematic errors in calibration, elevation angle, and spectroscopic parameters. The statistical error dominates for all the molecules presented in the table. We also present in Table 1 the calculated photolysis half-life of HOCl and the ClO abundance estimated using equation (5). The ClO confidence limits include the uncertainties in HO_2, HOCl, and OH, but not the uncertainties in the reaction rate constants or photolysis cross section.

In Figure 1 we show a comparison of our estimated ClO profile with a profile obtained simultaneously by the SLS instrument [*Stachnik et al.*, 1992]. The measured and estimated profiles are in good agreement above 24 km, having a χ^2 of 3.4 with 4 degrees of freedom (indicating agreement at the 49% confidence level). There appears to be a significant difference between measured and estimated ClO at 20 km. However, due to the low precision of our HO_2 and HOCl measurements at this altitude, we feel that it is more meaningful to use equation (5) to estimate HOCl from the measured ClO and HO_2 and then compare the estimate with the measured HOCl. In this way we avoid comparing one high precision measurement (ClO) with the ratio of two measurements statistically close to 0 (HOCl and HO_2). The estimated HOCl, 46 ± 32 ppt, is in good agreement with the measured value of 8 ± 11 ppt ($\chi^2 = 1.4$ with 1 degree of freedom). For the complete data set the χ^2 is 4.8 with 5 degrees of freedom, corresponding to agreement at the 44% confidence level (the probability of the χ^2 exceeding 4.8 is 0.44) over the full range of the measurements, 20–38 km.

It is worth examining whether or not a modification

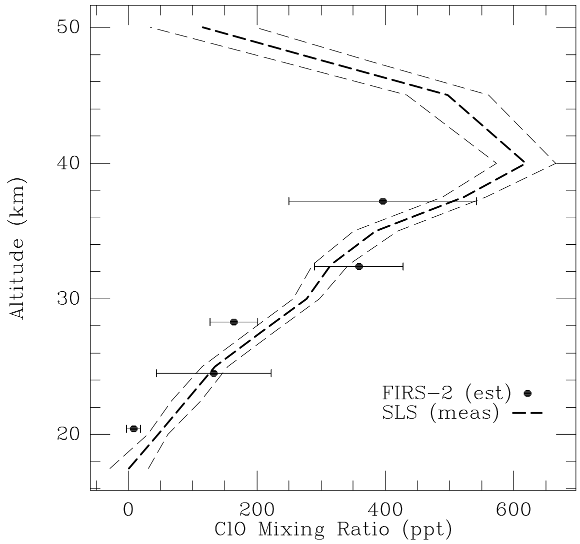

Figure 1. A comparison of estimated and measured ClO mixing ratio profiles for the balloon flight of September 29, 1992. The measurements were made over a period of 2.6 hours with an average solar zenith angle of 55°. The SLS measurements of ClO are represented by the heavy dashed line, with the confidence limits indicated by the light dashed lines. ClO mixing ratios estimated using equation (5) are plotted as solid circles. All errors are 1σ.

of our simple model might improve the agreement between measured and estimated ClO. The numerator in equation (5) is dominated by the photolysis rate, but an error in the photolysis rate is unlikely to change the shape of the estimated ClO profile since the rate changes slowly with altitude. The rate of reaction 2 would have to be much higher before it would have a significant effect on the estimated ClO distribution. Increasing k_2 by a factor of 10 over that given in JPL92-20 would increase the estimated ClO by 11% at 37 km, but would also increase the estimate by 6% at 32 km and so would not significantly improve agreement with the measured ClO. The rate of the next most rapid reaction, HOCl + Cl, would need to be increased by a factor of 50 to cause a 10% increase in the estimated ClO at 37 km. We conclude that no simple change to equation (5) would improve the agreement between measured and modeled ClO.

The effect of errors in j_3 and k_1 is potentially quite large. The estimated uncertainty in the total photolysis cross section is 40% [*DeMore et al.*, 1992]. Due to uncertainty in the temperature dependence the value of k_1 at 215 K is known only to within a factor of 2 or 3. Ignoring

Table 1. Measured and Calculated Profiles from FIRS-2

z, km	P, mbar	T, K	O_3, ppm	HO_2, ppt	OH, ppt	HOCl, ppt	$t_{1/2}$, m	Estimated ClO, ppt
20.4	54.0	212	1.9 ± 0.3	13 ± 8	2.8 ± 1.1	7 ± 9	36	8 ± 11
24.5	28.2	219	4.8 ± 0.2	10 ± 6	3.0 ± 0.8	40 ± 8	33	133 ± 89
28.3	15.8	224	6.3 ± 0.3	35 ± 7	7.6 ± 1.0	79 ± 9	29	164 ± 37
32.4	8.55	232	8.5 ± 0.4	68 ± 11	30.0 ± 2.0	141 ± 14	26	359 ± 69
37.2	4.22	238	7.9 ± 0.4	128 ± 30	120.0 ± 8.0	108 ± 31	22	396 ± 146

the uncertainty in k_2, the abundance of ClO as estimated by equation (5) could be off by as much as a factor of 4. The good agreement in Figure 1 indicates that the systematic error is much smaller than this, and probably is comparable to the measurement uncertainties (25–35%).

Having verified the relationship between ClO, HOCl, and HO_2, we can use FIRS data from other balloon flights to look for trends in ClO. We have retrieved measurements of HOCl and HO_2 (as well as HCl and other species) for 6 balloon flights covering the period 1988 through 1994 and plan to compare the increase in stratospheric chlorine due to anthropogenic emissions with our ClO estimates. We also note that we have an extensive set of measurements both before and after the eruption of Mt. Pinatubo in 1991, which gives us the opportunity to investigate the effects of the eruption on chlorine partitioning.

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