A test of the partitioning between ClO and ClONO2 using simultaneous UARS measurements of ClO, NO2, and ClONO2

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Abstract. The photochemical theory of the partitioning between the chlorine species ClONO2 and ClO in the lower and mid stratosphere is tested for the first time using simultaneous measurements of ClO, NO2, and ClONO2. The theory suggests that over most of the day the production of ClONO2 through the three-body reaction of ClO and NO2 is balanced by the loss of ClONO2 through photolysis. Our analysis tests this theory by utilizing simultaneous measurements of these species from instruments aboard the Upper Atmosphere Research Satellite (UARS), as well as calculations of the photolysis rate of ClONO2 and laboratory measurements of the rate constant for the reaction between ClO and NO2. Between 32 and 10 hPa (~24 and 32 km), averaged instantaneous production and loss rates of ClONO2 agree within ~10%. At 46 hPa (~21 km), the agreement between averaged instantaneous production and loss of ClONO2 is poorer than at higher altitudes, but still within uncertainties. This analysis provides no evidence for any problems in our understanding of the partitioning between the chlorine species ClONO2 and ClO over the range of pressures (46 to 10 hPa) and latitudes (60°S to 60°N) considered here.

Introduction

An understanding of the effect of chlorine on the stratosphere is among the most important questions facing atmospheric scientists today. Except in the perturbed polar vortices, inorganic chlorine (Cl_y) in the lower and mid stratosphere is principally bound in the molecules HCl and ClONO2, which together make up more than 90% of Cl_y. The ClO radical makes up a significant fraction of the remainder. How much of Cl_y is bound in each member of Cl_y is important because the ClO radical is involved in catalytic loss cycles that regulate the ozone loss over much of the stratosphere [*World Meteorological Organization*, 1995] while HCl and ClONO2 are not involved in cycles that destroy ozone. An assessment of how Cl_y partitions between its member species is therefore necessary to determine the role that Cl_y plays in regulating stratospheric O_3.

The focus in this paper is on the interaction between the species ClO and ClONO2 between ~21 and 32 km and 60°N and 60°S. Our current understanding of the photochemistry of ClO and ClONO2 implies that because of the

slow formation and destruction rate of HCl, the sum of mixing ratios of the species ClO and ClONO2 in an air parcel is constant on a time scale of days to weeks. While their sum is constant, these species interconvert with a time scale of hours. During daylight, ClONO2 is destroyed through photolysis, which most often severs the Cl-O bond [*DeMore et al.*, 1994]. The Cl atom formed reacts rapidly (e-folding time << 1 s) with O_3 to form ClO, while the NO_3 molecule is rapidly photolyzed (e-folding time ~ 10 s) to form NO2. We will therefore assume in this paper that ClONO2 photolysis yields ClO and NO2,

$$ClONO_2 + h\nu \longrightarrow ClO + NO_2 \qquad (1)$$
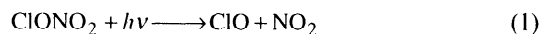
In addition to photolysis, at high altitudes the oxidation of ClONO2 by O and Cl atoms and the OH radical becomes a significant loss pathway for ClONO2. At 10, 15, and 22 hPa, model estimates indicate that these radicals are responsible for ~10%, 7%, and 3% of ClONO2 loss, respectively.

ClONO2 is reformed via the three-body reaction,

$$ClO + NO_2 \xrightarrow{\ M\ } ClONO_2 \qquad (2)$$
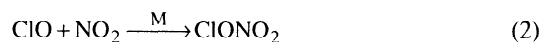
During most of the day, the production and loss of ClONO2 balance and the system is in steady state [*Kawa et al.*, 1992]. As the sun sets, photolysis of ClONO2 slows and eventually ceases, while reaction (2) continues, causing ClO to be depleted with an e-folding time of an hour or less. At sunrise, photolysis of ClONO2 resumes. The ClO abundance quickly rises and steady state is achieved in an hour or less.

Previous analyses have tested this theory in the lower stratosphere near 20 km altitude. *Brune et al.* [1990] demonstrated that the sunrise variation of ClO abundance is consistent with the photolysis of ClONO2 in a zero-dimensional photochemical model. Extending on this,

Stimpfle et al. [1994] used lower-stratosphere ClO measurements and NO₂ derived from measurements of NO to demonstrate that ClO is inversely correlated with NO₂, consistent with the formation and photolysis of ClONO₂. *Allen and Delitsky* [1991] used measurements of ClONO₂ and NO₂ by ATMOS to infer a ClO profile. Comparisons with measurements show that the calculated ClO profile is too high. A modeling paper by *Salawitch et al.* [1994] concluded that lower-stratosphere measurements of ClO and NO₂ are adequately reproduced by models incorporating heterogeneous chemistry on sulfate aerosols, but that modeled HCl was a factor of two larger than measurements. To explain these and other measurements of HCl that were significantly lower than model predictions, *Webster et al.* [1994] proposed that overestimates by a factor of three to ten in calculation of the photolysis rate of ClONO₂ (J_{ClONO_2}) cause ClO in models to be overestimated relative to ClONO₂. This overprediction of ClO, coupled with the subsequent reactions,

$$Cl O + NO \longrightarrow Cl + NO_2$$
$$\tag{3}$$
$$Cl + CH_4 \longrightarrow HCl + CH_3$$
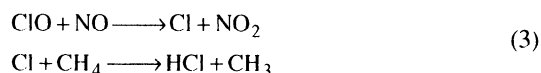
produces a higher formation rate of HCl in models than in the atmosphere, resulting in an overprediction of HCl by models.

None of the previous analyses utilized simultaneous measurements of ClO, NO₂, and ClONO₂. In this paper we will use newly available simultaneous measurements of these species to test the theory that we have discussed above and thereby attempt to confirm the processes that control the relative abundances of ClO and ClONO₂ over the altitude range of 21 to 32 km.

Data

ClO and ClONO₂

Level 3AT constituent data from the Upper Atmosphere Research Satellite (UARS) are used in this analysis. The data are from the 46-, 32-, 22-, 15-, and 10-hPa pressure surfaces, corresponding approximately to the altitude range of 21 to 32 km. The data in our analysis extend from 60°N to 60°S and were obtained between January 1 and April 15, 1993.

Measurements of ClO were made by the Microwave Limb Sounder (MLS) at 46, 22, and 10 hPa; 32- and 15-hPa abundances are obtained by interpolation. Minor adjustments have been applied to the version 3 data according to *Waters et al.* [1996]. The systematic uncertainty in the measurement can be a scaling error, where the error is a constant fraction of the observation, or a bias, in which case the true and measured value differ by a constant amount. Outside of the winter polar regions the bias can be as much as 0.2 parts per billion by volume (ppbv) at pressures of 46 hPa. This bias affects both day and night measurements and its magnitude can therefore be determined by examining MLS ClO measurements at night when ClO is zero. To account for the bias, we first calculate average nighttime ClO (solar zenith angles > 100°) as a function of latitude for each pressure level, using all of the data obtained between January 1 and April 15, 1993.

The average nighttime ClO measurement is approximately -100 parts per trillion by volume (pptv) over the range of altitudes and latitudes used in this analysis. Then, for each daytime ClO measurement used in this analysis, we subtract the average nighttime MLS ClO value at the latitude and pressure of the daytime measurement. All ClO data used in this analysis have been adjusted following this procedure.

On the basis of our comparison between MLS ClO and the difference between night and day ClONO₂ (Figure 1, discussed below) and the analysis presented by *Waters et al.* [1996, Figure 35], we estimate an upper limit of the bias uncertainty in the day minus night ClO data to be 50 pptv. We estimate the total accuracy of the ClO data to be the root-sum-of-squares of this 50 pptv bias uncertainty and an 8% scaling uncertainty estimated by *Waters et al.* [1996] (all uncertainties discussed in this paper are ~68% confidence limits, i.e., "1σ"). This corresponds to a total accuracy estimate ranging from ±70% at 46 hPa to ±21% at 10 hPa. Note that the precision uncertainty of any one MLS measurement is large compared to this (±300-400 pptv). Our analysis, however, averages a sufficient number of measurements to reduce the precision uncertainty to levels far below the accuracy estimate.

ClONO₂ data measured by the Cryogenic Limb Array Etalon Spectrometer (CLAES) (version 7) have a stated accuracy ranging from ±23% at 46 hPa to ±28% at 10 hPa [*Mergenthaler et al.*, 1996]. Simultaneous measurements of both ClO and ClONO₂ allow us to perform internal consistency checks on these data to supplement the accuracy estimates provided in the literature. Because ClO is primarily produced during the day from the photolysis of ClONO₂, we have,

$$\langle ClO \rangle^{day} \cong \langle ClONO_2 \rangle^{night} - \langle ClONO_2 \rangle^{day} \tag{4}$$

where the angled brackets (<>) indicate an average over the day or night, as indicated. Model simulations indicate that conversion of ClO into HOCl during the day introduces an error into equation (4) of less than 7%.

Figure 1 shows daytime average MLS ClO (left-hand side of equation (4)) versus the difference between average nighttime and average daytime CLAES ClONO₂ (right-hand side of equation (4)). The error bars represent the accuracy estimates; a sufficient number of measurements have been averaged in this plot so that precision uncertainty is negligible. The agreement between MLS ClO and the diurnal difference of CLAES ClONO₂ is better than 50 pptv at all pressure levels. A linear fit to the data produces a line with a slope very close to one (0.95) and a small y intercept (28 pptv). At 22, 15, and 10 hPa, the difference between daytime average ClO and the diurnal difference of ClONO₂ is less than 10%, much smaller than the uncertainty. At 46 and 32 hPa, the differences are 54 and 38%, respectively, but are small in absolute terms (less than 50 pptv) and within the uncertainty estimates.

A second test of the chlorine data is obtained from an analysis of the Halogen Occultation Experiment (HALOE) HCl and nighttime CLAES ClONO₂, whose sum closely approximates Cl$_y$ at the altitudes being considered. Figure 1 of *Dessler et al.* [1995] (not shown) compares the sum of HCl and nighttime ClONO₂ from UARS with Cl$_y$ derived from a relation based on aircraft data [*Woodbridge et al.*,
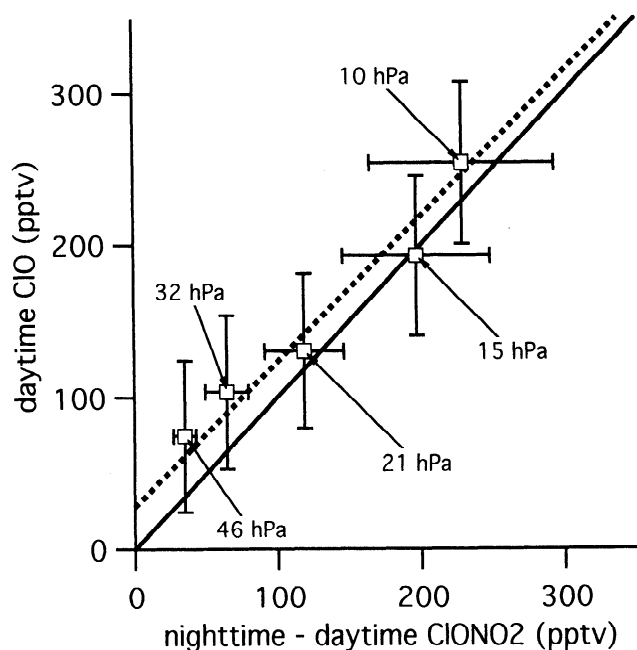
Figure 1. Daytime average Microwave Limb Sounder (MLS) ClO (pptv) versus nighttime average Cryogenic Limb Array Etalon Spectrometer (CLAES) ClONO₂ minus daytime average CLAES ClONO₂ (pptv). Daytime is defined as solar zenith angles less than 80°, nighttime as solar zenith angles greater than 100°. The solid line is the one-to-one line. The dotted line is a least squares fit to the UARS comparison (MLS=0.95*CLAES+28 pptv). For each pressure level, daytime average ClO and ClONO₂ are computed for 10°-wide latitude bins using simultaneously measured ClO and ClONO₂. Nighttime ClONO₂ is also averaged in 10°-wide latitude bins. Then, the daytime average ClONO₂ concentration is subtracted from the nighttime ClONO₂ average at the same latitude. The latitude bins are then averaged to produce a single average ClO and average nighttime minus daytime ClONO₂ for the entire pressure surface. The error bars represent the accuracy estimates and are the root-sum-of-squares of an 8% scaling uncertainty and a 50 pptv bias uncertainty for ClO and a 23-28% scaling uncertainty for nighttime minus daytime ClONO₂. Data were obtained between January 1 and April 15, 1993, and cover the latitude range between 60°N and 60°S.

1995]. The agreement between Cl_y and the sum of HCl and nighttime ClONO₂ between potential temperatures of 550 and 800 K (~46 and 10 hPa) provides supportive evidence that the ClONO₂ and HCl measurements are accurate. Note that these internal consistency checks use measurements from different instruments utilizing different measurement techniques and different retrieval algorithms to perform simple conservation tests on the data set. The ability to perform such tests as well as the good agreement found underscores the usefulness of the UARS data set.

NO₂

Measurements of NO₂ by the CLAES are made simultaneously with the ClO and ClONO₂ data. However, these version 7 CLAES NO₂ data have not been validated at the pressures used in this analysis. To address this issue, we

use NO and NO₂ measurements (both version 17) from the HALOE to adjust the CLAES NO₂ data. HALOE is a solar occultation instrument and it therefore makes all of its measurements at solar zenith angles of 90°. At this solar zenith angle, NO and NO₂ are rapidly interconverting and it is most convenient to deal with the sum of NO and NO₂, which is traditionally denoted as NO_x.

We first compare the CLAES NO₂ data with the HALOE NO_x data. Because NO is converted to NO₂ at night with a time scale of minutes, NO_x at night is constituted almost entirely of NO₂. Therefore HALOE sunset NO_x is comparable to CLAES NO₂ measured just after sunset; HALOE sunrise NO_x is comparable to CLAES NO₂ measured just before sunrise. Figure 2 compares the ratio of near-sunset to near-sunrise NO₂ from CLAES with ratio of sunset to sunrise NO_x in HALOE. One complication of this comparison is that NO_x decreases through the night because of the reaction

$$NO_2 + O_3 \longrightarrow NO_3 + O_2 \tag{5}$$
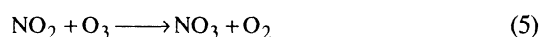
Thus, NO₂ measured just after sunset will be slightly smaller than sunset NO_x, and NO₂ measured just before
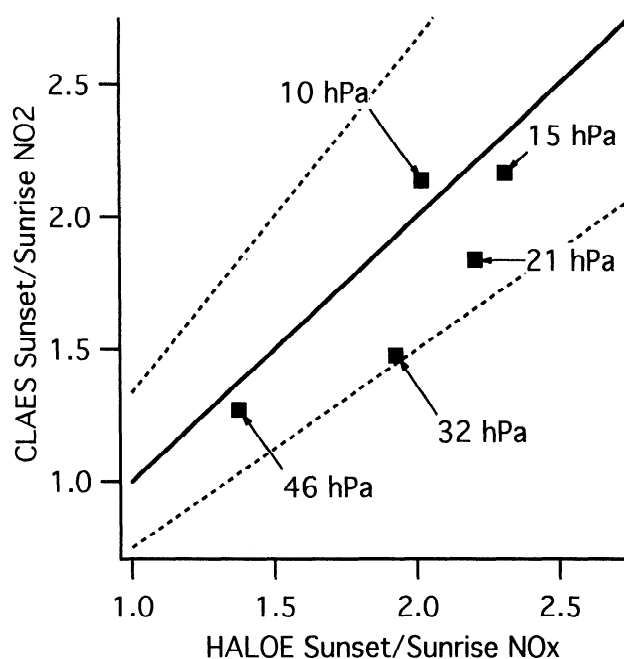

Figure 2. The ratio of CLAES NO₂ measured just after sunset (averaged over solar zenith angles between 95° and 110°) to CLAES NO₂ averaged over those same solar zenith angles just before sunrise versus the ratio of HALOE sunset NO_x to sunrise NO_x. The CLAES data have been adjusted for the small change in NO₂ between the measurement time and sunset/sunrise due to the reaction with ozone (see text). For each pressure level, zonally averaged CLAES and HALOE ratios are computed for 10°-wide latitude bins. These are then averaged to produce one value for each pressure surface, and these average values are plotted as squares. The solid line is the one-to-one line. The dashed lines are ±25%. Data in these plots were obtained between January 1 and April 15, 1993, and between 60°N and 60°S. Because a small offset in the NO₂ measurements at low concentrations could result in a large percent error, we have not included data between 20°N and 20°S on the 46, 32, and 22-hPa surfaces.

sunrise will be slightly larger than sunrise NO_x. We account for this effect by adjusting the near-sunset/sunrise CLAES NO_2 data by $2k_{NO_2+O_3}[O_3]\Delta t$, the fraction of NO_x depleted through reaction (5) in a length of time Δt. The factor of two arises because each NO_3 formed via equation (5) quickly reacts with another NO_2 to form N_2O_5. We calculate this correction factor using zonally-averaged monthly-mean O_3 and temperature, both measured by MLS (version 3). This adjustment increases the diurnal difference in the CLAES data by ~10%. Figure 2 shows general agreement between the magnitudes of the diurnal cycles in the HALOE NO_x and CLAES NO_2 data. The agreement is within 10% at 10, 15, and 46 hPa and within 17% and 24% at 22 and 32 hPa, respectively.

While the relative magnitude of the diurnal cycle is similar in the two data sets, comparisons of the absolute magnitude of the CLAES NO_2 and the HALOE NO_x show differences of as much as a factor of two. This suggests that these CLAES data are internally consistent but have an absolute calibration error. To correct the CLAES NO_2 data, we first determine the ratio of zonally averaged HALOE NO_x to zonally averaged CLAES NO_2 at sunrise and sunset as a function of latitude and pressure. Note that the CLAES NO_2 measurements are taken from just before sunrise and just after sunset and adjusted to sunrise and sunset as discussed previously. Then, each daytime CLAES NO_2 measurement is multiplied by the average of the sunrise and sunset ratios at the measurement's latitude and pressure. In other words, we are creating an NO_2 data set that uses the information from the CLAES about the relative changes in NO_2 throughout the day and information about the absolute calibration information from the HALOE. We will hereinafter refer to the CLAES NO_2 data that has been adjusted by the HALOE data as the "adjusted NO_2 data".

The accuracy of both the HALOE NO and NO_2 measurements is estimated to be ±15% [*Gordley et al.*, 1996], leading to a root-sum-of-squares of the uncertainty in NO_x of ±21%. From Figure 2 we estimate the uncertainty in the diurnal cycle of the CLAES NO_2 data to be ±25%. Combining these uncertainties, we calculate that the overall uncertainty in the adjusted NO_2 data is ±33%. Figure 3 is a plot of diurnal cycle of the adjusted NO_2 data. The shape of the profile is in good agreement with that seen by *Webster et al.* [1990]. Also shown is an average of the unadjusted version 7 CLAES NO_2 data and the HALOE NO_x data used to adjust the CLAES NO_2 data.

Ancillary Data

Temperature measurements by the CLAES are used in this analysis [*Gille et al.*, 1996]. The accuracy of these measurements is estimated to be ±2 K. Comparisons between the CLAES data with temperatures from the National Meteorological Center (NMC) Climate Analysis Center [*Nagatani et al.*, 1990 and references therein] interpolated to the location of the CLAES measurements reveal average disagreements smaller than 1% at both 10 and 46 hPa. The rms disagreement is 3% and 1% at 10 and 46 hPa, respectively. Temperatures are used to calculate the ambient number density, the rate constant for the three-body reaction between ClO and NO_2, and the cross section of $ClONO_2$. The uncertainty in the temperature is negli-
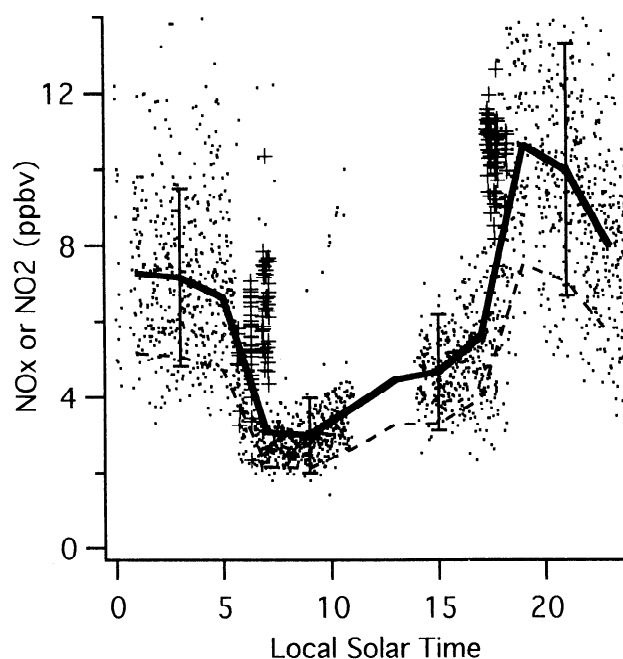

Figure 3. NO_2 and NO_x versus local solar time at 10 hPa. Individual adjusted NO_2 data (dots), the average of the adjusted data (solid line), and average of unadjusted CLAES NO_2 data (dashed line) are shown. The error bars on the adjusted NO_2 average line are ±33% and represent the accuracy of the data. Also shown are HALOE NO_x measurements (+) at sunrise and sunset. CLAES data were obtained between February 12 and March 16, 1993, and between 25°N and 35°N. HALOE data were obtained between January 20 and April 10, 1993, and between 25°N and 35°N.

gible compared to the other sources of uncertainty in this analysis and will not be considered further.

The rate constant for the three-body reaction between ClO and NO_2 (reaction (2)) is taken from the JPL 94 assessment of *DeMore et al.* [1994]. Using information in this source we estimate the 1σ error is ~±30%. The photolysis rate of $ClONO_2$, J_{ClONO_2}, is calculated as a function of pressure, temperature, overhead O_3, and solar zenith angle. The photolysis rate routine is taken from the Goddard three-dimensional chemical transport model [*Kawa et al.*, 1995] and is based on radiative transfer calculations from the model of *Anderson and Lloyd* [1990]. The $ClONO_2$ cross section is from the JPL 94 assessment of *DeMore et al.* [1994] and is temperature dependent. Overhead ozone is determined from a zonally averaged, monthly climatology of MLS O_3 measurements (205 GHz, version 3) obtained between January 1 and April 30, 1993. The radiation calculations are for clear-sky conditions and a surface albedo of 0.3. We estimate the uncertainty in the cross section of $ClONO_2$ to be ±15% [*Burkholder et al.*, 1994]. We estimate uncertainties in the radiative calculation to also be ±15%, leading to a combined 1σ uncertainty for J_{ClONO_2} of ±21%.

Balance Between Production and Loss of ClONO₂

To investigate our understanding of the ClO - $ClONO_2$ system, we compare the instantaneous production and loss

rate of $ClONO_2$. Loss of $ClONO_2$ is primarily through equation (1), photolysis of $ClONO_2$, and the rate of this process is $J_{ClONO_2}[ClONO_2]$. Production of $ClONO_2$ is through equation (2), the three-body reaction of ClO and NO_2, and the rate of this process is $k[ClO][NO_2][M]$. Figure 4a shows this comparison on the 22-hPa surface. There are approximately ten thousand points in this plot; each one represents a simultaneous measurement of ClO, NO_2, and $ClONO_2$ and a calculation of the J_{ClONO_2} and k. The data show considerable scatter, forming a cloud around the one-to-one line. The origin of the scatter in Figure 4a is not variability in the atmosphere but is predominantly due to the large precision uncertainty of the ClO data, the statistics of which have been discussed by *Schoeberl et al.* [1993] and *Waters et al.* [1996].

To eliminate the precision uncertainty, we average the instantaneous production and loss rates. The average production and loss rate for this pressure surface appears in Figure 4a as the square. Note that the average falls very close to the one-to-one line, indicating that production and loss of $ClONO_2$ balance. Figure 4b shows a close-up of the averaged value, graphically displaying the agreement between averaged instantaneous production and loss of $ClONO_2$. Also shown are the accuracy error bars, obtained from propagation of the uncertainties listed in Table 1.

Despite the large spread in the raw data, the precision uncertainty of the average is only a few percent, insignificant compared to the accuracy uncertainty.

Figure 5 compares the averaged instantaneous production and loss rates of $ClONO_2$ for the five pressure levels considered. For each pressure level, the individual measurements have been averaged, as discussed in the last paragraph, and only the averaged value for each pressure level is plotted. The error bars again represent the accuracy estimate of the average. In general the agreement is quite good. At 32 and 22 hPa, production and loss agree to within 1%. At 15 and 10 hPa, production exceeds loss by 13 and 23%, respectively. Part of this discrepancy results from our neglect of the loss of $ClONO_2$ at high altitudes through reactions with O, Cl, and OH. We estimate that these oxidation pathways contribute 7 and 10% to the loss of $ClONO_2$ at 15 and 10 hPa, respectively. Considering these neglected oxidation processes, the agreement between the averaged production and loss rates at 15 and 10 hPa is ~6 and 13%, respectively. At 46 hPa, production exceeds loss by about 50%. While within uncertainty limits, this agreement is much poorer than at higher altitudes.

We conclude from our analysis that there is no evidence to support missing chemistry, a significant error in the rate constant for the reaction of ClO and NO_2, or errors in our
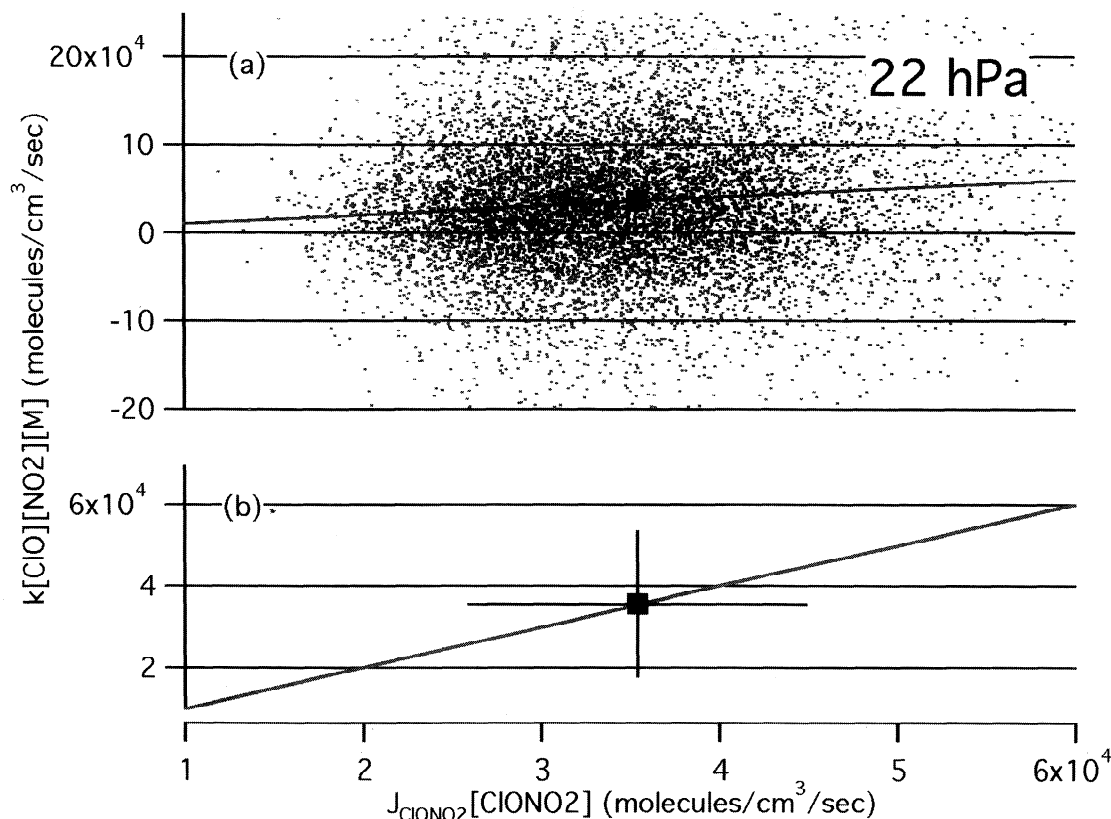

Figure 4. (a) Instantaneous production of $ClONO_2$ ($k[ClO][NO_2][M]$) versus loss of $ClONO_2$ ($J_{ClONO_2}[ClONO_2]$) on the 22-hPa pressure surface. Each dot represents a simultaneous measurement of ClO, NO_2, and $ClONO_2$ and a calculation of J_{ClONO_2} and k. The square is the average production and loss rate. The line is the one-to-one line. (b) Close-up of average production and loss rate. Error bars represent accuracy estimates; precision uncertainty is negligible and not considered. Note the agreement between average production and loss. The data in both Figures 4a and 4b were obtained between January 1 and April 15, 1993, and between 20° and 60° latitude in both hemispheres.

Table 1. Errors

Measurement	Accuracy, %
ClONO$_2$	±23-28
ClO	±21-70
Adjusted NO$_2$	±33
J	±21
k	±30
J[ClONO$_2$]	±31-35
k[ClO][NO$_2$][M]	±49-83

These uncertainties refer to ~68% confidence limits; that is, they are "1σ".

calculation of the photolysis rate of ClONO$_2$. In particular, we see no evidence to support previous suggestions of large pressure-dependent errors in calculations of the photolysis rate of ClONO$_2$ [Webster et al., 1994]. Note that the 46-hPa data show production exceeding loss. This is opposite to the effect suggested by Webster et al. [1994], who would predict loss of ClONO$_2$ exceeding production when using standard J_{ClONO_2} calculations. Our analysis of the raw 46-hPa data suggests that the degraded agreement between production and loss at 46 hPa is a result of uncertainty in the UARS data at this altitude and is not likely related to problems with our theoretical understanding of the ClO - ClONO$_2$ system.

We have shown in this figure that the production and loss rates of ClONO$_2$ balance on average. Because of the precision uncertainty in the data we cannot demonstrate balance on a point-by-point basis. However, while we cannot rule out the possibility that production exceeds loss in some region of the atmosphere and loss exceeds production in another region of the atmosphere such that the imbalances cancel each other, there is no a priori reason to believe that an imbalance in one region of the atmosphere would be canceled to within a few percent by an opposite imbalance in some other region of the atmosphere. We conclude therefore that it is unlikely for ClONO$_2$ production and loss rates to deviate significantly from balance on a point-by-point basis, although this point deserves further research.

A natural question arising from this analysis is how big a missing source or sink of ClONO$_2$ would be consistent with our analysis. Because our estimate of the production and loss rates of ClONO$_2$ balance to within ~10% between 10 and 32 hPa, any significant missing source or sink of ClONO$_2$ must fortuitously cancel (to within ~10%) an opposite systematic error in the data over the entire altitude extent of the missing chemistry. If we assume that the missing chemistry affects only one of the pressure levels in our data set, then we cannot rule missing chemistry that
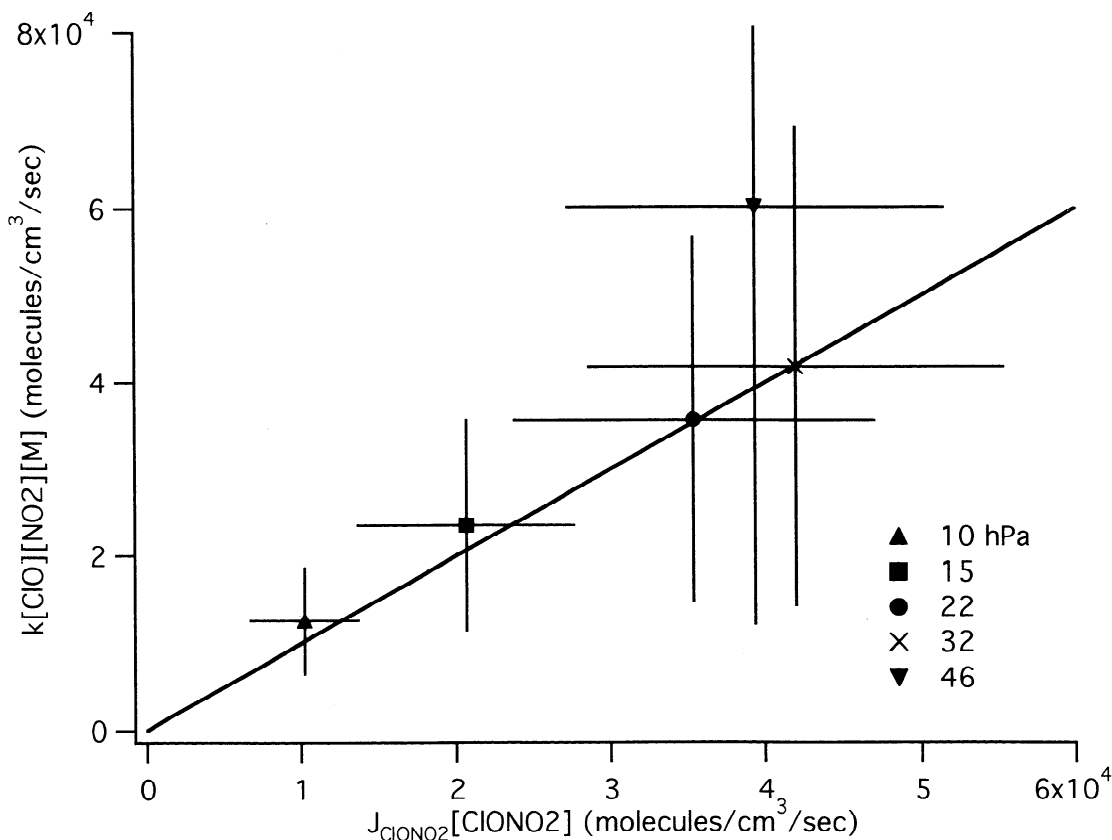

Figure 5. Production of ClONO$_2$ (k[ClO][NO$_2$][M]) versus loss of ClONO$_2$ (J_{ClONO_2}[ClONO$_2$]) for the five pressure levels analyzed in this paper. The data have been binned and averaged as discussed in text. Error bars represent accuracy estimates; precision uncertainty is negligible and not considered. The solid line is the one-to-one line. Note the agreement between production and loss. The data were obtained between January 1 and April 15, 1993. The 15 and 10-hPa data cover the latitude range between 60°N and 60°S. The 46-, 32-, and 22-hPa data cover the latitude range between 20° and 60° in each hemisphere.

is smaller than the error bars shown in Figure 5 for that level. However, missing chemistry that affects only one of our pressure levels is unlikely and puts sharp constraints on the potential mechanisms. Missing chemistry with a significant vertical extent (e.g., affecting several pressure levels) would require canceling systematic errors in the data on several pressure levels. Based on analyses of the retrieval algorithms, we estimate that the systematic errors for each given pressure level are largely uncorrelated with the systematic errors on other pressure levels. We believe therefore that any missing chemistry affecting several pressure levels must be significantly smaller than the error bars on any one level indicate. Without information about the altitude dependence of the missing chemistry, however, it is impossible to quantitatively evaluate the probability of the existence of the missing chemistry.

Due to the constraint of steady state, our analysis has been limited to investigating solar zenith angles of less than 80°. We have seen no evidence to suggest problems with our understanding of the production and loss of $ClONO_2$ at solar zenith angles less than 80°. However, the partitioning of Cl_y between HCl and $ClONO_2$ has a time constant that is weeks to months in the lower and mid stratosphere and is therefore a function of the production and loss rates of $ClONO_2$ averaged over all daytime solar zenith angles, including those greater than 80°. Calculations using the radiative model, however, indicate that solar zenith angles greater than 80° contribute only ~10 to 20% to the daytime-averaged production and loss of $ClONO_2$ over the latitude range of 60°N to 60°S. In conjunction with our analysis, we therefore conclude that the daytime-averaged production and loss of $ClONO_2$ are similarly well understood (within our uncertainties) and are unlikely to be significantly in error.

Conclusions

We have tested the partitioning between the chlorine species $ClONO_2$ and ClO using simultaneous measurements of ClO, NO_2, and $ClONO_2$ for the first time. We conclude the following:

1. Between 32 and 10 hPa (~24 and 32 km), average production and loss rates of $ClONO_2$ agree within a few percent, as expected by photochemical theory. At 46 hPa (~21 km), the agreement between averaged production and loss rates of $ClONO_2$ is poorer than at higher altitudes but still within uncertainties.

2. We see no evidence for any problems in our understanding of the partitioning between the chlorine species $ClONO_2$ and ClO over the range of pressures (46 to 10 hPa) and latitudes (60°S to 60°N) considered here. We conclude that our understanding of the chemical mechanisms, photolysis rate of $ClONO_2$, and the rate constant for the reaction between ClO and NO_2 is good within the uncertainties of this analysis.

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