

The response of ClO radical concentrations to variations in NO₂ radical concentrations in the lower stratosphere

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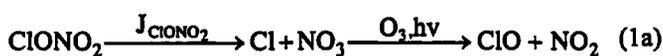
Abstract. The response of ClO concentrations to changes in NO₂ concentrations has been inferred from simultaneous observations of [ClO], [NO], [NO₂] and [O₃] in the mid-latitude lower stratosphere. This analysis demonstrates that [ClO] is inversely correlated with [NO₂], consistent with formation and photolysis of [ClONO₂]. A factor of ten range in the concentration of NO₂ was sampled (0.1 to 1 × 10⁹ mol/cm³), with a comparable range in the ratio of [ClO] to total available inorganic chlorine (1% ≤ [ClO]/[Cl_x] ≤ 5%). This analysis leads to an estimate of [ClONO₂]/[Cl_x] = 0.12 (×/±2), in the mid-latitude, lower-stratospheric air masses sampled.

Introduction

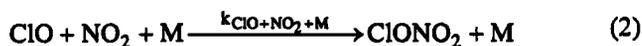
Photochemical removal of ozone in the stratosphere is controlled by reactions of hydrogen, halogen, nitrogen and oxygen radicals [WMO, 1985]. In the lower (17-20 km), mid-latitude (30-60° N) stratosphere, halogen-catalyzed removal of ozone constituted about 1/3 of the total photochemical removal rate in the Spring of 1993 [Wennberg *et al.*, 1994]. Extrapolating these results to other seasons, latitudes, and altitudes requires a mechanistic understanding of the photochemistry controlling the radical abundances. In this letter we present an analysis of the coupling of [ClO] to [NO₂] in the mid-latitude lower stratosphere. We demonstrate that [ClO] is inversely correlated with [NO₂]. Because [ClO] dominates reactive chlorine ([Cl_x] = [Cl] + [ClO] + 2 × [ClOOCl] + [HOCl]) and [NO₂] is proportional to reactive nitrogen ([NO_x] = [NO] + [NO₂] + [NO₃]) for the air masses considered here, these results may be more broadly interpreted as a demonstration of the control of [Cl_x] by [NO_x]. Gaining insight into the value of d[ClO]/d[NO₂] from atmospheric measurements is of great importance in understanding the sensitivity of calculated O₃ loss rates to

seasonal, latitudinal and altitudinal variations of [NO₂] and to perturbations of [NO₂] resulting from injections of volcanic debris or aircraft engine effluent.

In the mid-latitude lower stratosphere [ClO] is produced primarily by photolysis of chlorine nitrate:



and removed by reaction with NO₂,



where J_{ClONO_2} (sec⁻¹) is the photolysis rate, $k_{\text{ClO}+\text{NO}_2+\text{M}}$ (cm⁶ mol⁻² sec⁻¹) is the rate constant for the recombination reaction, and [M] is the number density of air. The photolysis of ClONO₂ proceeds approximately equally via the channels 1a and 1b [Minton *et al.*, 1992]. During the day (solar zenith angle (SZA) ≤ 70°) ClO and ClONO₂ are close to photochemical steady-state [Kawa *et al.*, 1992] and typically the sum of [ClO] and [ClONO₂] is conserved (= [ClONO₂]^{night}) so that [ClO] may be expressed as:

$$[\text{ClO}] = \frac{J_{\text{ClONO}_2} ([\text{ClONO}_2]^{\text{night}} - [\text{ClO}])}{k_{\text{ClO}+\text{NO}_2+\text{M}} [\text{M}] [\text{NO}_2]} \quad (3a)$$

$$[\text{ClO}] = \frac{J_{\text{ClONO}_2} [\text{ClONO}_2]^{\text{night}}}{J_{\text{ClONO}_2} + k_{\text{ClO}+\text{NO}_2+\text{M}} [\text{M}] [\text{NO}_2]} \quad (3b)$$

Eqn. 3b may be simplified to reflect the inverse relationship between [ClO] and [NO₂] when $J_{\text{ClONO}_2} \ll k_{\text{ClO}+\text{NO}_2+\text{M}} [\text{M}] [\text{NO}_2]$. For the air masses considered here the ratio of $J_{\text{ClONO}_2}/k_{\text{ClO}+\text{NO}_2+\text{M}} [\text{M}] [\text{NO}_2]$ ranges from about 1/13 to 1/2. The purpose of this paper is to demonstrate the validity of Eqn. 3b with in situ measurements. We note that Eqn. 3 will not describe the principal control over [ClO] in winter polar regions when [Cl_x] is large compared to [NO₂] and the ClO dimer is important. We restrict our analysis to mid-latitude air where the effect of this chemistry may be neglected. The effect of HOCl is not explicitly included because we have no direct experimental measurement of [HOCl] and to simplify the analysis. A more detailed treatment of ClO abundances that includes estimated [HOCl] (= $k_{\text{ClO}+\text{HO}_2} [\text{ClO}][\text{HO}_2]/J_{\text{HOCl}}$) does not affect the conclusions drawn here.

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Analysis of simultaneous, *in situ* measurements obtained from the NASA ER-2 aircraft of [ClO], [NO], [NO₂], [O₃] and a variety of chemical and dynamical tracers provides a means to test Eqn. 3 over a wide dynamic range. The number of ER-2 based observations in the mid-latitudes has expanded with the recently completed Stratospheric, Photochemistry, Aerosols, and Dynamics Expedition (SPADE) [Wofsy *et al.*, 1994] and its predecessor, the Second Airborne Arctic Stratospheric Expedition (AASE-II) [Anderson and Toon, 1993]. Although the absence of *in situ* [ClONO₂] measurements hinders the analysis, we are able to provide strong evidence that measured [ClO] is inversely proportional to [NO₂] over a wide range in [NO₂] (0.1 to 1 × 10⁹ mol/cm³). The extensive range of [NO₂] sampled here is the result of seasonal and latitudinal variations as well as reductions in [NO_x] due to heterogeneous chemistry following the eruption of Mt. Pinatubo [Fahey *et al.*, 1993 and references therein; Koike *et al.*, 1994]. An increase in [ClO] (presumably due to reductions in NO_x) coincident with the dramatic increase in sulfate aerosol loading has been noted for measurements obtained during AASE-II [Wilson *et al.*, 1993; Avallone *et al.*, 1993]. Here we demonstrate that the variability of [ClO] is driven directly by changes in [NO₂].

Observations and Inferences

The SPADE flights took place out of NASA Ames, Mountain View, CA (37°N, 122°W) in November, 1992 and April-May, 1993. The AASE-II campaign took place from September, 1991 through March, 1992 from NASA Ames, Fairbanks, AK (65°N, 147°W) and Bangor, ME (45°N, 69°W). We include in the analysis AASE-II data from seven flights that did not sample polar vortex-like air and that had similar latitude coverage to that of the SPADE flights. Polar air masses are excluded by eliminating flights for which [N₂O] < 180 ppb.

[ClO] is measured using resonance fluorescence detection of Cl atoms at 118.9 nm, generated by chemical conversion of ambient ClO to Cl by NO addition, with an accuracy of 30 - 35 % (2σ) [Brune *et al.*, 1989]. [NO] is measured via chemiluminescence following reaction of ambient NO with added O₃, with an accuracy of 10-20% [Fahey *et al.*, 1989]. Two different measurement techniques for [NO₂] were implemented for SPADE. The NOAA chemiluminescent technique detects NO₂ with an accuracy of 60% by photolyzing NO₂ to produce NO that is detected as above [Gao *et al.*, 1994]. The JPL Aircraft Laser Infrared Absorption Spectrometer (ALIAS) detects [NO₂], in addition to [HCl], [N₂O], and [CH₄], with an accuracy for [NO₂] of 25% to 50% for concentrations near 7 × 10⁸ mol/cm³ (0.4 ppb) and less than 2 × 10⁸ mol/cm³ (0.1 ppb), respectively [Jaegle *et al.*, 1994]. [N₂O] is measured with the NASA/Ames Airborne Tunable Laser Absorption Spectrometer (ATLAS) with 10% accuracy [Podolske and Loewenstein, 1993]. [O₃] is detected by UV absorption with an accuracy of 3% [Proffitt *et al.*, 1983]. Temperature and pressure are measured by the Meteorological Measurement System instrument [Scott *et al.*, 1990].

Direct measurements of total inorganic chlorine and photolysis rates are not available. [Cl_y] (= [Cl₂] + [HCl] + [ClONO₂]) is calculated as a function of [N₂O]

using relationships derived from measurements of [N₂O] and eight halogenated organic compounds obtained during AASE-II [Woodbridge *et al.*, 1994]. Cl_y estimated using these formulae is expected to be accurate to 30%. Photolysis rates (J values) for ClONO₂ and NO₂ used in this analysis are calculated using a radiative-transfer model [Salawitch *et al.*, 1994] and absorption cross-sections and quantum yields based upon the current photochemical recommendation [DeMore *et al.*, 1992]. The computed photolysis rates take into account variations in overhead ozone and albedo along the flight track using measurements from the Total Ozone Mapping Spectrometer (TOMS).

Since [NO₂] was not measured during AASE-II and the measurements during SPADE were less frequent than those of [ClO], [NO₂] densities are calculated from the photochemical steady-state relation,

$$[\text{NO}_2]^* = 0.7 \times \frac{[\text{NO}] \times (k_{\text{NO}+\text{O}_3}[\text{O}_3] + k_{\text{NO}+\text{ClO}}[\text{ClO}])}{J_{\text{NO}_2}} \quad (4)$$

where an asterisk is used to distinguish inferred from measured [NO₂]. SPADE measurements of [NO₂] from ALIAS are consistently lower than the photochemical steady-state prediction [Jaegle *et al.*, 1994]. Preliminary results reported by the NOAA instrument [Gao *et al.*, 1994] are lower than expected as well. The cause of the imbalance is not understood at this time. However, in order to base this analysis on measurements, the factor of 0.7 (±35%) is introduced that brings the inferred value into better agreement with the measurements. The correction is applied to the AASE-II data as well.

Analysis

In Figure 1, we plot [ClO]/[Cl_y] vs. [NO₂]* × (k_{ClO+NO₂+M} [M] / J_{ClONO₂}). Here J_{ClONO₂} refers to the J value derived from data in the current photochemical recommendation, which assumes a quantum yield (Φ_{ClONO₂}) of 100% for the photolysis of ClONO₂. The data shown were collected at constant [O₃], 3.0 ± 0.1 × 10¹² mol/cm³, and for SZA ≤ 70°. This limit on SZA assures that ClO is within 10% of its photochemical steady-state value of Eq. 3 [Kawa *et al.*, 1992]. The [ClO] measurements have been median-filtered over an 80 sec interval to achieve higher signal-to-noise.

Figure 1 illustrates the central conclusion that [ClO]/[Cl_y] is inversely correlated with [NO₂]. The three curves in Figure 1 are lines that conform to Eqn. 3 using values of [ClONO₂]^{night}/[Cl_y] equal to 0.07 (lower dashed), 0.12 (solid line) and 0.17 (upper dashed). By visual inspection these lines provide a simple estimate of the most probable value and the error for [ClONO₂]^{night}/[Cl_y] = 0.12 ± 0.05. Propagating the error due to uncertainty (1σ) in the ordinate, [ClO]/[Cl_y] (±40%) and the abscissa, [NO₂]* × (k_{ClO+NO₂+M} [M] / J_{ClONO₂}) (±90%) [Kawa *et al.*, 1992], by adding the above errors in quadrature leads to [ClONO₂]^{night}/[Cl_y] = 0.12 (×/+2). The data are restricted to values of [ClO]/[Cl_y] ≤ 0.05 where estimated [HOCl] is small (< 20%) compared to estimates of [ClONO₂] during the day.

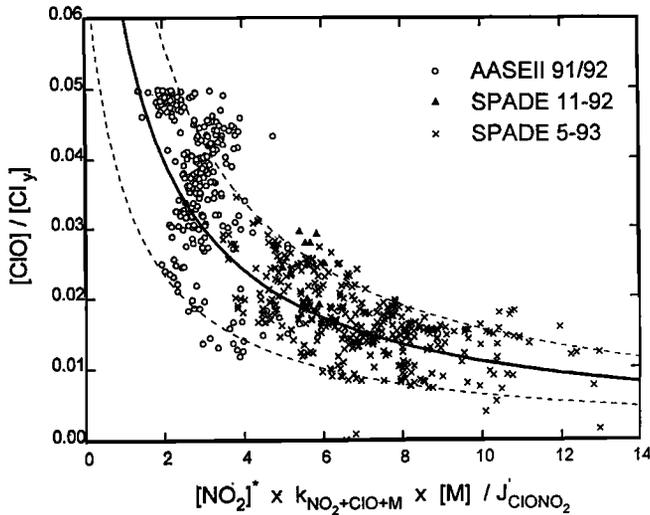


Figure 1. The observed ratio of $[ClO]/[Cl_v]$ versus $[NO_2]^* \times (k_{ClO+NO_2+M} [M]/J_{ClONO_2})$. Data from AASE-II (open circles), 910917 (17 September 1991), 911004, 911014, 911208, 920112, 920222, 920322; SPADE Fall (solid triangles) 921109, 921116; SPADE Spring (\times symbols) 930430, 930501, 930503, 930506, 930507, 930511, 930512, 930514, 930518. The measurements were obtained under the conditions: $25 \leq \text{latitude} \leq 58^\circ N$, $1.7 \times 10^{18} \leq [M] \leq 2.5 \times 10^{18} \text{ mol/cm}^3$, $205 \leq \text{temperature} \leq 220K$, $4.1 \times 10^{11} \leq [N_2O] \leq 7 \times 10^{11} \text{ mol/cm}^3$, $1.3 \times 10^9 \leq [Cl_v] \leq 3.5 \times 10^9 \text{ mol/cm}^3$, $0.6 \times 10^{10} \leq [NO_y] \leq 1.2 \times 10^{10} \text{ mol/cm}^3$, $0.5 \leq \text{aerosol surface area} \leq 30 \mu\text{m}^2 \text{ cm}^{-3}$, and $0.4 \times 10^{-4} \leq J_{ClONO_2} \leq 1.0 \times 10^{-4} \text{ sec}^{-1}$.

The measurements in Figure 1 are direct evidence for an inverse relationship between $[ClO]$ and $[NO_2]$, provided we can verify the following assumptions: 1) $[ClO]$ is linearly related to J_{ClONO_2} as described by the steady state equation, 2) the reaction of $ClO + NO_2$ is the only significant loss term for ClO , and 3) the ratio of $[ClONO_2]^{night}/[Cl_v]$ is a constant for the data shown. Here we discuss each of these assumptions in turn:

1) Diurnal $[ClO]$ measurements obtained on two consecutive days (a sunrise flight on 11 May 1993 and a sunset flight on 12 May 1993) during SPADE in air that had nearly constant values of $[Cl_v]$, $[NO_y]$, $[O_3]$, $[M]$ and temperature provide a test of J_{ClONO_2} , as shown in Figure 2. By inference, the $[ClO]$ measurements were obtained for nearly constant $[ClONO_2]$. Since all of the remaining terms on the left hand side of Eqn. 3 are approximately constant ($[ClONO_2]^{day} \cong [ClONO_2]^{night}$ since $[ClO]/[Cl_v] \leq 2\%$) this plot is a test of whether the J_{ClONO_2} has the correct solar zenith angle dependence to represent the measurements. The similarity of J_{ClONO_2} and ClO is a strong indication that $ClONO_2$ photolysis is the source of ClO during the day. This result does not depend on the absolute magnitude of J_{ClONO_2} , a test of which would require knowledge of $[ClONO_2]$.

2) Measurements of the rate of decay of $[ClO]$ after sunset (when the source term due to $ClONO_2$ photolysis is negligible) by *Brune et al.* (1990) and during SPADE show that the rate constant k_{ClO+NO_2+M} suggested by the current photochemical recommendation predicts the rate of disappearance of ClO under stratospheric conditions. The observed decay rate for ClO measured after sunset on the SPADE 930507 flight ($k^I = 0.7 \pm 0.3 \times 10^{-3} \text{ sec}^{-1}$) agrees within experimental error with the decay rate calculated from the NO_2 data obtained by the ALIAS instrument ($k^I = k_{ClO+NO_2+M} \times [M] \times [NO_2] = 1.2 \pm 0.8 \times 10^{-3} \text{ sec}^{-1}$).

3) The final requirement for a test of Eq. 3, that the ratio of $[ClONO_2]^{night}/[Cl_v]$ is constant for the data shown in Figure 1, cannot be unequivocally demonstrated without a simultaneous $[ClONO_2]$ measurement. The measurements of $[HCl]$ by ALIAS do not indicate a trend in chlorine partitioning for the data in Figure 1. The data shown were selected at constant $[O_3]$ because the partitioning of $[ClONO_2]/[Cl_v]$ is strongly dependent on $[O_3]$. A series of plots for different values of $[O_3]$ conforms to the same inverse relationship, although as expected the derived value of $[ClONO_2]^{night}/[Cl_v]$ increases with $[O_3]$. This dependence is the subject of another paper currently in preparation.

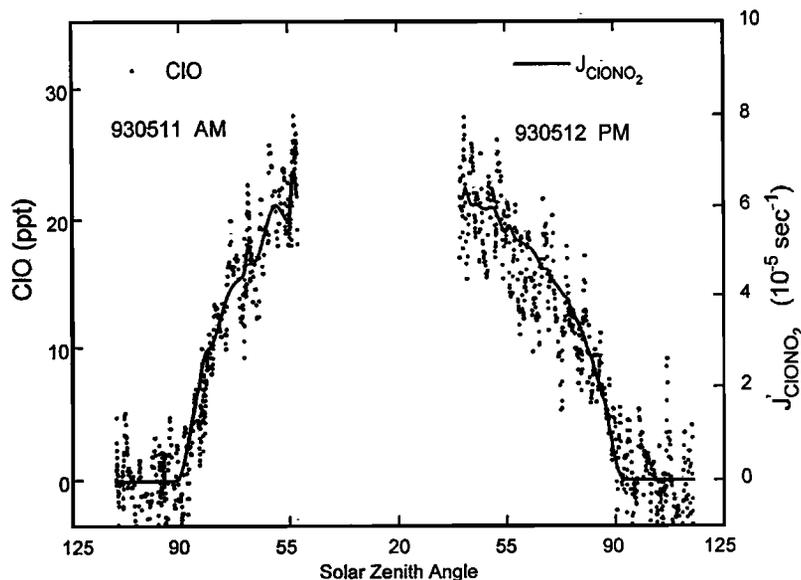


Figure 2. Observed ClO (solid circles) and calculated J_{ClONO_2} versus solar zenith angle for two SPADE diurnal flights: sunrise on 930511 (left) and sunset on 930512 (right).

Conclusions

Simultaneous in situ measurements of [ClO], [NO], [NO₂], [O₃], [N₂O] and other variables have been used to draw two conclusions. First, the demonstration that ClO is inversely correlated with [NO₂] provides confidence that the control of [ClO] by [NO₂] ($d[\text{ClO}]/d[\text{NO}_2]$) through the formation of ClONO₂ is prescribed correctly in current models. Therefore modeling of O₃ loss rates due to halogen reactions as a function of variable [NO_x] may be correctly described. It is crucial to recognize that Figure 1 shows the measured response of [ClO] to [NO₂] independent of whether the chemistry connecting ClO to Cl_y is completely correct.

Secondly, this analysis provides an estimate of $[\text{ClONO}_2]_{\text{night}}/[\text{Cl}_y]=0.12$ ($\times/\div 2$) assuming Φ_{ClONO_2} is equal to unity. We note that this result is not consistent with the simultaneous measurements of [HCl] given that $[\text{Cl}_y] = [\text{Cl}_x] + [\text{HCl}] + [\text{ClONO}_2]$; measured [HCl] and [ClONO₂] estimated here do not sum to [Cl_y] for SPADE and AASE-II [Webster et al., 1993]. This discrepancy in our understanding of the chlorine budget remains unresolved at this time.

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