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

R. M. Stimpfle¹, J. P. Koplow¹, R. C. Cohen¹, D. W. Kohn¹, P. O. Wennberg¹, D. M. Judith¹, D. W. Toohey¹, L. M. Avallone¹, J. G. Anderson¹, R. J. Salawitch³, E. L. Woodbridge⁴, C. R. Webster⁵, R. D. May³, M. H. Proffitt⁴, K. Aiken⁴, J. Margitan⁵, M. Loewenstein⁵, J. R. Podolske⁵, L. Pfister⁴, K. R. Chan⁶

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 x 10⁹ mol/cm³), with a comparable range in the ratio of [ClO] to total available inorganic chlorine (1% _ [ClO]/[Cl] _ 5%). This analysis leads to an estimate of [ClONO₂]/[Cl] -- 0.12 (x/.'-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] = [Cl] + [ClO] + 2 x [ClOCl] + [HOCI]) and [NO₂] is proportional to reactive nitrogen ([NO₂] = [NO] + [NO] + [NO₂]) for the air masses considered here, these results may be more broadly interpreted as a demonstration of the control of [ClO] by [NO₂]. 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:

\[ \text{ClONO}_2 \rightarrow \text{Cl} + \text{NO}_3 + \text{O}_3 \rightarrow \text{Cl} + \text{NO}_2 + \text{O}_3 \] (la)

\[ \text{ClO} + \text{NO}_2 \rightarrow \text{Cl} + \text{NO}_3 + \text{M} \rightarrow \text{ClO} + \text{NO}_2 + \text{M} \] (lb)

where J_{ClONO₂} (sec⁻¹) is the photolysis rate, k_{ClO+NO₂+M} (cm³ mol⁻¹ 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]ₑₐₙ) so that [ClO] may be expressed as:

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

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

Eqn. 3b may be simplified to reflect the inverse relationship between [ClO] and [NO₂] when J_{ClONO₂} ≪ k_{ClO+NO₂+M} [M] [NO₂]. For the air masses considered here the ratio of J_{ClONO₂}/k_{ClO+NO₂+M} [M] [NO₂] 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] 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 HOCI is not explicitly included because we have no direct experimental measurement of [HOCI] and to simplify the analysis. A more detailed treatment of ClO abundances that includes estimated [HOCI] (≈ k_{ClO+H₂O} [ClO][H₂O]/k_{HOCI}) does not affect the conclusions drawn here.
Analysis of simultaneous, in situ measurements obtained from the NASA ER-2 aircraft of \([\text{ClO}], [\text{NO}], [\text{NO}_2], [\text{O}_3]\) 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) \([\text{Wofsy et al.}, 1994]\) and its predecessor, the Second Airborne Arctic Stratospheric Expedition (AASE-II) \([\text{Anderson and Toon}, 1993]\). Although the absence of \textit{in situ} \([\text{ClONO}_2]\) measurements hinders the analysis, we are able to provide strong evidence that measured \([\text{ClO}]\) is inversely proportional to \([\text{NO}_3]\) over a wide range in \([\text{NO}_2]\) (0.1 to \(1 \times 10^5 \text{ mol/cm}^3\)). The extensive range of \([\text{NO}_2]\) sampled here is the result of seasonal and latitudinal variations as well as reductions in \([\text{NO}_2]\) due to heterogeneous chemistry following the eruption of Mt. Pinatubo \([\text{Fahey et al.}, 1993\text{ and references therein}; \text{Koike et al.}, 1994]\). An increase in \([\text{ClO}]\) (presumably due to reductions in \([\text{NO}_2]\)) coincident with the dramatic increase in sulfate aerosol loading has been noted for measurements obtained during AASE-II \([\text{Wilson et al.}, 1993; \text{Avallone et al.}, 1993]\). Here we demonstrate that the variability of \([\text{ClO}]\) is driven directly by changes in \([\text{NO}_2]\).

Observations and Inferences

The SPADE flights took place out of NASA Ames, Mountain View, CA (37ºN, 122ºW) in November, 1992 and April-May, 1993. The AASE-II campaign took place from September, 1991 through March, 1992 from NASA Ames, Fairbanks, AK (65ºN, 147ºW) and Bangor, ME (45ºN, 69ºW). 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 \([\text{NO}_2] < 180 \text{ ppb}\).

\([\text{ClO}]\) is measured using resonance fluorescence detection of Cl atoms at 118.9 nm, generated by chemical conversion of ambient CIO to Cl by NO addition, with an accuracy of 30 - 35% \((\sigma)\) \([\text{Brune et al.}, 1989]\). \([\text{NO}]\) is measured via chemiluminescence following reaction of ambient NO with added O$_3$, with an accuracy of 10-20% \([\text{Fahey et al.}, 1989]\). Two different measurement techniques for \([\text{NO}_2]\) were implemented for SPADE. The NOAA chemiluminescent technique detects \([\text{NO}_2]\) with an accuracy of 60% by photolyzing \([\text{NO}_2]\) to produce NO that is detected as above \([\text{Gao et al.}, 1994]\). The JPL Aircraft Laser Infrared Absorption Spectrometer (ALIAS) detects \([\text{NO}_2]\) in addition to \([\text{HCl}], [\text{N}_2\text{O}], \text{and} \ [\text{CH}_4]\), with an accuracy for \([\text{NO}_2]\) of 25% to 50% for concentrations near \(7 \times 10^7 \text{ mol/cm}^3\) (0.4 ppb) and less than \(2 \times 10^8 \text{ mol/cm}^3\) (0.1 ppb), respectively \([\text{Jaeglé et al.}, 1994]\). \([\text{N}_2\text{O}]\) is measured with the NASA/Ames Airborne Tunable Laser Absorption Spectrometer (ATLAS) with 10% accuracy \([\text{Podolske and Loewenstein}, 1993]\). \([\text{O}_3]\) is detected by UV absorption with an accuracy of 3% \([\text{Profitt et al.}, 1983]\). Temperature and pressure are measured by the Meteorological Measurement System instrument \([\text{Scott et al.}, 1990]\).

Direct measurements of total inorganic chlorine and photolysis rates and are not available. \([\text{Cl}_2] = ([\text{Cl}_2] + [\text{HCl}] + [\text{ClONO}_2])\) is calculated as a function of \([\text{NO}_2]\) using relationships derived from measurements of \([\text{N}_2\text{O}]\) and eight halogenated organic compounds obtained during AASE-II \([\text{Woodbridge et al.}, 1994]\). \([\text{Cl}_2]\) estimated using these formulae is expected to be accurate to 30%. Photolysis rates \((J)\) values for \([\text{ClONO}_2]\) and \([\text{NO}_2]\) used in this analysis are calculated using a radiative-transfer model \([\text{Salawitch et al.}, 1994]\) and absorption cross-sections and quantum yields based upon the current photochemical recommendation \([\text{DeMore et al.}, 1992]\). 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 \([\text{NO}_2]\) was not measured during AASE-II and the measurements during SPADE were less frequent than those of \([\text{ClO}], [\text{NO}_2]\) densities are calculated from the photochemical steady-state relation,

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

where an asterisk is used to distinguish inferred from measured \([\text{NO}_2]\). SPADE measurements of \([\text{NO}_2]\) from ALIAS are consistently lower than the photochemical steady-state prediction \([\text{Jaegle et al.}, 1994]\). Preliminary results reported by the NOAA instrument \([\text{Gao et al.}, 1994]\) 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 \(0.7 \pm 35\%\) 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 \([\text{ClO}] / [\text{Cl}_2] \) vs. \([\text{NO}_2]^* \times k_{\text{ClO}+\text{NO}_2+M} \times M / J_{\text{ClONO}_2}\). Here \(J_{\text{ClONO}_2}\) refers to the \(J\) value derived from data in the current photochemical recommendation, which assumes a quantum yield \((\Phi_{\text{ClONO}_2})\) of 100% for the photolysis of \([\text{ClONO}_2]\). The data shown were collected at constant \([\text{O}_3]\), \(3.0 \pm 0.1 \times 10^{22} \text{ mol/cm}^3\), and for \(SZA \leq 70\\text{ø}\). This limit on \(SZA\) assures that \([\text{ClO}]\) is within 10% of its photochemical steady-state value of Eq. 3 \([\text{Kawa et al.}, 1992]\). The \([\text{ClO}]\) measurements have been median-filtered over an 80 sec interval to achieve higher signal-to-noise.

Figure 1 illustrates the central conclusion that \([\text{ClO}] / [\text{Cl}_2] \) is inversely correlated with \([\text{NO}_2]\). The three curves in Figure 1 are lines that conform to Eqn. 3 using values of \([\text{ClONO}_2}] \times k_{\text{NO}+\text{O}_3} \times M / J_{\text{ClONO}_2} = 0.12 \pm 0.05\). Propagating the error due to uncertainty \((\sigma)\) in the ordinate, \([\text{ClO}] / [\text{Cl}_2] \) \((\pm 40\%)\) and the abscissa, \([\text{NO}_2]^* \times k_{\text{ClO}+\text{NO}_2+M} \times M / J_{\text{ClONO}_2} \) \((\pm 90\%)\) \([\text{Kawa et al.}, 1992]\), by adding the above errors in quadrature leads to \([\text{ClONO}_2}] \times k_{\text{NO}+\text{O}_3} \times M / J_{\text{ClONO}_2} = 0.12 \pm 0.05\). The data are restricted to values of \([\text{ClO}] / [\text{Cl}_2] \leq 0.05\) where estimated \([\text{HOCI}]\) is small \((< 20\%)\) compared to estimates of \([\text{ClONO}_2}\) during the day.
The measurements in Figure 1 are direct evidence for an inverse relationship between [CIO] and [NO₂], provided we can verify the following assumptions: 1) [CIO] is linearly related to $J_{\text{CIONO}_2}$ as described by the steady state equation, 2) the reaction of CIO + NO₂ is the only significant loss term for CIO, and 3) the ratio of $[\text{CIONO}_2]^\text{night}/[\text{Cl}]$ is a constant for the data shown. Here we discuss each of these assumptions in turn:

1) Diurnal [CIO] 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], [NO₂], [O₃], [M] and temperature provide a test of $J_{\text{CIONO}_2}$, as shown in Figure 2. By inference, the [CIO] measurements were obtained for nearly constant [CIONO₂]. Since all of the remaining terms on the left hand side of Eqn. 3 are approximately constant ($[\text{CIONO}_2]^\text{night} \\equiv [\text{CIONO}_2]^{0}$ since [CIO]/[Cl] ≤ 2%) this plot is a test of whether the $J_{\text{CIONO}_2}$ has the correct solar zenith angle dependence to represent the measurements. The similarity of $J_{\text{CIONO}_2}$ and CIO is a strong indication that CIONO₂ photolysis is the source of CIO during the day. This result does not depend on the absolute magnitude of $J_{\text{CIONO}_2}$, a test of which would require knowledge of [CIONO₂].

2) Measurements of the rate of decay of [CIO] after sunset (when the source term due to CIONO₂ photolysis is negligible) by Brune et al. (1990) and during SPADE show that the rate constant $\kappa_{\text{CIO}+\text{NO}_2+\text{M}}$ suggested by the current photochemical recommendation predicts the rate of disappearance of CIO under stratospheric conditions. The observed decay rate for CIO measured after sunset on the SPADE 930507 flight ($k = 0.7 \pm 0.3 \times 10^{-3} \text{ sec}^{-1}$) agrees within experimental error with the decay rate calculated from the NO₂ data obtained by the ALIAS instrument ($k = k_{\text{CIO}+\text{NO}_2+\text{M}} \times [\text{M}] \times [\text{NO}_2] = 1.2 \pm 0.8 \times 10^{-3} \text{ sec}^{-1}$).

3) The final requirement for a test of Eq. 3, that the ratio of $[\text{CIONO}_2]^\text{night}/[\text{Cl}]$ is constant for the data shown in Figure 1, cannot be unequivocally demonstrated without a simultaneous [CIONO₂] 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 [O₃] because the partitioning of [CIONO₂]/[Cl] is strongly dependent on [O₃]. A series of plots for different values of [O₃] conforms to the same inverse relationship, although as expected the derived value of $[\text{CIONO}_2]^\text{night}/[\text{Cl}]$ increases with [O₃]. This dependence is the subject of another paper currently in preparation.
Conclusions

Simultaneous in situ measurements of [CIO], [NO], [NO], [O], [N2O] and other variables have been used to draw two conclusions. First, the demonstration that CIO is inversely correlated with [NO] provides confidence that the control of [CIO] by [NO] (d[CIO]/d[NO]) through the formation of CINO3 is prescribed correctly in current models. Therefore modeling of O3 loss rates due to halogen reactions as a function of variable [NO] may be correctly described. It is crucial to recognize that Figure 1 shows the measured response of [CIO] to [NO] independent of whether the chemistry connecting CIO to ClO is completely correct.

Secondly, this analysis provides an estimate of [CINO3] + [CINO2] = 0.12 (x±2) assuming Φ(CIO) is equal to unity. We note that this result is not consistent with the simultaneous measurements of [HCl] given that [Cl2] = [Cl2] + [HCl] + [CINO2]; measured [HCl] and [CINO2] estimated here do not sum to [Cl2] 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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D.W. Toohey, L.M. Avallone, Earth System Science, University of California, Irvine, CA 92717.
R.J. Salawitch, Division of Applied Sciences, Harvard University, Cambridge, MA 02138.
E.L. Woodbridge, M.H. Proffitt, K. Aiken, NOAA Aeronomy Laboratory and Cooperative Institute for Environmental Research, Boulder, CO 80303.
C.R. Webster, R.D. May, J. Margitan, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109.

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