Observations of HO x and its relationship with NO x in the upper troposphere during SONEX

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Observations of HO\(_x\) and its relationship with NO\(_x\) in the upper troposphere during SONEX

Ian Faloona, David Tan, William H. Brune, Lyatt Jaelge, Daniel J. Jacob, Y. Kondo, M. Koike, Robert Chatfield, Rudolf Pueschel, Guy Ferry, Glen Sachse, Stephanie Vay, Bruce Anderson, John Hannon, and Henry Fuelberg

Abstract. Simultaneous measurements of the oxides of hydrogen and nitrogen made during the NASA Subsonic Assessment, Ozone and Nitrogen Oxide Experiment (SONEX) afforded an opportunity to study the coupling between these two important families throughout the free troposphere and lowermost stratosphere. Moreover, the suite of measurements made during the campaign was unprecedented in its completeness, thus providing a uniquely detailed picture of the radical photochemistry that drives oxidation and ozone production in this part of the atmosphere. On average, observed hydrogen oxides (HO\(_x\) = OH + HO\(_2\)) agree well with both instantaneous and diel steady-state models; however, there is a persistent deviation of the observations that correlates with the abundance of nitrogen oxides (NO\(_x\) = NO + NO\(_2\)) in the sampled air mass. Specifically, the observed HO tends to exceed the model predictions in the presence of high NO concentrations, by as much as a factor of 5 (>500 pptv NO\(_x\)), and is sometimes as little as half that expected by steady state at lower NO\(_x\) levels. While many possibilities for these discrepancies are discussed, it is argued that an instrumental artifact is not probable and that the discrepancy may bespeak a shortcoming of our understanding of HO\(_x\) chemistry. The consistently elevated HO in the presence of elevated NO\(_x\) leads directly to greater ozone production than expected, thereby extending the NO\(_x\)-limited regime of the upper troposphere. These results could thus have bearing on the predicted impacts of increasing NO\(_x\) emissions into this region of the atmosphere from, for example, the growth of global air traffic.

1. Introduction

During the months of October and November 1997, NASA carried out an experimental deployment in its subsonic aircraft assessment (SASS) program focusing on the chemical impact of commercial aircraft emissions over the North Atlantic flight corridor (NAFC). The Subsonic Assessment Ozone and Nitrogen Oxide Experiment (SONEX) was a unique airborne mission for many reasons. Two of the singular features of the experiment were, first, that it occurred in the late Northern Hemisphere autumn at predominantly high latitudes where the atmosphere is not very photochemically active and, second, that the data set it engendered is one of the first to include most of the tropospheric trace gases, specifically HO\(_x\) and HO\(_x\) sources, thought to be consequential in atmospheric oxidation and ozone production. The NASA DC-8 aircraft was the main platform for the study, and it operated for over 120 hours, including two transcontinental flights and 12 others based from Bangor, Maine, Shannon, Ireland, and the Azores. A summary of the mission can be found in the work of Singh et al. [1999].

The central importance of OH and HO in the chemistry of the atmosphere has been known for several decades [Levy, 1972; Logan et al., 1981], but it is only recently that in situ, simultaneous measurements of both of these extremely reactive and, consequently, very short-lived species have become available to test our understanding of the oxidative cycles in the atmosphere [Wennberg et al., 1995; Poppe et al., 1997; Folkins et al., 1997; Brune et al., 1998]. Comparisons of measurements made in the planetary boundary layer with steady-state models have been somewhat inconclusive in assessing whether or not an accurate understanding of the chemical cycles that give rise to the instantaneous levels of HO\(_x\) in the troposphere is extant, or for that matter, if steady state is an applicable assumption [Crosley, 1995]. Experiments in the planetary boundary layer have shown that in general, the observations of OH are lower than expected [Perner et al., 1987; Eisele et al., 1996; Comes et al., 1997]. This led many researchers to invoke the presence of some unbeknown chemical sink, most probably hydrocarbon in form, which was not included in the chemical box models. Comes et al. [1997] even notice that the deviations of the model in their experiment in the Canary Islands seem to correspond to the NO:NO\(_2\) ratio, but the relationship is not fully developed, and they too suggest a missing biogenic hydrocarbon sink of OH.
Meanwhile, stratospheric observations have shown the budget of \( \text{HO}_2 \), to be fairly well understood in that region of the atmosphere [Stimpfle et al., 1989; Wennberg et al., 1995; Pickett and Peterson, 1996]. The former two in situ studies did, however, help confirm the absence of two important heterogeneous processes in photochemical models at the time: the hydrolysis of \( \text{N}_2\text{O}_5 \) to \( \text{HNO}_3 \) and the nighttime conversion of \( \text{NO}_2 \) to nitrous acid (HONO) on sulfate aerosols. The latter mechanism provides a longer wavelength photolysis source of \( \text{HO}_2 \), in the early morning at high solar zenith angles, and tentative evidence of this was observed in the upper troposphere during SONEX as well [Jaegle et al., this issue]. Further measurements of \( \text{HO}_2 \) in the upper troposphere and lower stratosphere (UT/LS) provided evidence of other previously unrecognized players in the \( \text{HO}_2 \) budget in these dry environments, namely, the photolysis of acetone and peroxides [Singh et al., 1995; Jaeglé et al., 1997; Folkins et al., 1998]. Brune et al. [1998] observed evidence of these precursors convectively lofted from Asia and transported to the upper troposphere [Stimpfle et al., 1989; Wennberg et al., 1995; R. B. Chatfield et al., unpublished data, 1999]. The SONEX payload, on the other hand, provided an unprecedented suite of observations of \( \text{HO}_2 \), in conjunction with simultaneous measurements of all of the sources thought to be important (i.e., hydrogen peroxide, methylhydroperoxide, formaldehyde, and acetone) as well as ozone, water vapor, and direct spectroradiometric observations of actinic fluxes. Moreover, the experiment represents the first time such thoroughly constrained tropospheric observations were made in the presence of considerably elevated \( \text{NO}_x \) (over 3 ppbv in some instances.) The \( \text{NO} \), encountered in a given air mass may have predominantly originated from lightning, the stratosphere, convective injection from the polluted, continental boundary layer, or from aircraft emissions of the approximately 700 commercial flights that traverse the NAFC each day. Of course, in most cases the observed \( \text{NO} \), was from some complicated superposition of all three of these sources [Thompson et al., 1999; Liu et al., 1999; R. B. Chatfield et al., unpublished data, 1999 (hereinafter referred to as C99)].

The models and measurements of \( \text{HO}_2 \), are thus put to the test in a wide variety of chemical and meteorological environments. Aside from merely absolute agreement between the two, the experimental data set provides an opportunity to try to analyze weak points one or the other may have in certain chemical regimes. We began by seeking trends in the magnitude and direction of the discrepancy between the observations and the model predictions and then attempting to surmise what factors might be driving such trends.

In the following section we present a brief overview of the experimental techniques employed in the measurements and the two types of steady-state models to which the data were compared. Section 3 begins with a brief summary of the overall agreement between the \( \text{HO}_2 \) observations and the models and then goes on to demonstrate that there is a persistent trend in the way the observations and models deviate from one another. Further, it is established that the principal determinant of this bias is the atmospheric abundance of \( \text{NO}_x \). The second part of section 3 presents evidence of this relationship in several atmospheric regimes. We then turn to plausible reasons for this \( \text{NO}_x \)-dependent discrepancy, specifically examining possible instrumental interferences in section 4, as well as positing a misunderstanding of the underlying chemistry.

2. Experimental Methods

2.1. Aircraft Instrumentation

The \( \text{HO}_2 \) measurements were made onboard the DC-8 with the Penn State Airborne Tropospheric Hydrogen Oxides Sensor (ATHOS) instrument. SONEX was the second deployment of this instrument, originally developed in 1996 and flown onboard the DC-8 during the SUCCESS mission of that year. ATHOS is an in situ laser induced fluorescence (LIF) \( \text{OH} \) detection system based on fluorescence assay by gas expansion (FAGE) [Hard et al., 1984]. The instrument operates at reduced pressures, typically 4-10 hPa, by drawing air from below the aircraft through a small orifice into a low-pressure detection chamber. The air passes through the 1.57 mm orifice and undergoes a supersonic expansion followed by rapid development of a laminar flow profile inside a heated inlet tube (approximately 50 cm in length) which leads to two detection chambers in series. At the first detection cell the sample is probed with a pulsed, 308 nm dye laser beam in a multispas White cell. The pump laser is operated at a 5 kHz repetition rate, and after each laser pulse clears the detection cell, a fast-switching microchannel plate PMT (Hamamatsu Corp.) is biased into a high gain state, and photons from the resonce fluorescence \((A \Sigma-\Sigma, v'=0 \rightarrow v''=0)\) of the OH molecules in the sample are counted. In transit to the second detection cell, \( \text{NO} \) is injected into the flow to rapidly convert the ambient \( \text{HO}_2 \) to \( \text{OH} \), and a second identical measurement is made to quantify the total \( \text{HO}_2 \). The dye laser is tuned alternately on and off the \( \text{OH} \) absorption line every 10 s by means of an intracavity etalon which is controlled by an electronic feedback loop that monitors an \( \text{OH} \) reference cell. The photon counting, instrument control, automatic diagnostic/calibration procedures and monitoring of the instrumental parameters are all conducted by the data acquisition/power supply and motor control system designed and built in-house at Penn State. Other descriptions of the technique may be found in the work of Stevens et al. [1994], as well as a comprehensive instrumental description of ATHOS in particular by W. H. Brune et al. (manuscript in preparation, 1999).

Currently, we estimate the absolute accuracy of the ATHOS \( \text{HO}_2 \) measurements to be no worse than \( \pm 40\% \). This value is an upper limit to the combination of all of the measurement uncertainties that go into the instrumental calibration. Such an error would appear in the data as a more or less uniform bias from the models. A systematic bias, however, is not apparent in the data set. The precision, on the other hand, is well defined by the Poisson statistics of photon counting and as such depends on the integration time of the measurement and the shot noise that determines the background signal. The standard deviations of the 1 min data reported for SONEX were usually below 0.015 parts per trillion by volume (pptv) for \( \text{OH} \) and less than 0.03 pptv for \( \text{HO}_2 \). The magnitude of these \( 1\sigma \) values are too small to influence the \( \text{HO}_2 \), comparisons of the forthcoming analysis. The total \( \text{HO}_2 \), mixing ratios are typically between 1 and greater than 2 orders of magnitude larger than the \( 1\sigma \) precision.
NO and NO₂ measurements were made with a two channel O₃–NO chemiluminescence method, in which one channel is passed through a heated gold tube with the addition of CO in order to catalytically reduce all NO₂ species to NO. The NO measurement is estimated to possess an accuracy of 8% at a nitric oxide mixing ratio of 100 pptv [Kondo et al., 1997]. At the sampling altitudes characteristic of SONEX the 1 min NO data have a 2σ precision of approximately 11% at 20 pptv and less than 3% at 100 pptv. Aerosols and large particles were detected by the Forward Scattering Spectrometer Probe (FSSP) which measures the laser light scattered in the forward direction by such particles. The detection range of the FSSP is 0.4 to 20 μm effective diameter [Pueschel et al., 1994].

### 2.2. Computer Steady-State Models

The HOx observations made during SONEX were compared with two different steady-state models. The first is a zero-dimensional box model which solves for the expected levels of HOx, assuming that the instantaneous production and loss are in balance. The instantaneous steady-state (ISS) concentration of HOx is derived from the nonnegative roots of the following quadratic equation:

\[
L_2[\text{HO}_x]_2 + L_1[\text{HO}_x] - P_{\text{an}} = 0 \tag{1}
\]

where \(P_{\text{an}}\) is the sum of all directly measured HOx production rates (mostly photolytic), and \(L_1\) is the sum of all the first-order OH and HOx loss rates:

\[
\text{OH} + \text{NO} \rightarrow \text{HNO}_2, \tag{2}
\]

\[
\text{OH} + \text{HNO}_3 \rightarrow \text{NO}_3 + \text{H}_2\text{O}, \tag{3}
\]

\[
\text{OH} + \text{HNO}_3 \rightarrow \text{NO}_3 + \text{H}_2\text{O}, \tag{4}
\]

\[
\text{HO}_2 + \text{NO} \leftrightarrow \text{HNO}_2. \tag{5}
\]

Thermal dissociation of peroxynitric acid (the reverse of reaction (5)) is included as a HOx production term in the \(L_1\) of equation (1). Furthermore, because NO₂ and peroxynitric acid (PNA) were not measured directly, their concentrations were estimated to be the photostationary state values predicted by the measured \(O_3\), \(NO\), \(J(\text{NO}_2)\), \(OH\), and \(HO_2\). The sum of the loss rates of second order in HOx comprise \(L_2\) in equation (1), namely,

\[
\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2, \tag{6}
\]

\[
\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2. \tag{7}
\]

These self-reactions furnish the main losses of HOx in clean, low NO environments but become less important as NOx increases due to the acceleration of reactions (2) through (5). Because more than 85% of the observed HO₂:OH ratios were greater than 10, the calculation makes the assumption that all of the HOx is HO₂. The predicted HO₂:OH ratio, \(R_{\text{HOx}}\), is based primarily on the concentrations of CO, NO, and \(O_3\):

\[
R_{\text{HOx}} = \left( k_{\text{OH-CO}}[\text{CO}] + k_{\text{OH-CH}_4}[\text{CH}_4] + k_{\text{OH-NO}_2}[\text{O}_3] \right) / \left( k_{\text{HO}_2:NO_2}[\text{NO}] + k_{\text{HO}_2:NO}[\text{O}_3] \right), \tag{8}
\]

where the \(k\) values represent the HOx reaction rate coefficients with each of the constituent concentrations. The ISS OH concentration is thus estimated from the HOx (calculated from equation (1)) by means of this estimated ratio (\(OH = \text{HOx}/R_{\text{HOx}}\)).

The calculation is constrained by all measured quantities onboard the DC-8 where available (including photolysis frequencies, NO, \(O_3\), H₂O, HNO₃, acetone, and peroxides.) Values of the peroxides and formaldehyde were estimated as half of their respective detection limits when the measurements were below such limits. The respective limits of detection for the H₂O, CH₃OH, and HCHO measurements aboard SONEX were 15, 25, and 50 pptv [Lee et al., 1995]. Jaquelep et al. [this issue] show that the DSS model estimates of these species are, on average, similar to the one-half limit of detection values, indicating that the assumption may be reasonable. In order to maximize concurrent data coverage, acetone and formaldehyde levels were interpolated between their integrated measurement points with a cubic spline algorithm, except during ascent or descent of the aircraft. All of the chemical reaction rate data used in the model comes from DeMore et al. [1997], except the parameters for nitric acid formation, reaction (2), for which the most recent assessment by Dransfield et al. [1999] was used.

The second HO calculation used in this study was that from the diel steady-state (DSS) model of Jacob et al. [1996]. This photochemical model is run for every minute of each flight and is constrained with the observed \(O_3\), CO, CH₄, H₂O, acetone, hydrocarbons (ethane, methane, and C₄ alkanes), temperature, pressure, aerosol surface area, \(J(\text{NO}_2)\), and \(J(O_3)\). NO, (=NO+NO₂+HNO₃+HNO₂+NO+2N₂O₅) is kept fixed for each calculation point such that NO calculated by the model matches the observed NO at the time of day of the observations. The chemical mechanism in the DSS photochemical model is based on the Jet Propulsion Laboratory (JPL) recommendations [DeMore et al., 1997]. More up-to-date data for the quantum yields of acetone and \(O_3\rightarrow\text{O}(\text{D})\) are from Gierczak et al. [1998] and Talukdar et al. [1998], respectively. The hydrolysis of N₂O₅ on sulfate aerosols, with an uptake coefficient (\(\theta\)) of 0.1, was the only heterogeneous reaction included in this version of the model. See Jacob et al. [1996] for further details of the diel steady-state model.

To ensure that the HO deviations were not simply attributable to the DSS estimation of longer-lived, yet measured molecular species, a similar analysis was run for another Harvard model product of 3-5 min data in which the diel steady-state values of OH and HOx were fully constrained by the observations of HNO₃, peroxycetyl nitrate (PAN), H₂O₂, and CH₂OOH (when above their detection limits.) The average ratio of measured to calculated HO in this smaller data set was 0.86, and the general trends with NOx presented here with the less constrained model did not change significantly. For this study we used the analysis with the former, less constrained DSS model because of the greater data abundance.

### 3. Results of Observation and Model Comparison

#### 3.1. General Agreement

Table 1 presents a summary of the comparisons between the model predictions and the observations of HOx, OH, and the HOx:OH ratio for each flight in which concurrent data exist. The total body of 1 min data presented have been filtered to exclude periods when the solar zenith angle (SZA) was greater than 80° and when the DC-8 was thought to be sam-
HO, In the following analysis the HOx deviation refers to the ratio of the observed value over that of the model prediction. Generally account for over 80% of the observed variability in HOx for the entire data set is 0.99 and respectively. Moreover, the $r^2$ values imply that the models generate a steady-state calculation (Table 1). In fact, the average ratio of the observed value to the modeled value.

For the case of the HOx/OH ratio the deviation represents the quotient of the measured ratio to the model’s calculated ratio. Notice that for all flights the average HOx/OH deviation is within 25% of unity and that similarly, the HOx deviations all remain below 35%, except for the November 12 transcontinental flight. The overall agreement is well within the absolute accuracy of the HOx observations, currently estimated at ± 40%; and all the more so when the combined uncertainties from both the measurements and the models (typically of comparable magnitude, 35%-50%) are considered. The large excursions from the ISS model in early November are a result of the paucity of formaldehyde data for these flights; their absence omits a significant source of HOx in the model and results in a systematic underprediction. Nonetheless, on a flight-by-flight basis there is significant variability in the amounts and directions of the HOx deviations.

The development of the ISS model was not undertaken in order to compare the performance of the two models in any systematic way. Rather it was intended as a second, independent approach to predicting the steady-state HOx levels, and more importantly to the present analysis, to reproduce the persistent underestimation of HOx under high NOx conditions. The fact that both models exhibit similar behavior as a function of NO seems to indicate that the underlying assumptions about HOx chemistry in the UT may require modification and more importantly to the present analysis, to reproduce the persistent underestimation of HOx under high NOx conditions. The computational treatment of the photochemical system.

**Table 1. Comparison Between Models and Observations of HOx, OH, and the HOx/OH Ratio for the Entire SONEX Flight Series (Constrained to Data When Solar Zenith Angle < 80° and Outside of Clouds)**

<table>
<thead>
<tr>
<th>SONEX Flight Date (1997)</th>
<th>Number of 1 min Data Points</th>
<th>HOx Deviations $^{ab}$</th>
<th>OH Deviations $^{ab}$</th>
<th>HOx/OH Ratio Deviations $^{ab}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Harvard DSS</td>
<td>Penn State ISS</td>
<td>Harvard DSS</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Obs/Mod $^c$</td>
<td>$r^2$</td>
<td>Obs/Mod $^c$</td>
</tr>
<tr>
<td>Oct. 13</td>
<td>88</td>
<td>0.61 0.95 0.68 0.85</td>
<td>N/A N/A N/A N/A</td>
<td>N/A N/A</td>
</tr>
<tr>
<td>Oct. 15</td>
<td>156</td>
<td>0.64 0.94 0.61 0.91</td>
<td>0.83 0.92 0.79 0.91</td>
<td>0.81 0.97 0.84 0.97</td>
</tr>
<tr>
<td>Oct. 18</td>
<td>165</td>
<td>0.85 0.93 1.09 0.82</td>
<td>0.79 0.87 0.91 0.81</td>
<td>1.12 0.96 1.20 0.96</td>
</tr>
<tr>
<td>Oct. 20</td>
<td>184</td>
<td>0.74 0.94 0.90 0.84</td>
<td>0.65 0.93 0.85 0.91</td>
<td>1.22 0.95 1.30 0.96</td>
</tr>
<tr>
<td>Oct. 25</td>
<td>144</td>
<td>1.26 0.93 0.98 0.93</td>
<td>1.29 0.88 1.13 0.93</td>
<td>1.10 0.92 1.17 0.90</td>
</tr>
<tr>
<td>Oct. 28</td>
<td>155</td>
<td>0.76 0.96 0.63 0.94</td>
<td>0.73 0.89 0.61 0.90</td>
<td>0.90 0.90 0.80 0.87</td>
</tr>
<tr>
<td>Oct. 29</td>
<td>162</td>
<td>0.68 0.96 0.68 0.88</td>
<td>0.66 0.90 0.67 0.95</td>
<td>1.02 0.95 1.05 0.94</td>
</tr>
<tr>
<td>Oct. 31</td>
<td>84</td>
<td>0.95 0.97 0.80 0.96</td>
<td>1.32 0.79 1.27 0.70</td>
<td>0.75 0.83 0.74 0.89</td>
</tr>
<tr>
<td>Nov. 3</td>
<td>158</td>
<td>1.06 0.95 2.26 0.89</td>
<td>1.13 0.93 2.07 0.87</td>
<td>0.93 0.93 1.00 0.94</td>
</tr>
<tr>
<td>Nov. 5</td>
<td>258</td>
<td>1.13 0.95 1.76 0.87</td>
<td>1.07 0.87 1.65 0.73</td>
<td>0.94 0.92 1.01 0.92</td>
</tr>
<tr>
<td>Nov. 9</td>
<td>68</td>
<td>1.32 0.88 1.92 0.83</td>
<td>1.14 0.92 1.54 0.83</td>
<td>1.14 0.94 1.23 0.93</td>
</tr>
<tr>
<td>Nov. 10</td>
<td>156</td>
<td>1.26 0.94 1.16 0.91</td>
<td>1.20 0.83 1.03 0.89</td>
<td>0.99 0.92 1.03 0.93</td>
</tr>
<tr>
<td>Nov. 12</td>
<td>83</td>
<td>2.18 0.86 1.71 0.86</td>
<td>2.09 0.56 1.55 0.80</td>
<td>1.16 0.79 1.06 0.90</td>
</tr>
<tr>
<td>Average</td>
<td>1861 $^a$</td>
<td>0.99 0.94 1.20 0.88</td>
<td>0.99 0.83 1.14 0.81</td>
<td>1.00 0.93 1.05 0.93</td>
</tr>
</tbody>
</table>

$^a$Obs/Mod, the average ratio of the observed value to the modeled value. $^b$Values are for linear fits of observed to modeled data which are constrained to include the origin. The weighting is logarithmic such that the fractional deviation, not the absolute deviation, is critical to the calculation.

1. Number of 1 min average values which goes into observed/DSS model comparison; the number pertinent to the observed/ISS model comparison could be slightly different.

2. Total number of data points that comprise the averages.

pling inside clouds. The presence of cloud particles was determined by the measurement of significant particle concentrations with a mean diameter greater than 0.9 μm. This information was gleaned from the FSSP onboard the DC-8. In the absence of this particle size distribution data, the saturation ratios with respect to ice (S) were calculated, and episodes of supersaturation were excluded. These two criteria were used to filter the data because we wanted to separate out the effects of longer-wavelength radiation [Wennberg et al., 1999] as well as those of heterogeneous reactions on ice crystals which are thought to exert considerable influence on HOx levels in the atmosphere [Jaegle et al., this issue; Faloona et al., 1998; Mauldin et al., 1998]. Three quarters of all the 1 min data collected during SONEX, where both calculated and observed HOx measurements were available, passed through the filter and were used in this study, establishing a data set of over 31 flight hours representing predominantly homogeneous, daytime chemistry of the upper troposphere and lower stratosphere (more than 90% of the data reported were collected at or above 6 km above mean sea level).

Taken in their entirety, the data indicate a very close correspondence between the measured levels of HOx and the steady-state calculations (Table 1). In fact, the average ratio of observed to modeled HOx for the entire data set is 0.99 and 1.18 for the Harvard DSS and the Penn State ISS models, respectively. Moreover, the $r^2$ values imply that the models generally account for over 80% of the observed variability in HOx. In the following analysis the HOx deviation refers to the ratio of the observed value over that of the model prediction.
are listed in Table 2. These are averages for the filtered data used in this analysis as described above. 

The ratio of $\text{HO}_2$ to $\text{OH}$ agrees more closely with the model predictions, and the agreement exhibits less variation from flight to flight. The fact that the ratio is well predicted attests to a good understanding of the processes that control the $\text{HO}_2$ and $\text{OH}$ equilibration (equation (8)). In the upper troposphere the partitioning of $\text{HO}_x$ is controlled primarily by the relative rates of the two reactions

\begin{align}
\text{OH} + \text{CO} + \text{O}_2 & \rightarrow \text{HO}_2 + \text{CO}_2, \\
\text{HO}_2 + \text{NO} & \rightarrow \text{OH} + \text{NO}_2. 
\end{align}

These reactions represent an exchange between $\text{OH}$ and $\text{HO}_2$ and, typically, occur on timescales of about 6 s in the UT over the North Atlantic. Near the tropopause and in the lowermost stratosphere, however, the rapid interchange becomes increasingly dominated by the reactions

\begin{align}
\text{OH} + \text{O}_3 & \rightarrow \text{HO}_2 + \text{O}_2, \\
\text{HO}_2 + \text{O}_3 & \rightarrow \text{OH} + 2\text{O}_2, 
\end{align}

because $\text{O}_3$ tends to be more abundant, while CO tends to be less abundant. These reactions interchange $\text{HO}_x$ on timescales of about 1 min in the lowermost stratosphere. Regardless then of the exact composition and history of a given air parcel, the $\text{HO}_2$ to $\text{OH}$ ratio should be determined quickly by these readily measured species: $\text{NO}$, $\text{CO}$, and $\text{O}_3$. Moreover, the measurement of the ratio is not so prone to instrumental artifacts because systematic biases tend to cancel out, and the quantity is greatly independent of the absolute calibration of ATHOS. We estimate the uncertainty in the measurement of the $\text{HO}_2$ to $\text{OH}$ ratio to be no more than 20%, particularly when extremely low $\text{OH}$ levels (higher SZA) are excluded. Beyond filtering the data for daytime conditions, observations of the ratio were not included in the comparisons if the $\text{OH}$ concentration dropped below approximately one-half its 1σ value.

### Table 2. Average Chemical and Meteorological Conditions for the Filtered SONEX Data Set (Constrained to Data When Solar Zenith Angle < 80° and Outside of Clouds)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>PI, Institution</th>
<th>Measurement Type</th>
<th>Units</th>
<th>Median</th>
<th>Mean</th>
<th>s.d.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td>Sachse, NASA LaRC</td>
<td>diode laser hygrometer</td>
<td>ppmv</td>
<td>136</td>
<td>284</td>
<td>470</td>
</tr>
<tr>
<td>$\text{O}_3$</td>
<td>Gregory, NASA LaRC</td>
<td>NO+O$_3$ chemiluminescence</td>
<td>ppbv</td>
<td>57.0</td>
<td>78.0</td>
<td>61.0</td>
</tr>
<tr>
<td>$\text{CO}$</td>
<td>Sachse, NASA LaRC</td>
<td>diode laser spectrometer</td>
<td>ppbv</td>
<td>84.0</td>
<td>82.0</td>
<td>23.0</td>
</tr>
<tr>
<td>$\text{NO}$</td>
<td>Kondo, Nagoya U.</td>
<td>NO+O$_3$ chemiluminescence</td>
<td>pptv</td>
<td>57.0</td>
<td>101.0</td>
<td>157.0</td>
</tr>
<tr>
<td>$\text{HNO}$</td>
<td>Talbot, U. New Hampshire</td>
<td>ion chromatography</td>
<td>pptv</td>
<td>117.0</td>
<td>214.0</td>
<td>232.0</td>
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<td>Kondo, Nagoya U.</td>
<td>NO+O$_3$ chemiluminescence</td>
<td>pptv</td>
<td>401.0</td>
<td>505.0</td>
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<td>$\text{PAN}$</td>
<td>Singh, NASA ARC</td>
<td>gas chromatography (GC)</td>
<td>pptv</td>
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<td>84.0</td>
<td>66.0</td>
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<td>Shetter, NCAR</td>
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<td>2.70</td>
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<td>whole air canister, GC</td>
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<td>674.0</td>
<td>713.0</td>
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<td>$\text{CN}$</td>
<td>Anderson, NASA LaRC</td>
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Figure 1. Ratio of observed HOx to modeled HOx as a function of NOx for 12 flights. The one-to-one line (solid) and the ±40% lines (dashed) are shown in each plot for reference. The ratio to the Harvard diel steady-state model (open squares) tend to be closer to 1 than the ratio to the Penn State instantaneous steady-state model (x), but both tend to significantly underpredict the observations at higher NOx.
Figure 1 demonstrates that the NO$_x$ correlation exists in most instances for all flights, independent of the average agreement on any particular day. Although the more sophisticated diel steady-state model tends to predict the HO$_x$ levels more accurately than the simple steady-state calculation, similar relationships are evident in both deviations with respect to NO$_x$. Because the observations deviate from both models in a similar fashion, and if, as we argue in section 4.1, it is not an instrumental phenomenon, then the discrepancy may result from a misconception in our understanding of HO$_x$ chemistry in the troposphere, be it in the rate and equilibrium constants used in this range of pressures and temperatures, or in the actual reactions that participate in HO$_x$ production and/or loss. The average slopes of the HO$_x$ deviation for the DSS model is 28% per 100 pptv NO$_x$ and 41% per 100 pptv NO$_x$ for the ISS model.

3.3. Evidence From SUCCESS

There is evidence of just this sort of NO$_x$ dependence in another airborne data set of ours. Figure 2 is a composite of all flights made during the SUCCESS mission in the spring of 1996. Most flights took place over the central United States, but two were carried out offshore of the Pacific Northwest. Although the model calculations performed in support of this campaign were not so tightly constrained by a full suite of chemical measurements (e.g., acetone, peroxides, and photolytic fluxes were not measured), a definite relationship with NO$_x$ is apparent. Moreover, the general shape of the relationship bears a very strong resemblance to the one derived from the SONEX data. Above about 300 pptv NO$_x$, the deviation appears to increase linearly with NO$_x$, as it does in the SONEX data and clusters around this line all the way up to several
parts per billion by volume of NO\textsubscript{x}. High levels of NO\textsubscript{x} were attained during three chase flights (May 3, 4, and 7) in which the DC-8 flew directly in the exhaust trails of a Boeing 757. In a study of the HO\textsubscript{x} balance in these aircraft plumes, Tan et al. [1997] discuss the observation of anomalously high HO\textsubscript{x} concentrations in the exhaust plumes (a steady-state treatment predicts that all of the HO\textsubscript{x} would react away in the NO\textsubscript{x}-rich plumes within a matter of seconds). The authors suggested that an incomplete mixing process of the long-lived plumes could be one possible explanation for the discrepancy. It is interesting to note that when viewed in the present light the underprediction of the models in the exhaust plumes is merely the extension of a phenomenon that is present in ambient air with levels of NO\textsubscript{x} that exceed a few hundred parts per trillion by volume. Unfortunately, this evidence of the NO\textsubscript{x} dependence comes from the same measurement (ATHOS) and does not therefore temper the possibility of an instrumental effect.

In a recent study by Folkins et al. [1997], HO\textsubscript{x} observations aboard the NASA ER-2 are compared with photochemical steady-state models in two descents of the aircraft through upper tropospheric biomass burning plumes encountered over the western Pacific equatorial region. The results indicate that the measured HO\textsubscript{x} is always greater than the models in these high NO\textsubscript{x} regimes (50-600 pptv) even when an (unmeasured and therefore hypothetical) acetone source is included in the model. Careful inspection of the small data set gathered during these plume crossings [Folkins et al., 1997, Figures 2 and 4] does reveal evidence, though, of a NO\textsubscript{x} dependence in the deviation of the model. In one case (Figure 4 of the work cited above) the HO\textsubscript{x} deviation goes from less than 2 at ~70 pptv NO\textsubscript{x} to well over 10 near 700 pptv. Interestingly, the change in deviation is not nearly as large in the other crossing. The main difference between the two episodes seems to be that the period of the largest deviations coincides with the largest predicted HO\textsubscript{x} sinks involving nitric and peroxynitric acids (reactions (2)-(5)), rather than reaction (6). It is important to examine other data sets in which HO\textsubscript{x} and NO\textsubscript{x} are measured simultaneously to explore the possibility that this phenomenon is atmospheric rather than instrumental.

3.4. Evidence From the Lower Stratosphere

In considering the extent to which the NO\textsubscript{x} effect could be applicable, it is important to determine whether measurements display this tendency in a variety of environments. If the apparent NO\textsubscript{x} influence were, for example, the result of some unknown, unmeasured HO\textsubscript{x} source that happened to be spatially correlated with NO\textsubscript{x}, then it might exhibit variability depending on the particular source of NO\textsubscript{x} and its residence time.
in the atmosphere. In the SONEX data set then it is possible to establish the existence of the NOx dependence in the lower stratosphere, away from the complicating influence of other species such as water, aerosol surfaces, and hypothetical HOx precursors which would most probably come from surface emissions.

Figure 3 shows a compilation of the SONEX measurements as, again, the ratio of observed NOx to that predicted by the DSS model, made in air of elevated potential vorticity (PV). The data are from intervals from three separate flights (i.e., October 15, 20, and 29, 1997) in which the potential vorticity was measured to be greater than 8.8 PV units. The potential vorticity reported is a scaled Ertel’s PV, a scalar quantity derived from the projection of the absolute vorticity of the air onto the potential temperature gradient. In terms of standard meteorological units, one PV unit is equivalent to 1x10^4 K s^-1 mbar^-1. PV is a dynamically conserved quantity that possesses a strong gradient at the tropopause and as such is frequently used as a tracer for air of stratospheric origin. Typically, values of this scaled quantity greater than 3-5 are considered to be indicative of stratospheric air in midlatitude regions. In this analysis we use PV values much larger than that (>8.8) to examine a subset of the data from the most unambiguously stratospheric flight legs of the mission.

Figure 3 clearly illustrates a similar correspondence in the HOx deviation ratios with NOx as is apparent in the entire data set. The linear relationship exhibited in each of the three sets of data are remarkably similar, and the slope appears to be about twice as strong as the average slope for the entire data set (60% per 100 pptv NOx as opposed to 28%). The average mixing ratio and surface area concentration for these combined intervals are 43 ppmv and 11 μm^2/cm^2, respectively. These data thus represent a strong example of the hypothetical surface precursors.

Evidence from other experiments with different instrumentation compared with different steady-state models would lend considerable support to the validity of these observations. A preliminary search through the POLARIS ER-2 data yielded a small data set of only eight 3 min points in which all necessary measurements and model results were publicly available and where the O3 levels were sufficiently “tropospheric” in magnitude (<300 ppbv). In this small sample, however, the HOx deviation ratio grows from about 0.85 at 70 pptv NO to 1.8 at over 200 pptv. We encourage further investigation of these and other apropo data sets.

3.5. Evidence in Differing Types of NOx

There has been much consideration of the individual NOx sources in the SONEX data set [Thompson et al., 1999; Liu et al., 1999; C99]. These authors try to assign certain fractions of observed NOx to the various sources operative during the mission and evaluate the impact that air traffic has on the NOx budget. In general, the NOx sampled in flight had originated from a variety of sources: convection from areas where considerable surface sources were present, lightning production during convective events from both continental, polluted regions as well as from cleaner marine environments, aircraft engine exhaust, and to a smaller extent the stratosphere. The consistent features of the NOx dependence seen in Figure 1 underscore the ubiquity of this effect in the atmosphere. The NOx influence seems to persist independent of origins of NOx, in a given air mass.

Figure 4 shows three time series examples of the variation of the HOx deviation with ambient NOx, levels. The solid line corresponds to the measured NOx (NO + NO2 estimated from the ISS model), and the symbols are the deviation ratios of HOx with respect to each model predicted NOx. The top example is from a period on November 3, at an altitude of 12 km, when air traffic exhaust is thought to be the dominant NOx source, by approximately a factor of 3-4. Although the Harvard DSS model tends to predict the measured HOx levels more accurately, both models fluctuate very faithfully with the NOx in the air mass. During this flight no formaldehyde data were taken, and consequently, the ISS model is consistently low due to this missing HOx source. The second time series is from the flight of November 9 when very high levels of NOx were encountered, up to 3 ppbv. The majority of this NOx is thought to have originated from recent convection that took place off the northeastern seaboard of the United States and Nova Scotia. Aside from the model predictions of lightning influence, the NO/NOx ratio measured at the NOx peak near 18.9 hours was about two thirds, indicating a very recent emission. Again, a strong correlation is seen in the model underpredictions (up to 20 times too small!) with the elevated NOx levels. The last period is from the October 28 flight across the southern portion of the NAFC. The NOx contributions during this period seem to be a mixture of surface sources transported from North America over the course of several days and recent aircraft emissions from the flight corridor. The relationship in each episode depicted in Figure 4 is striking, and it appears that the expounded NOx relationship is independent of the origin of the nitrogen oxides. The absolute HOx levels are typically between 0.5 and 1.0 pptv during these periods of elevated NOx. Such concentrations are some 10-15 times greater than the 1 min 1σ precision of the HOx measurement and therefore are not considered to be near the instrumental limit of detection.

4. Possible Causes of the Discrepancy

4.1. Instrumental Concerns

An obvious candidate for the explanation of the NOx influence is that of a measurement artifact. A plausible mechanism for biasing the HOx measurements is the existence of an interfering species in the atmosphere that might somehow give rise to OH and HO2 when inside the instrument. However, it is important to note that the very good agreement among the measured and modeled HOx:OH ratio implies that to within experimental uncertainty, such an interference would need to produce both HO2 and OH signals and would need to do so in proportional amounts consistent with their expected ratio defined by equation (8). Because the residence time inside the instrument, approximately 45 ms, is much shorter than the equilibration timescale of the HOx:OH system (=6 s) and the fact that the reduced internal pressure slows bimolecular reaction rates by at least 2000 times, the relaxation of any internally created HOx to the expected HOx:OH ratio is not likely. This fact notwithstanding the most plausible interference is that from thermal dissociation of peroxynitric acid, or PNA (HO2NO2). PNA is a thermally labile peroxyacid formed in the atmosphere by the combination of HOx and NOx.
The inlet tube of the ATHOS instrument is kept at a constant temperature, usually near 275 K, in an effort to maintain an equilibrium between possible HOx species physisorbed on the inlet walls and those in the sample air stream. Because this temperature tends to be warmer than the ambient air of the middle to upper troposphere, the possibility exists that PNA could be thermally dissociating on its brief journey to the detection chambers. Furthermore, the reduced pressure of the instrument serves to push the PNA equilibrium toward dissociation. Simple lifetime considerations using the equilibrium constant and rate of forward reaction of reaction (5) from DeMore et al. [1997] yields an e-folding time for PNA dissociation of about 1 min at typical operating temperatures and pressures. The transit time from the inlet pinhole to the second, HOx, detection axis is about 45 ms, so the theoretical conversion rate of PNA to HO2 is only 0.07 pptv per 100 pptv of ambient PNA. The magnitude of such an artifact is not nearly sizeable enough to account for the NOx dependence observed, since typical HO2 abundances measured at lower solar zenith angles (<80) ranged from 1 to 5 pptv. Typical model estimates of ambient PNA levels during SONEX are of the order of 60 pptv [Jaegle et al., this issue].

Another test of a possible PNA interference came during the predawn flight leg of November 12, 1997. As part of a series of diagnostic tests performed on the instrument in the dark, the inlet tube was heated and then allowed to cool gradually over the range of 35°. During such “baking” conditions, a significant signal is produced within the instrument, presumably due to the desorption of HOx, or precursor species, from the interior walls of the inlet. As the inlet tube cools down, the signal decays away, and the influence of any hypothetical PNA interference should change due to the strong temperature dependence of the dissociation constant, \( \Delta E/R = 10,900 \) K [DeMore et al., 1997]. Conservatively, assuming that the high-temperature signal arises solely from the dissociation of PNA and extrapolating such an effect back to normal operating temperatures, the greatest possible contribution is less than 0.08 pptv per 100 pptv of PNA. Furthermore, the correlations of the HOx deviation with the model-predicted concentrations of PNA are small compared to that of the correlation with NOx. The total normalized covariances for the entire filtered data set between the HOx deviation ratio and NOx is 0.70, whereas the covariances with PNA and peroxyacetylnitrate (PAN), another possible interfering species, are just 0.19 and -0.11, respectively.

Another possible instrumental effect could be the presence of an HO2 offset. The OH and the HO2 measurements are made by taking the difference of the photon counts accumulated between the interval (usually 10 s) when the dye laser is tuned to an OH absorption peak and the counts when the laser is tuned off line. The spectral separation between the on-line and the off-line positions is kept small, approximately 10 GHz, to minimize any changes in the laser background from one position to the next. Nonetheless, it is possible that a consistent bias exists between the background signals collected from each laser setting. Repeated zero air tests in the labora-
Figure 5. Comparison of 1 min observed HO2 and DSS-modeled HO2 for the entire flight of October 13. The data are separated into low NOx conditions, < 100 pptv (diamonds), and higher NOx conditions, >100 pptv (pluses). The one-to-one line (solid) and the ±40% margins (dashed) are included for reference. All of the data for which the observations are greater than the model occur at higher NOx, and this holds true for a wide range of HO2 levels (from 2 to 8 pptv.)

A signal artifact of this nature would become most obvious at low HO2 levels; and because HO2 and NO are negatively correlated due to their rapid reaction (10), an instrumental offset would appear as model underpredictions at high NO. A counterexample of this proposed bias presents itself in the data from the flight of October 13, 1997. During this flight over the continental United States, convected HOx precursors were abundant enough to allow for the coexistence of higher NOx along with greater levels of HO2. Figure 5 is a scatterplot of the observed versus the modeled HO2 concentrations partitioned into two groups: one where the air contained high levels of NOx along with greater levels of HO2. Figure 5 is a scatterplot of the observed versus the modeled HO2 concentrations partitioned into two groups: one where the air contained high levels of NO (>100 pptv) and the other where less than 100 pptv NO was present. All of the points that lie on the side of the one-to-one line indicating model underprediction are in the high NO category, and this distinction holds over a range of HO2 concentrations from 2 to 7.5 pptv. Any hypothetical HO2 offset would be far less noticeable at these large concentrations, and yet the underprediction by the model persists. This relationship indicates that higher observation deviations at greater NOx levels are not merely the influence of an instrumental offset.

4.2. Missing or Misunderstood Chemistry

The other principal candidates that could explain the NOx dependence of the HOx deviations are actual chemical features of the atmosphere that are either completely neglected in the models or are incorrectly parameterized. Most likely, these could take the form of missing HO source terms that are somehow correlated with NOx concentrations, or alternately could be explained by some sort of biased overestimation of HOx sink terms. If for example, despite the analysis presented in section 3.5, the deviation was a result of only aircraft-generated NOx, then the answer could lie in an unaccounted combustion source of HOx that may be bound up in a slowly released compound (e.g., HNO3 or HOxNOy). If such a hypothetical species were not measured during SONEX, then their additional HOx source contributions would be undetected by the models. On the other hand, the two principal loss routes of HOx at high NOx (over a couple hundred pptv) involve NO2 and HO2NO2 through equations (2) and (5). As pointed out earlier, these two species were not measured during the campaign and therefore their estimated HOx loss rates rely on steady-state calculations that prescribe their abundances.

HOx in the upper troposphere is an extremely buffered chemical system [Wennberg et al., 1998]. The losses of OH and HO2 tend to be predominantly quadratic in nature; that is, they depend on the square of HO concentrations, especially at the low NOx levels typical of background conditions in the upper troposphere. The oxidation of methane and other hydrocarbons by the hydroxyl radical, \(\text{OH} + \text{CH}_4 + \text{NO} + \text{O}_2 \rightarrow \rightarrow \text{HO}_2 + \text{CH}_2\text{O} + \text{H}_2\text{O}\), is part of the HOx exchange cycling...
and it usually yields more than one molecule of HO₂ by its production of formaldehyde; thus, once photochemically generated in the atmosphere, HO₂ begets more HO₂ in the presence of hydrocarbons and a little NO. Such autocatalytic amplification coupled with quadratic loss rates leads to a system whose equilibrium concentrations are tightly constrained; consequently, HO₂ levels in the atmosphere can remain relatively constant while other species vary drastically. Because of the high degree of buffering, explanations of our measured HO₂ discrepancy in terms of incorrect kinetics data require drastic changes to laboratory reaction rates.

Peroxynitric acid is a reasonable suspect because its concentrations were not confirmed by measurements and its equilibrium constant has a large uncertainty at the low temperatures of the UT. The uncertainty in the equilibrium constant reported by DeMore et al. [1997] is as high as a factor of five at 220 K (Sander, personal communication). Running the ISS model with an equilibrium constant a factor of five smaller yields a change in the overall slope of the HO₂ deviation ratio with NO from 29% per 100 ppt NO, to 23% per 100 ppt NO. This sort of change is clearly not large enough to account for the entire discrepancy. In fact, significantly reduced correlations between the HO₂ deviation ratio and NO were not obtained until the PNA equilibrium constant was altogether eliminated. Artificially suppressing the formation of HO₂NO₂ in the model in this way reduced the slope to one-third its original magnitude or about 10% per 100 ppt NO.

The Penn State ISS model uses the recently reported reaction rate for OH + NOₓ from Dransfield et al. [1999] which is some 20% lower than the 1997 JPL recommendation at the conditions of the UT. This reaction is the principal sink of OH at high levels of NO, where the measurements outpace the model predictions by as much as a factor of 5. The use of this slower nitric acid formation did not alter the overall NO₂ dependence by more than a couple of percent.

5. Concluding Summary

Taken as a whole the measurements of HO₂ in the upper troposphere made during SONEX compare fairly well with the expectations of photostationary state models. However, most flights seem to have consistent biases which need to be investigated further to determine what is interfering with or otherwise lacking in the measurements or what is missing from the models. The observations seem to persistently overestimate the model predictions in conditions of high NO. This relationship was also borne out of the SUCCESS data set, and it may prove instructive to research other cases of such dependence in other data from different instrumentation and different models. If the observed NO₂ dependence is a true atmospheric phenomenon, then ozone production rates in the upper troposphere and lower stratosphere may be considerably higher than currently predicted. In this case, increased NO₂ emissions to that part of the atmosphere, where the O³ lifetime is long and its longwave radiative forcing is strongest, could have a profound and unanticipated impact on the global environment.

Acknowledgments. We thank the many fine staff members at Penn State, including Dianne Taylor, Robert Lesher, Christopher Frame, and Jeremy Basis. Also thanks are in order to the SONEX mission scientists Hanwant Singh and Anne Thompson, the pilots and crew of the DC-8, and the other investigators onboard for their willingness to work in the predawn hours. This work was supported by NASA grant NAG 2-1117. Further support to the first author was received in the form of a NASA Earth System Science Fellowship (reference 1995-GlobalCh000086), and he wishes to thank the supportive program scientists Ghassam Asrar and Ming-Ying Wei.

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(Received April 7, 1999; revised July 15, 1999; accepted August 19, 1999.)