Observations of HOx and its relationship with NOx in the upper troposphere during SONEX

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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 (HOx = OH + HO2) 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 (NOx = NO + NO2) 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 NOx), and is sometimes as little as half that expected by steady state at lower NOx 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 HOx chemistry. The consistently elevated HO in the presence of elevated NOx leads directly to greater ozone production than expected, thereby extending the NOx-limited regime of the upper troposphere. These results could thus have bearing on the predicted impacts of increasing NOx 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 HOx and NOx 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 HO2 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 HOx 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; Armerding et al., 1997]. This led many researchers to invoke the presence of some unknown 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: NOx 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 HO, 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 N₂O₅ to HNO₃ and the nighttime conversion of NO₂ species to nitrous acid (HONO) on sulfate aerosols. The latter mechanism provides a longer wavelength photolysis source of HO, in the early morning at high solar zenith angles, and tentative evidence of this was observed in the upper troposphere during SONEX as well [Jaeglé et al., this issue]. Further measurements of HO, in the upper troposphere and lower stratosphere (UT/LS) provided evidence of other previously unrecognized players in the HO, budget in these dry environments, namely, the photolysis of acetone and peroxydes [Singh et al., 1995; Jaeglé et al., 1997; Folkins et al., 1998].

Bruné et al. [1998] observed evidence of these precursors convectively lofted from Asia and transported to the upper troposphere over northern California. Jaeglé et al. [1997] demonstrated this effect over the central United States in the two, the experimental data set provides an opportunity to try data from the NASA Subsonic Aircraft Contrail and Cloud Pickett and Peterson, 1996]. The former two in situ studies budget of HOx to be fairly well understood in that region of the two types of steady-state models to which the data were better defined by the Poisson statistics of photon counting and the apparent in the data set. The precision, on the other hand, is generally 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 NO, was from some complicated superposition of all 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 HO, 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 HO, 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 NO₂. The second part of section 3 presents evidence of this relationship in several atmospheric regimes. We then turn to plausible reasons for this NO₂-dependent discrepancy, specifically examining possible instrumental interferences in section 4, as well as posing a misunderstanding of the underlying chemistry.

2. Experimental Methods

2.1. Aircraft Instrumentation

The HO, 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) 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 a 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 multistage 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 resonance fluorescence (AΣ-XΠ, v"=0 -> v'=0) of the OH molecules in the sample are counted. In transit to the second detection cell, NO is injected into the flow to rapidly convert the ambient HO, to OH, and a second identical measurement is made to quantify the total HO, The dye laser is tuned alternately on and off the OH absorption line every 10 s by means of an intracavity etalon which is controlled by an electronic feedback loop that monitors an 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. Bruné et al. (manuscript in preparation, 1999).

Currently, we estimate the absolute accuracy of the ATHOS HO, measurements to be no worse than ±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 OH and less than 0.03 pptv for HO, The magnitude of these 1σ values are too small to influence the HO, comparisons of the forthcoming analysis. The total HO, mixing ratios are typically between 1 and greater than 2 orders of magnitude larger than the 1σ precision.

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NO and NO\textsubscript{2} measurements were made with a two channel O\textsubscript{3}–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 NO\textsubscript{x} 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 2\sigma 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 \textmu m effective diameter [Pueschel et al., 1994].

2.2. Computer Steady-State Models
The HO\textsubscript{x} 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 HO\textsubscript{x} assuming that the instantaneous production and loss are in balance. The instantaneous steady-state (ISS) concentration of HO\textsubscript{x} is derived from the nonnegative roots of the following quadratic equation:

\[ L_1[\text{HO}_x]^2 + L_2[\text{HO}_x] - P_{ax} = 0 \] (1)

where \( P_{ax} \) is the sum of all directly measured HO\textsubscript{x} production rates (mostly photolytic), and \( L_2 \) is the sum of all the first-order OH and HO\textsubscript{2} loss rates:

\[
\begin{align*}
\text{OH} + \text{NO} &\rightarrow \text{HNO}_3, \\
\text{OH} + \text{HNO}_3 &\rightarrow \text{NO}_3 + \text{H}_2\text{O}, \\
\text{OH} + \text{HNO}_2 &\rightarrow \text{NO}_3 + \text{H}_2\text{O}, \\
\text{HO}_2 + \text{NO}_2 &\leftrightarrow \text{HNO}_4.
\end{align*}
\] (2-5)

Thermal dissociation of peroxytrinitic acid (the reverse of reaction (5)) is included as a HO\textsubscript{x} production term in the \( P_{ax} \) of equation (1). Furthermore, because NO\textsubscript{2} and peroxytrinitric acid (PNA) were not measured directly, their concentrations were estimated to be the photostationary state values predicted by the measured NO, NO\textsubscript{2}, J(NO\textsubscript{2}), OH, and HO\textsubscript{2}. The sum of the loss rates of second order in HO\textsubscript{x} comprise \( L_2 \) in equation (1), namely,

\[
\begin{align*}
\text{OH} + \text{HO}_2 &\rightarrow \text{H}_2\text{O} + \text{O}_2, \\
\text{HO}_2 + \text{HO}_2 &\rightarrow \text{H}_2\text{O}_2 + \text{O}_2.
\end{align*}
\] (6-7)

These self-reactions furnish the main losses of HO\textsubscript{x}, so in clean, low NO\textsubscript{x} environments but become less important as NO\textsubscript{x} increases due to the acceleration of reactions (2) through (5). Because more than 85\% of the observed HO\textsubscript{2}:OH ratios were greater than 10, the calculation makes the assumption that all of the HO\textsubscript{x} is HO\textsubscript{2}. The predicted HO\textsubscript{2}:OH ratio, \( R_{\text{HO}_2/\text{OH}} \), is based primarily on the concentrations of CO, NO, and O\textsubscript{3}:

\[
R_{\text{HO}_2/\text{OH}} = \left( k_{\text{OH} + \text{CO}} + k_{\text{OH} + \text{CH}_4} + k_{\text{OH} + \text{O}_3}[\text{O}_3] \right) / \left( k_{\text{HO}_2 + \text{NO}}[\text{NO}] + k_{\text{HO}_2 + \text{OH}}[\text{OH}] \right).
\] (8)

where the \( k \) values represent the HO\textsubscript{x} reaction rate coefficients with each of the constituent concentrations. The ISS OH concentration is thus estimated from the HO\textsubscript{2} (calculated from equation (1)) by means of this estimated ratio (OH = HO\textsubscript{2}/\( R_{\text{HO}_2/\text{OH}} \)).

The calculation is constrained by all measured quantities onboard the DC-8 where available (including photolysis frequencies, NO, O\textsubscript{3}, H\textsubscript{2}O, HNO\textsubscript{3}, 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 H\textsubscript{2}O, CH\textsubscript{2}OH, and HCHO measurements aboard SONEX were 15, 25, and 50 pptv [Lee et al., 1995]. Jaegle 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\textsubscript{x} 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\textsubscript{3}, CO, CH\textsubscript{4}, H\textsubscript{2}O, acetone, hydrocarbons (ethane, methane, and C\textsubscript{4} alkanes), temperature, pressure, aerosol surface area, J(NO\textsubscript{2}), and J(O\textsubscript{3}). NO\textsubscript{y} (=NO+NO\textsubscript{2}+HNO\textsubscript{3}+H\textsubscript{2}O\textsubscript{2}+NO\textsubscript{2}N\textsubscript{2}O\textsubscript{5}) 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\textsubscript{3}--O\textsubscript{1}(D) are from Gierczak et al. [1998] and Talukdar et al. [1998], respectively. The hydrolysis of N\textsubscript{2}O\textsubscript{5} on sulfate aerosols, with an uptake coefficient \( q \) 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\textsubscript{x} 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 HO\textsubscript{2} were fully constrained by the observations of HNO\textsubscript{3}, peroxyacetyl nitrate (PAN), H\textsubscript{2}O\textsubscript{2}, and CH\textsubscript{3}OH (when above their detection limits.) The average ratio of measured to calculated HO\textsubscript{2} in this smaller data set was 0.86, and the general trends with NO\textsubscript{x} 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 HO\textsubscript{2}, OH, and the HO\textsubscript{2}:OH ratio for each flight in which concurrent data existed. 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-

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The presence of cloud particles was determined by the measurement of significant particle concentrations with a mean diameter greater than 0.9 \mu m. 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_I) 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 HO levels in the atmosphere [Jaegld 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 HO, measurements were available, passed through the filter and were used in this study, establishing a 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 HO and the steady-state calculations (Table 1). In fact, the average ratio of observed to modeled HO, 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 HO. In the following analysis the HO deviation refers to the ratio of the observed value over that of the model prediction. For the case of the HO2:OH ratio the deviation represents the quotient of the measured ratio to the model's calculated ratio. Notice that for all flights the average HO2:OH deviation is within 25% of unity and that similarly, the HO, deviations all remain below 35%, except for the November 12 transcontinental flight. The overall agreement is well within the absolute accuracy of the HO, observations, currently estimated at \( \pm 40\% \); 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 HO, 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 HO, 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 HO, levels, and more importantly to the present analysis, to reproduce the persistent underestimation of HO, under high NOx conditions. The fact that both models exhibit similar behavior as a function of NOx seems to indicate that the underlying assumptions about HO, chemistry in the UT may require modification and that the problem does not lie merely within the particular computational treatment of the photochemical system.

Average values of trace gas species and meteorological parameters measured over the course of the SONEX experiment.
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>H2O</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>O3</td>
<td>Gregory, NASA LaRC</td>
<td>NO+O, chemiluminescence</td>
<td>ppbv</td>
<td>57</td>
<td>78</td>
<td>61</td>
</tr>
<tr>
<td>CO</td>
<td>Sachse, NASA LaRC</td>
<td>diode laser spectrometer</td>
<td>ppbv</td>
<td>84</td>
<td>82</td>
<td>23</td>
</tr>
<tr>
<td>NO</td>
<td>Kondo, Nagoya U.</td>
<td>NO+O, chemiluminescence</td>
<td>pptv</td>
<td>57</td>
<td>101</td>
<td>157</td>
</tr>
<tr>
<td>HNO3</td>
<td>Talbot, U. New Hampshire</td>
<td>ion chromatography</td>
<td>pptv</td>
<td>117</td>
<td>214</td>
<td>232</td>
</tr>
<tr>
<td>NO</td>
<td>Kondo, Nagoya U.</td>
<td>NO+O, chemiluminescence</td>
<td>pptv</td>
<td>401</td>
<td>505</td>
<td>335</td>
</tr>
<tr>
<td>PAN</td>
<td>Singh, NASA ARC</td>
<td>gas chromatography (GC)</td>
<td>pptv</td>
<td>64</td>
<td>84</td>
<td>66</td>
</tr>
<tr>
<td>J(NO2)</td>
<td>Shetter, NCAR</td>
<td>scanning spectroradiometry</td>
<td>x10^3 1/s</td>
<td>8.0</td>
<td>8.1</td>
<td>2.0</td>
</tr>
<tr>
<td>OH</td>
<td>Brune, Penn State</td>
<td>laser-induced fluorescence</td>
<td>pptv</td>
<td>0.09</td>
<td>0.10</td>
<td>0.06</td>
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<tr>
<td>HO2</td>
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<td>laser-induced fluorescence</td>
<td>pptv</td>
<td>2.52</td>
<td>2.70</td>
<td>1.44</td>
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<tr>
<td>H2O2</td>
<td>Heikes, U. Rhode Island</td>
<td>HP liquid chromatography</td>
<td>pptv</td>
<td>74</td>
<td>106</td>
<td>94</td>
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<tr>
<td>C2H5</td>
<td>Blake, U. California Irvine</td>
<td>whole air canister, GC</td>
<td>pptv</td>
<td>674</td>
<td>713</td>
<td>305</td>
</tr>
<tr>
<td>CN</td>
<td>Anderson, NASA LaRC</td>
<td>butanol CN counter</td>
<td>#/cm³</td>
<td>1840</td>
<td>3020</td>
<td>4670</td>
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<tr>
<td>Acetone</td>
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<td>gas chromatography (GC)</td>
<td>pptv</td>
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<td>503</td>
<td>199</td>
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<td>SZA</td>
<td>Jacob, Harvard U.</td>
<td>calculated</td>
<td>degrees</td>
<td>68</td>
<td>66</td>
<td>11</td>
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<tr>
<td>Temperature</td>
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<td>234</td>
<td>14</td>
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<tr>
<td>PV</td>
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<td>1.8</td>
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<tr>
<td>Tropopause</td>
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<td>microwave temp. profiler</td>
<td>km</td>
<td>11.9</td>
<td>12.3</td>
<td>1.8</td>
</tr>
</tbody>
</table>

are listed in Table 2. These are averages for the filtered data used in this analysis as described above. Jaegle et al. [this issue] tabulate similar measurements, and the median values in Table 2 correspond fairly well to their classification of background air (for further breakdowns by air mass, see Jaegle et al. [this issue]). Large differences between the medians and means indicate that many spikes in those species were encountered. This is true of NO and CN, in particular, due to the high occurrence of air traffic corridor crossings made during the mission.

The ratio of HO2 to 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 HO2 and OH equilibration (equation (8)). In the upper troposphere the partitioning of HOx is controlled primarily by the relative rates of the two reactions

\[ \text{OH} + \text{CO} + \text{O}_2 \rightarrow \text{HO}_2 + \text{CO}_2, \]  
\[ \text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2. \]

These reactions represent an exchange between OH and HO2 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

\[ \text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2, \]
\[ \text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + \text{2O}_2, \]

because O3 tends to be more abundant, while CO tends to be less abundant. These reactions interchange HOx on timescales of about 1 min in the lowermost stratosphere. Regardless then of the exact composition and history of a given air parcel, the HO2:OH ratio should be determined quickly by these readily measured species: NO, CO, and O3. 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 HO2:OH ratio to be no more than 20%, particularly when extremely low 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 OH concentration dropped below approximately one-half its 1σ value.

3.2. Dependence of HOx Deviation on NOx

For the present purposes we define the HOx deviation as the ratio of the observed HOx to the model-predicted HOx. Figure 1 is an overview of the HOx deviation as a function of NO, for 12 of the 13 fights. The flight of October 31, 1997, is not included in the figure because the average NO measured during this flight was only 30 pptv, and consequently, the NO dependence is not clearly demonstrated. The normalized covariance of the HOx deviation (from the Harvard DSS model) and the NOx concentration is 0.70 for the entire data set (filtered for SZA<80 and outside of clouds). An inspection of the covariance matrix between the HOx deviation and all of the other 211 parameters included in the merged data set (which includes the DSS model calculations of many unmeasured species) reveals this covariance with NOx to be the largest. The covariance with NO, a directly observed quantity, is slightly smaller than for that with NOx (0.61 and 0.70, respectively.) In general, all of the figures presented in this paper do not appear very different when plotted as a function of NO as opposed to NOx. Because of the fact that the NO levels depend in part on solar zenith angle, the selection of NOx as the independent variable in Figures 1-3 was merely an attempt to avoid convolution of SZA into the study.
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 NOx 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 HOx levels more accurately than the simple steady-state calculation, similar relationships are evident in both deviations with respect to NOx. 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 HOx 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 HOx production and/or loss. The average slopes of the HOx deviation for the DSS model is 28% per 100 pptv NOx, and 41% per 100 pptv NOx for the ISS model.

3.3. Evidence From SUCCESS

There is evidence of just this sort of NOx 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 NOx 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 ppt NOx, the deviation appears to increase linearly with NOx, as it does in the SONEX data and clusters around this line all the way up to several

Figure 2. (a) Log-log plot of the HOx observation to HOx modeled ratios for eight flights during the Subsonic Assessment, Ozone and Nitrogen Oxide Experiment (SUCCESS) of April/May 1996 and (b) all of the filtered data from SONEX for comparison. Penn State ATHOS instrument measured the HOx, and the model predictions were generated by the Harvard DSS model in both experiments. The NOx was measured in the SUCCESS mission by Weinheimer, Campos, and Ridley of the National Center for Atmospheric Research.
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{2} concentrations in the exhaust plumes (a steady-state treatment predicts that all of the HO\textsubscript{2} 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 $1 \times 10^6$ 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 water mixing ratio and surface area concentration for these combined intervals are 43 ppmv and 11 $\mu$m$^2$/cm$^2$, respectively. These data thus represent a strong example of the supposed NOx effect at work in the atmosphere in the absence of available heterogeneous chemical pathways and 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 O$_3$ 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 apropos 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: conversion 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 + NOy estimated from the ISS model), and the symbols are the deviation ratios of HOx with respect to each model predicted HOx. 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/NOy 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 expended 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 HOx 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 HOx 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 HO2: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 HO2:OH ratio is not likely. This fact notwithstanding the most plausible interference is that from thermal dissociation of peroxylic 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, \( \Delta E/R = 10,900 \text{ K} \) [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 peroxyacetyl nitrate (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 laboratory...
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 NO conditions, < 100 pptv (diamonds), and higher NO 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 NO, and this holds true for a wide range of HO2 levels (from 2 to 8 pptv.)

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 NO concentrations, or alternately could be explained by some sort of biased overestimation of HO 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 HO2NO2). 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 HOx 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, OH + CHx + NO + O2 → HOx + CHxO + H2O, is part of the HOx exchange cycling
and it usually yields more than one molecule of HO\textsubscript{2} by its production of formaldehyde; thus, once photochemically generated in the atmosphere HO\textsubscript{2} begets more HO\textsubscript{2} in the presence of hydrocarbons and a little NO\textsubscript{2}. Such autocatalytic amplification coupled with quadratic loss rates lead to a system whose equilibrium concentrations are tightly constrained; consequently, HO\textsubscript{2} levels in the atmosphere can remain relatively constant while other species vary drastically. Because of the high degree of buffering, explanations of our measured HO\textsubscript{2} 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 HO\textsubscript{2} deviation ratio with NO\textsubscript{2} from 29% per 100 ppt NO\textsubscript{2} to 23% per 100 ppt NO\textsubscript{2}. This sort of change is clearly not large enough to account for the entire discrepancy. In fact, significantly reduced correlations between the HO\textsubscript{2} deviation ratio and NO were not obtained until the PNA equilibrium constant was altogether eliminated. Artificially suppressing the formation of HO\textsubscript{2}NO\textsubscript{2} in the model in this way reduced the slope to one-third its original magnitude or about 10% per 100 ppt NO\textsubscript{2}.

The Penn State ISS model uses the recently reported reaction rate for OH + NO\textsubscript{2} 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\textsubscript{2} 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 NO\textsubscript{2} dependence by more than a couple of percent.

5. Concluding Summary

Taken as a whole the measurements of HO\textsubscript{2} 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 over-shoot the model predictions in conditions of high NO\textsubscript{2}. 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 NO\textsubscript{2} 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 NO\textsubscript{2} emissions to that part of the atmosphere, where the \O\textsubscript{3} lifetime is long and its longwave radiative forcing is strongest, could have a profound and unanticipated impact on the global environment.

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