Measurement of HO₂ NO₂ in the free troposphere during the Intercontinental Chemical Transport Experiment North America 2004

Permalink
https://escholarship.org/uc/item/4pr327c0

Journal
Journal of Geophysical Research, 112(D12)

ISSN
0148-0227

Authors
Kim, S.
Huey, L. G
Stickel, R. E
et al.

Publication Date
2007-02-10

DOI
10.1029/2006jd007676

License
https://creativecommons.org/licenses/by/4.0/ 4.0

Peer reviewed
Measurement of HO$_2$NO$_2$ in the free troposphere during the Intercontinental Chemical Transport Experiment–North America 2004


Received 20 June 2006; revised 20 October 2006; accepted 14 November 2006; published 10 February 2007.

[1] The first direct in situ measurements of HO$_2$NO$_2$ in the upper troposphere were performed from the NASA DC-8 during the Intercontinental Chemical Transport Experiment–North America 2004 with a chemical ionization mass spectrometer (CIMS). These measurements provide an independent diagnostic of HO$_x$ chemistry in the free troposphere and complement direct observations of HO$_x$ because of the dual dependency of HO$_2$NO$_2$ on HO$_x$ and NO$_x$. On average, the highest HO$_2$NO$_2$ mixing ratio of 76 pptv (median = 77 pptv, σ = 39 pptv) was observed at altitudes of 8–9 km. Simple steady state calculations of HO$_2$NO$_2$, constrained by measurements of HO$_x$, NO$_x$, and J values, are in good agreement (slope = 0.90, R$^2$ = 0.60, and z = 5.5–7.5 km) with measurements in the midtroposphere where thermal decomposition is the major loss process. Above 8 km the calculated steady state HO$_2$NO$_2$ is in poor agreement with observed values (R$^2$ = 0.20) and is typically larger by a factor of 2.4. Conversely, steady state calculations using model-derived HO$_x$ show reasonable agreement with the observed HO$_2$NO$_2$ in both the midtroposphere (slope = 0.96, intercept = 7.0, and R$^2$ = 0.63) and upper troposphere (slope = 0.80, intercept = 32.2, and R$^2$ = 0.58). These results indicate that observed HO$_2$ and HO$_2$NO$_2$ are in poor agreement in the upper troposphere but that HO$_2$NO$_2$ levels are consistent with current photochemical theory.


1. Introduction

[2] Perinitric acid (HO$_2$NO$_2$) is formed in the atmosphere by an association reaction that couples the HO$_x$ and NO$_x$ families [Niki et al., 1977]:

$\text{(R1)} \quad \text{HO}_2 + \text{NO}_2 + M \rightarrow \text{HO}_2\text{NO}_2 + M$

The thermal decomposition of HO$_2$NO$_2$, R-1, is a strong function of temperature with the lifetime for this process varying from approximately 20 s in the boundary layer to 8 hours at 8 km. Consequently, at lower and mid latitudes HO$_2$NO$_2$ is only expected to build up to significant concentrations in the upper troposphere, whereas photolysis and reaction with OH are expected to be the dominant loss processes.

$\text{(R2)} \quad \text{HO}_2\text{NO}_2 + h\nu \rightarrow \text{Products}$

$\text{(R3)} \quad \text{OH} + \text{HO}_2\text{NO}_2 \rightarrow \text{H}_2\text{O} + \text{NO}_2 + \text{O}_2$

[3] The potential impact of HO$_2$NO$_2$ on upper tropospheric photochemistry (z = 8–12 km) has been discussed by several investigators [Brune et al., 1999; Wennberg et al., 1999; Faloona et al., 2000; Jaeglé et al., 2000]. In particular, Jaeglé et al. [2000] noted the importance of HO$_2$NO$_2$ as a sink for HO$_x$ at intermediate levels of NO$_x$ (100–500 pptv) via R3. However, these studies were unconstrained by observations of HO$_2$NO$_2$. The only previous direct measurements of HO$_2$NO$_2$ are in the South Pole boundary layer during Austral Summer 2000 and 2003 [Slusher et al., 2002; Jostad et al., 2004]. These results demonstrated that HO$_2$NO$_2$ was present in significant levels (on average 25 pptv in 2000; 42 pptv in 2003) and could be
the dominant sink for HOx via deposition to the snowpack and R3. The only in situ airborne HO2NO2 data were obtained during the TOPSE campaign from the NCAR C-130 at altitudes of 0 to 7 km. Murphy et al. [2003] derived levels of HO2NO2 + CH3ONO2 from their sum of peroxy nitrates channel (ΔPN) by subtracting independent measurements of peroxy acyl nitrates (PANs). They compared the derived HO2NO2 to photochemical calculations (with and without an overtone photolysis rate of 10^-5 s^-1) and demonstrated the importance of the overtone photodissociation channel as a loss mechanism for HO2NO2 [Roehl et al., 2002; Wennberg et al., 1999]. Observations of pernitric acid by remote sensing have been reported but are confined to the stratosphere (20–40 km) [Rinsland et al., 1996; Sen et al., 1998].

[4] Here we present the first direct in situ observations of HO2NO2 in the free troposphere. These measurements were performed in the summer of 2004 with a chemical ionization mass spectrometer from the NASA DC-8 during INTEX-NA field experiment. The INTEX-NA study sought to characterize and investigate the transport and transformation of both aerosol and gas-phase species over large spatial scales and altitude ranges. Flights were based out of California, Illinois, and New Hampshire. The sampling domain included much of the U.S., parts of Canada, and areas off the eastern and western coasts of North America. A detailed description of the DC-8 payload and the INTEX-NA campaign is presented by Singh et al. [2006]. In this work our understanding of the chemistry of HO2NO2 over the altitude range of 4–12 km is investigated by comparison of observations with highly constrained steady state calculations and photochemical models.

2. Methods

2.1. Instrumentation

[5] The instrument used to measure HO2NO2 and SO2 from the NASA DC-8 during INTEX-NA is nearly identical to that described by Slusher et al. [2004]. The instrument comprises an inlet, a flow tube ion molecule reactor, a collisional dissociation chamber (CDC), an octopole ion guide and a quadrupole mass spectrometer as shown in Figure 1. SF6 ion chemistry is utilized to selectively ionize HO2NO2 and SO2 (R4 and R5) in the CIMS [Slusher et al., 2001; Huey et al., 1995, 2004; Huey, 2006].

\[
\text{(R4)} \quad \text{SF}_6 + \text{HO}_2\text{NO}_2 \rightarrow \text{NO}_2^-(\text{HF}) + \text{SF}_5
\]

\[
\text{(R5)} \quad \text{SF}_6 + \text{SO}_2 \rightarrow \text{F}_2\text{SO}_2 + \text{SF}_4
\]

Air was delivered to the CIMS through an all perfluoroalkoxy Teflon inlet (i.d. = 0.95 cm, length = 80 cm) maintained at a constant temperature of 298 K. A relatively low inlet temperature was utilized as the pernitric acid signal was found to diminish above 318 K because of thermal decomposition. A flow of more than 5 s/s was maintained in the inlet to minimize both the gas residence time (t < 0.57 s) and wall interaction. The sampled air was periodically scrubbed of both HO2NO2 and SO2 with an activated carbon filter. The sensitivity of the instrument to SO2 was
continuously monitored by the addition of isotopically labeled calibration gas (850 ppbv ± 9.2%) [e.g., Bandy et al., 1993]. A typical example of the raw CIMS data is shown in Figure 2. The sensitivity of HO$_2$NO$_2$ relative to SO$_2$ was assessed post mission by a series of laboratory tests over the pressure and humidity conditions encountered on the DC-8. These tests demonstrated that the relative sensitivity of HO$_2$NO$_2$ to SO$_2$ was nearly identical to the ratio of the rate constants for reactions (R4) and (R5) [Slusher et al., 2001]. This indicates that the sensitivity for both of these species is dominated by the ion molecule chemistry and that the continuous SO$_2$ calibration provides a good relative measure of the HO$_2$NO$_2$ sensitivity. The estimated uncertainty for HO$_2$NO$_2$ levels well above detection limit was typically less than 30% with a detection limit of less than 5 pptv for a 1-min integration at altitudes greater than 3 km.

The methods used to obtain HO$_x$, NO$_2$, and J values during INTEX-NA have been described in detail elsewhere [Avery et al., 2001; Faloona et al., 2004; Thornton et al., 2000; Shetter and Müller, 1999].

2.2. Calculations

[6] HO$_2$NO$_2$ levels were estimated, assuming steady state, from the following equation.

$$[\text{HO}_2\text{NO}_2]_{ss} = \frac{k_1[\text{HO}_2][\text{NO}_2]}{k_2 + k_{-1} + k_3[\text{OH}]}$$  (1)

The rate constants for these calculations are taken from Christensen et al. [2004] for $k_1$, Sander et al. [2003] for $k_{-1}$ and Jiménez et al. [2004] for $k_3$. The NO$_2$ mixing ratios and the photolysis rate in the ultraviolet region were constrained by observations. Actinic fluxes in the near infrared were not measured during this campaign leaving the overtone photolysis rate unconstrained. For this reason, the overtone photolysis rate was estimated to be 10$^{-5}$ s$^{-1}$ [Murphy et al., 2003; Roehl et al., 2002; Wennberg et al., 1999]. The uncertainty of [HO$_2$NO$_2$]$_{ss}$ calculated from the estimated error of each input parameter, excluding overtone photolysis, in equation (1) is ~68% at 8 km. The error in this calculation is dominated by the uncertainties in the HO$_x$ measurement (~32%) and the rate constants $k_{-1}$ and $k_4$ (~30%). The uncertainty does depend on altitude and ranges from 40 to 68%. Nitric acid levels were calculated using both observed ([HO$_2$NO$_2$]$_{ss,obs}$) and model predicted ([HO$_2$NO$_2$]$_{ss,mod}$) levels of OH and HO$_2$. Model predicted HO$_2$ levels were obtained from the NASA Langley photochemical box model which was highly constrained to observations of photolysis rates and the concentrations of long-lived species (e.g., NO$_2$, O$_3$, CO, etc.) [Olson et al., 2004; Crawford et al., 1999].

[7] Time-dependent model calculations were also performed to assess the deviation of HO$_2$NO$_2$ from steady state for typical upper tropospheric conditions where its lifetime is of the order of 5 hours (Figure 3). This method assumed an initial injection of NO$_x$ into the upper troposphere and followed its temporal evolution and oxidation over the course of several days in 1-min time steps. Short-lived species such as radicals were predicted using the steady state assumption and the chemical scheme of

![Figure 2. Raw ion signal obtained during flight. (top) The $^{34}$SO$_2$ signal illustrates the periodic calibration to the isotopically labeled standard. (middle) Ambient $^{32}$SO$_2$ signal. (bottom) Variation of ambient signal HO$_2$NO$_2$ signal. The shaded area is a background measurement period.](image-url)
Longer-lived species such as CO based on both observed and KIM ET AL.: MEASUREMENT OF HO altitude profile for the INTEX-NA mission is 
\[ \mathrm{CO}_2 \] = 0.58, slope = 0.80, from the recent mixing ratio profile shows a maximum 
3 observations (Figure 5b, \( R^2 \)). Vertical distribution of the total lifetime of 
3 in this region, where thermal 
\[ \mathrm{C}_2 \mathrm{H}_4 \] = 0.60, slope = 0.90, intercept = 0.4 pptv) 
Journal of Geophysical Research, 
calculations are also graphed in Figure 4. The 
Sander et al. measurement alone. These 
Summary of Chemical Species Treated in the Time-Dependent Model 
are still highly correlated 
\[ x \] and individual lifetimes with respect to thermal 
\[ \mathrm{NO}_2 \] / \[ \mathrm{C}_2 \mathrm{H}_4 \] = 0.20, slope = 1.38, intercept = 
(\( x \)) and individual lifetimes with respect to thermal 
\[ \mathrm{NO}_2 \] / \[ \mathrm{C}_2 \mathrm{H}_4 \] = 0.1 for 
photolysis rates were found to be within 20% of observa-
tions typical of INTEX-NA (e.g., latitude, time of day, and date), and rate constants were taken from the JPL 
evaluation version 14 [Sander et al., 2003]. Calculated 
photolysis rates were found to be within 20% of observa-
during INTEX-NA.

3. Results and Analysis

[9] All reported data and analyses are based on a 1-min average merged data set (ftp:// ftp-air.larc.nasa.gov/pub/ INTEXA/DC8_AIRCRAFT/). The median observed 
\[ \mathrm{HO}_2 \mathrm{NO}_2 \] altitude profile for the INTEX-NA mission is presented in Figure 4, and the statistics of the vertical 
distribution are reported in Table 2. Median values of steady 
state calculations of \[ \mathrm{HO}_2 \mathrm{NO}_2 \] based on both observed and model predicted \[ \mathrm{HO}_x \] are also graphed in Figure 4. The 
observed \[ \mathrm{HO}_2 \mathrm{NO}_2 \] mixing ratio profile shows a maximum 
of \( \sim 76 \) pptv between 8 and 9 km. Permitric acid mixing 
ratios decrease below this altitude as expected because of 
large thermal dissociation rates. Above 10 km levels de-
crease primarily because of a weakening of the source 
strength. The mean concentration of permitric acid in the 
top troposphere (\( 8 \sim 12 \) km) was \( 67 \pm 37 \) pptv (2467 data 
points, \( 1 \sigma \)), which accounted for approximately 5% of the 
total reactive nitrogen (\([ \mathrm{NO}_3 \]) budget and approximately 
10% of the \([ \mathrm{HO}_x \) sink in this region as determined from the 
time-dependent modeling results described earlier (H. B. 
Singh et al., Reactive nitrogen distribution and budgets in the 
North American troposphere and lowermost strato-
phere, submitted to Journal of Geophysical Research, 
2006; X. Ren et al., unpublished manuscript, 2006).

[10] In the mid troposphere (\( 4 \sim 8 \) km) both of the calculated 
profiles are in reasonable agreement with observations 
(Figure 4). This is more clearly illustrated in Figure 5 which 
presents scatterplots of the steady state calculations versus 
observations. The calculations based on observed \([ \mathrm{HO}_x \) (Figure 5a, \( R^2 = 0.60, \) slope = 0.90, intercept = 0.4 pptv) 
and on model predicted \([ \mathrm{HO}_x \) (Figure 5b, \( R^2 = 0.63, \) slope = 
0.96 intercept = 7.0 pptv) are both well correlated to the 
observations. The median ratios for the calculations relative 
to the observations are 0.8 for observed \([ \mathrm{HO}_x \) and 1.1 for 
model predicted \([ \mathrm{HO}_x \). This level of agreement is well within 
the 30% error bar of the \([ \mathrm{HO}_2 \mathrm{NO}_2 \) measurement alone. These 
results indicate that we have a reasonable understanding of 
the chemistry of \([ \mathrm{HO}_2 \mathrm{NO}_2 \) in this region, where thermal 
decomposition dominates the lifetime (Figure 3). Very 
similar results were also derived using \( k_{-1} \) from the recent 
work of Gierczak et al. [2005]. Correlations between calcu-
lations and observations were essentially identical with 
calculated values rising by a factor of 1.5. However, these 
results are still within the uncertainty of the analysis.

[11] In the upper troposphere (\( 8 \sim 12 \) km) the agreement 
between the steady state calculations and observations is not 
as good as at lower altitudes. The \([ \mathrm{HO}_2 \mathrm{NO}_2 \) calculations 
based on model predicted \([ \mathrm{HO}_x \) are still highly correlated 
with the observations (Figure 6b, \( R^2 = 0.58, \) slope = 0.80, 
intercept = 32.2 pptv) but with a significant offset that 
yields a median ratio of calculated to observed of 1.3. 
Conversely, the correlation between \([ \mathrm{HO}_2 \mathrm{NO}_2 \) calculations 
based on observed \([ \mathrm{HO}_x \) and observations is significantly 
weaker (Figure 6a, \( R^2 = 0.20, \) slope = 1.38, intercept = 
72.4 pptv) with a median ratio of calculated to observed of 
2.4. These results indicate that our ability to predict \([ \mathrm{HO}_2 \mathrm{NO}_2 \) with simple steady state models at higher altitudes, where its 
lifetime is longer and controlled by photochemical processes 
(Figure 3), is not as good as at low altitudes. There is also a 
difference between upper tropospheric \([ \mathrm{HO}_x \) observations 
and predictions, especially around 10 km, with the permitric 
acid observations more in accord with the photochemical 
model results.

| Table 1. Summary of Chemical Species Treated in the Time-Dependent Model² |
|---------------------|---------------------|
| Category            | Species             |
| Constrained         | \( \mathrm{O}_3, \mathrm{CH}_4, \mathrm{CO}, \mathrm{CH}_3 \mathrm{OH}, \mathrm{H}_2\mathrm{O}, \mathrm{CH}_3\mathrm{C(O)CH}_3, \mathrm{H}_2\mathrm{O} \) |
| Steady state        | \( \mathrm{OH}, \mathrm{HO}_2, \mathrm{CHO}, \mathrm{O}^\cdot(\mathrm{D}), \mathrm{CH}_3\mathrm{O}, \mathrm{CH}_2\mathrm{C(O)O}_2 \) |
| Time dependent      | \( \mathrm{NO}, \mathrm{NO}_2, \mathrm{HNO}_3, \mathrm{HO}_2\mathrm{NO}_2, \mathrm{PAN}, \mathrm{NO}_3, \mathrm{N}_2\mathrm{O}_5 \) |

²Constrained species were held to median observed levels for the INTEX mission. The concentrations of the short-lived radicals (e.g., \( \mathrm{OH}, \mathrm{HO}_2 \), etc.) are calculated using the steady state assumption. The reactive nitrogen species (e.g., \( \mathrm{NO}, \mathrm{HNO}_3 \), etc.) are calculated in a time-dependent manner.
[11] At altitudes of 8–10 km the ratio of photochemical model predictions to observations (M/O) for OH and HO$_2$ are 1.8 and 1.0, respectively (X. Ren et al., unpublished manuscript, 2006). In the altitude range of 10–12 km the M/O ratio for OH and HO$_2$ are 1.5 and 0.5, respectively (X. Ren et al., unpublished manuscript, 2006). Consequently, there is a discrepancy between the measured and predicted HO$_2$/OH ratio that increases with altitude. However, this difference is primarily due to the high levels of NO$_x$ that also were observed to increase with altitude (T. H. Bertram et al., Direct measurements of the convective recycling of the upper troposphere, submitted to Science, 2006, hereinafter referred to as Bertram et al., submitted manuscript, 2006). The predicted ratio of [HO$_2$/OH] decreases much more strongly as a function of NO$_x$ than the observations (X. Ren et al., unpublished manuscript, 2006).

[12] At higher altitudes where thermal decomposition of pernitric acid is negligible the ratio of HO$_2$NO$_2$ to NO$_2$ should have a strong dependence on the [HO$_2$/OH] ratio. This is evident from equation (1) for those conditions where reaction with OH (R3) is the dominant loss. For the INTEX-NA mission the HO$_2$NO$_2$ loss due to OH dominates in the upper troposphere according to model predictions. However, if the model is incorrect the correlation between [HO$_2$/OH] and [HO$_2$NO$_2$/NO$_2$] should still be significant because of the dependence of OH levels on photolysis rates. Thus the observed [HO$_2$NO$_2$/NO$_2$] ratio provides an independent check of the [HO$_2$/OH] ratio. A strong correlation (R$^2 = 0.6$) is observed between model predicted [HO$_2$/OH] (Figure 7b) and observed [HO$_2$NO$_2$/NO$_2$]; however, the correlation decreases significantly with observed HO$_x$ (Figure 7a, R$^2 = 0.3$). The weaker correlation with the observations is primarily due to the insensitivity of the observed [HO$_2$/OH] ratio to higher NO$_x$ levels which corresponds to lower ratios of [HO$_2$NO$_2$/NO$_2$]. Consequently, the observed HO$_2$NO$_2$ levels are more consistent with the predicted [HO$_2$/OH] ratio.

[13] Finally, the INTEX-NA data set allows the investigation of the impact of high levels of ozone on the CIMS system. A potential problem with the SF$_6$/C0$_2$ CIMS system for measurement of HO$_2$NO$_2$ is a positive interference due to high ozone levels [Slusher et al., 2001]. This interference...
has been characterized in the laboratory and was found to be unimportant at levels of ozone up to several hundred ppbv [Slusher et al., 2001] but this has not been confirmed by field observations. The potential effect was investigated by examining the relationship of observed HO$_2$NO$_2$ with O$_3$.

Figure 8 plots observed HO$_2$NO$_2$ versus O$_3$ in the altitude range 8.5–9.5 km (i.e., highest HO$_2$NO$_2$) for both periods when the air was primarily of tropospheric (O$_3$ < 150 ppbv, H$_2$O > 120 ppmv) and stratospheric origin (O$_3$ > 200 ppbv, H$_2$O < 100 ppmv). There is a moderate correlation ($R^2 = 0.33$) between pernitric acid and ozone at lower ozone levels for the tropospheric air masses. At the higher ozone levels in the stratospherically influenced air masses there is essentially no correlation. This indicates that O$_3$ at levels of up to 250 ppbv are not a significant interference to the HO$_2$NO$_2$ measurement. The correlation between ozone and HO$_2$NO$_2$ in the tropospheric air masses is likely due to ozone production via the reaction of HO$_2$ with NO which is closely related to pernitric acid formation (R1). This suggests that HO$_2$NO$_2$ in this altitude range may be a good marker for recent ozone production.

4. Discussion

[14] Measurements of HO$_x$, NO$_x$, and HO$_2$NO$_2$ were consistent at altitudes below 7.5 km where thermal decomposition dominates the loss of pernitric acid. The thermal decomposition rates derived from Sander et al. [2003] and Gierczak et al. [2005] are both in reasonable agreement with the lower-altitude observations. These results indicate that the uncertainty in the HO$_2$NO$_2$ lifetime due to the thermal decomposition rate, $k_{-1}$, is less than a factor of two at temperatures greater than 250 K.

[15] Above 8 km the observations of HO$_x$ and HO$_2$NO$_2$ are less compatible with our understanding of photochemistry. The results indicate that the formation rate of HO$_2$NO$_2$ is overestimated or the loss rates are underestimated. Alternatively these results may suggest that the steady state calculations are problematic in this altitude range and the agreement between the model HO$_x$ calculations and observed HO$_2$NO$_2$ is fortuitous. There is strong evidence that the rate constant ($k_1$) for the formation of HO$_2$NO$_2$ is accurately known. The rate constant has recently been measured by Christensen et al. [2004] and found to be within 15% of the JPL recommendation [Sander et al., 2003], based on several previous studies, over a wide range of temperature and pressure. There has been speculation that the reaction of HO$_2$ with NO$_2$ could produce other products such as HONO, but this has been shown to be unimportant by Tyndall et al. [1995]. The rate constant, $k_3$, for the reaction of HO$_2$NO$_2$ with OH also appears to be known to better than 50% over a wide temperature range (218–335 K) [Jiménez et al., 2004; Smith et al., 1984]. This uncertainty is too little to bring the observed HO$_x$ and HO$_2$NO$_2$ at

Figure 6. Scatterplots of upper troposphere (8–12 km) HO$_2$NO$_2$ steady state calculations versus observed HO$_2$NO$_2$. The calculations are based on (a) observed and (b) model HO$_x$.

Figure 7. Correlation plot between [HO$_2$NO$_2$]/[NO$_2$] and [HO$_2$]/[OH] (a) from observed HO$_x$ and (b) from model predicted HO$_x$. 

D12S01 KIM ET AL.: MEASUREMENT OF HO$_2$NO$_2$ IN THE FREE TROPOSPHERE D12S01
higher altitudes into agreement. For these reasons, we have investigated other potential loss processes, reassessed our estimate of overtone photolysis rates, and performed time-dependent photochemical calculations to assess the magnitude of the deviation from steady state.

Pernitric acid could be lost by heterogeneous loss or uptake in the upper troposphere on either background sulfate aerosol or cirrus clouds [Evans et al., 2003]. However, we found no evidence for a relationship between aerosol surface area and HO$_2$NO$_2$ levels indicating that reaction on sulfate aerosol are not an important loss process. Evaluating the impact of cirrus clouds on pernitric acid levels is more problematic because of their relatively short lifetime (τ/C2 ≈ 1 hour). There were a few flight legs during the campaign in which the DC-8 sampled in cirrus clouds as evidenced by detection of large particles (>20 μm dia.). There was no obvious diminishment of pernitric acid in these air masses, but these data are limited and do not allow for a robust conclusion. For this reason, we think cirrus cloud processing of HO$_2$NO$_2$ is still an open question especially since pernitric acid has been shown to efficiently stick to ice at low temperatures [Li et al., 1996].

Overtone photolysis rates of HO$_2$NO$_2$ were estimated by calculating actinic fluxes using the SBDART (Santa Barbara DISORT Atmospheric Radiative Transfer) model [Ricchiazzi et al., 1998] and cross sections and quantum yields from Roehl et al. [2002]. Calculations of both direct and diffuse fluxes were performed for typical INTEX conditions as listed in Table 3. Note that sand was chosen as the surface to maximize the infrared albedo. A total photolysis rate of 8.0 x 10$^{-6}$ s$^{-1}$ was calculated which compares favorably with the value of 8.3 x 10$^{-6}$ s$^{-1}$ derived by Roehl et al. [2002] from the direct flux at the top of the atmosphere. These calculations indicate the photolysis rate (10$^{-5}$ s$^{-1}$) used in the steady state analysis is reasonable but is probably an upper limit. As the dominant overtone photolysis band, 2ν₁, for HO$_2$NO$_2$ overlaps a water transition [Rothman et al., 2005] the upward flux in this spectral range over clouds, ocean, and snowpack will be attenuated because of a decreased albedo in the near-IR. It is also worth noting that only one measurement [Roehl et al., 2002] of the quantum yield and cross section for the 2ν₁ band is available and should probably be confirmed.

The error in the HO$_2$NO$_2$ calculations was investigated by using a time-dependent photochemical model to estimate the deviation from steady state. Figure 9 shows a temporal plot of HO$_2$NO$_2$ at 9 km, for typical INTEX-NA conditions (28 July, latitude ~40°N), calculated using steady state and time-dependent methods. The time-dependent results are for the second day after a fresh injection of NO$_x$ into the upper atmosphere reflecting the relatively fresh air masses sampled during INTEX-NA (Bertram et al., submitted manuscript, 2006; H. E. Fuelberg et al., Meteorological conditions and anomalies during INTEX-NA, submitted to Journal of Geophysical Research, 2006; M. Porter et al., unpublished manuscript, 2006). However, the comparison of the time-dependent and steady state results was not found to depend strongly on the number of days after the NO$_x$ injection. In fact, the steady state values were found to be within 50% of the time-dependent

<table>
<thead>
<tr>
<th>Table 3. Parameters for Actinic Flux Calculations Using SBDART</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Local Time</strong></td>
</tr>
<tr>
<td>Latitude</td>
</tr>
<tr>
<td>Surface type</td>
</tr>
<tr>
<td>Atmosphere profile</td>
</tr>
<tr>
<td>Boundary layer type</td>
</tr>
</tbody>
</table>
calculations within approximately 5 hours after a fresh injection of NO. The shaded area in Figure 9 is the typical flight time from 0800 to 1800 LT. The largest difference is in the morning where the steady state model overpredicts HO2NO2 by ~50%. The disagreement diminishes through the day until there is a slight underestimation by the steady state model in the late afternoon. These effects were observed to a small extent in the data as the ratio of model predictions to observations before noon was approximately 10% greater than in the afternoon. On average the steady state model overpredicts the time-dependent results by 12% during typical DC-8 flight times. At higher altitudes the disagreement between steady state and time-dependent calculations is lower as HO2NO2 does not undergo signifi-

Figure 9. Temporal plot of HO2NO2 calculated using time-dependent (solid circle with solid line) and steady state HO2NO2 (open circle with dashed line) models. Shaded time zone is a typical flight time during INTEX-NA from 0800 to 1800 LT. 

Figure 10. (a) Altitude profile of the first-order rate constant for the additional loss of HO2NO2 derived from measured HOx. (b) Vertical profile of observed ([HO2NO2]obs) and predicted ([HO2NO2]ss_Obs. OH). The predicted HO2NO2 is derived from a steady state analysis using observed OH levels and the model predicted ratio of [HO2] to [OH].
cant thermal decomposition through the night. Consequently, steady state methods seem to be valid for predicting HO$_2$NO$_2$ levels in the upper troposphere with less than a 50% inherent error bar.

[19] Clearly, the measured HO$_2$NO$_2$ and HO$_x$ are not consistent with our current understanding of photochemistry in the upper troposphere. One possible explanation is that there are unidentified measurement errors in either or both the HO$_x$ and HO$_2$NO$_2$ measurements. These potential errors must be greater at either high altitude or high HO$_x$ levels, but at this point we are unaware of any mechanisms for these errors. Alternatively, a higher loss rate for pernitric acid would bring observations of HO$_2$NO$_2$ and HO$_x$ into better agreement. Figure 10a presents the vertical profile of the needed HO$_2$NO$_2$ first-order rate constant for the additional loss needed to bring observed HO$_2$NO$_2$ and HO$_x$ into accord. This additional loss rate generally increases with altitude with a maximum near 11 km. The needed loss rate is of a large magnitude and is unlikely to be explained by any single mechanism. One potential mechanism that could account for some of the additional loss is photolysis via weak electronic transitions as discussed by Mathews et al. [2005]. Finally, we determined if the measured OH and the model predicted [HO$_2$/OH] ratio are consistent with the observed HO$_2$NO$_2$. This was done with a steady state analysis using observed OH and HO$_x$ derived from the predicted HO$_x$ ratio. The median altitude profile for this data is shown in Figure 10b and shows excellent agreement with the observed profile. These data demonstrate that the observed HO$_2$NO$_2$ are inconsistent with the observed HO$_x$ ratio but not the observed OH levels.

5. Summary

[20] Our understanding of HO$_2$NO$_2$ in the free troposphere is examined with the first direct in situ observations from the NASA DC-8 during INTEX-NA 2004. Photochemical models and observed HO$_x$ levels can explain the HO$_2$NO$_2$ in the midtroposphere (4.5 – 8 km) where thermal decomposition is dominant. In the upper troposphere (8 – 12 km) there is a significant discrepancy between model predicted and observed HO$_x$. There is also significant disagreement between steady state calculations of HO$_2$NO$_2$ that use measured HO$_x$ levels and observations of HO$_2$NO$_2$ in the upper troposphere. Conversely, pernitric acid levels are reasonably well predicted by steady state calculations using photochemical model predicted HO$_x$ levels. Time-dependent modeling of HO$_2$NO$_2$ levels indicates that treating pernitric acid as in steady state is valid in the upper troposphere. The discrepancy between the observed HO$_x$ and HO$_2$NO$_2$ levels would be diminished if there is an unidentified loss process for HO$_2$NO$_2$ whose magnitude increases with altitude. This suggests that further investigation of potential HO$_2$NO$_2$ loss process may be needed.

[21] Acknowledgments. The authors gratefully acknowledge the financial support of NASA through contract NNG04GB62G and thank the DC-8 crew and support team. We also thank Paul Ricchiazzi of U.C. Santa Barbara for valuable advice on using SBDART.


M. Avery, G. Chen, J. H. Crawford, G. Diskin, and J. R. Olson, NASA Langley Research Center, Hampton, VA 23681, USA.

T. H. Bertram, R. C. Cohen, A. Perring, and P. J. Wooldridge, Department of Chemistry and Department of Earth and Planetary Science, University of California, Berkeley, CA 94720, USA.

W. H. Brune, R. Lesher, and X. Ren, Department of Meteorology, Pennsylvania State University, University Park, PA 16802, USA.

L. G. Huey, S. Kim, I. Sokolik, R. E. Stickel, and D. J. Tanner, School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA 30332, USA. (greg.huey@eas.gatech.edu)

B. L. Lefer, Department of Geosciences, University of Houston, Houston, TX 77204, USA.

R. E. Shetter, National Center for Atmospheric Research, Boulder, CO 80305, USA.