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# Measurements of the sum of $\text{HO}_2\text{NO}_2$ and $\text{CH}_3\text{O}_2\text{NO}_2$ in the remote troposphere

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**Abstract.** The chemistry of peroxyacetic acid ( $\text{HO}_2\text{NO}_2$ ) and methyl peroxyacetic acid ( $\text{CH}_3\text{O}_2\text{NO}_2$ ) is predicted to be particularly important in the upper troposphere where temperatures are frequently low enough that these compounds do not rapidly decompose. At temperatures below 240 K, we calculate that about 20% of  $\text{NO}_y$  in the mid- and high-latitude upper troposphere is  $\text{HO}_2\text{NO}_2$ . Under these conditions, the reaction of OH with  $\text{HO}_2\text{NO}_2$  is estimated to account for as much as one third of the permanent loss of hydrogen radicals. During the Tropospheric Ozone Production about the Spring Equinox (TOPSE) campaign, we used thermal dissociation laser-induced fluorescence (TD-LIF) to measure the sum of peroxyacetic acids ( $\Sigma\text{PNs} \equiv \text{HO}_2\text{NO}_2 + \text{CH}_3\text{O}_2\text{NO}_2 + \text{PAN} + \text{PPN} + \dots$ ) aboard the NCAR C-130 research aircraft. We infer the sum of  $\text{HO}_2\text{NO}_2$  and  $\text{CH}_3\text{O}_2\text{NO}_2$  as the difference between  $\Sigma\text{PN}$  measurements and gas chromatographic measurements of the two major peroxy acyl nitrates, peroxy acetyl nitrate (PAN) and peroxy propionyl nitrate (PPN). Comparison with  $\text{NO}_y$  and other nitrogen oxide measurements confirms the importance of  $\text{HO}_2\text{NO}_2$  and  $\text{CH}_3\text{O}_2\text{NO}_2$  to the reactive nitrogen budget and shows that current thinking about the chemistry of these species is approximately correct. During the spring high latitude conditions sampled during the TOPSE experiment, the model predictions of the contribution of ( $\text{HO}_2\text{NO}_2 + \text{CH}_3\text{O}_2\text{NO}_2$ ) to  $\text{NO}_y$  are highly temperature dependent: on average 30% of  $\text{NO}_y$  at 230 K, 15% of  $\text{NO}_y$  at 240 K, and <5% of  $\text{NO}_y$  above 250 K. The temperature dependence of the inferred concentrations corroborates the contribution of overtone photolysis to the photochemistry of peroxyacetic acid. A model that includes IR photolysis ( $J = 1 \times 10^{-5} \text{ s}^{-1}$ ) agreed with the observed sum

of  $\text{HO}_2\text{NO}_2 + \text{CH}_3\text{O}_2\text{NO}_2$  to better than 35% below 240 K where the concentration of these species is largest.

## 1 Introduction

Reactions of hydrogen radicals ( $\text{HO}_x \equiv \text{OH} + \text{HO}_2$ , and  $\text{RO}_2$ ) and nitrogen radicals ( $\text{NO}_x \equiv \text{NO} + \text{NO}_2$ ) affect atmospheric composition and climate by regulating global tropospheric ozone and the Earth's oxidative capacity. Peroxyacetic acids ( $\text{RO}_2\text{NO}_2$ ) link these chemical families, thereby influencing tropospheric ozone production and the abundance of OH in both the troposphere and stratosphere. Non-acyl peroxyacetic acids such as  $\text{HO}_2\text{NO}_2$  and  $\text{CH}_3\text{O}_2\text{NO}_2$  are increasingly important at temperatures below 240 K, because the molecules are very weakly bound ( $\sim 95 \text{ kJ/mol}$ ) and rapidly dissociate at higher temperature. Consequently these molecules are most important in the stratosphere and upper troposphere.

Knowledge of the chemistry of alkyl  $\text{RO}_2\text{NO}_2$  species is limited because they are difficult to isolate in the laboratory or to observe directly in the atmosphere. Remote sensing measurements of peroxyacetic acid concentrations in the stratosphere show that  $\text{HO}_2\text{NO}_2$  mixing ratios peak at approximately 200 ppt near 27 km altitude (Rinsland et al., 1986; Rinsland et al., 1996; Sen et al., 1998). The only other measurements are from the Antarctic surface where Slusher et al. (2001) used chemical ionization mass spectrometry to observe  $\text{HO}_2\text{NO}_2$  mixing ratios on the order of 20 ppt, showing they were nearly equal to nitric acid mixing ratios. Recent OH and  $\text{HO}_2$  measurements made in the lower stratosphere at high solar zenith angles (SZA) indicate that there is a source of  $\text{HO}_x$  that dissociates following absorption of low energy photons (Salawitch et al., 1994; Wennberg et al., 1999). Overtone photodissociation of  $\text{HO}_2\text{NO}_2$ , as

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suggested by Donaldson et al. (1997), can explain part of the HO<sub>x</sub> source required to account for these observations and some of the temporal variability seen in remote sensing of HO<sub>2</sub>NO<sub>2</sub> (Salawitch et al., 2002). These observations and calculations of HO<sub>2</sub>NO<sub>2</sub> abundances and their effect on stratospheric HO<sub>x</sub> have been the impetus for revisiting the long-wavelength photolysis and kinetics of peroxy nitrates in the laboratory (Knight et al., 2002; Roehl et al., 2002; Zhang et al., 2000).

Here we describe the first in situ measurements of these peroxy nitrates in the free troposphere. The measurements were made during the Tropospheric Ozone Production about the Spring Equinox (TOPSE) experiment (Atlas et al., 2003). TOPSE flights focused on tropospheric sampling over mid- to high-latitude continental North America during the winter and spring of 2000. Data used in this paper are limited to latitudes north of 50° N and altitudes above 500 m to avoid the effects of recent surface emissions or losses. The data were collected during the daytime at temperatures between 220 and 290 K. Analysis along chemical coordinates (Cohen et al., 2000), in this case temperature and NO<sub>2</sub>, and consideration of the NO<sub>y</sub> budget are used to evaluate current understanding of photolytic and thermal decomposition rates of HO<sub>2</sub>NO<sub>2</sub> and CH<sub>3</sub>O<sub>2</sub>NO<sub>2</sub>.

## 2 Instrumentation

NO<sub>y</sub> and its components were measured from the NCAR C-130 aircraft during the TOPSE experiment. Ridley et al. (2000) measured NO, NO<sub>2</sub> and NO<sub>y</sub> by conversion to NO followed by O<sub>3</sub>+NO chemiluminescence. The NO<sub>2</sub> measurements were precise to ± 4 ppt and accurate to 5%. C<sub>1</sub>–C<sub>4</sub> alkyl nitrates (ΣANs) were quantified by GC analysis of whole air samples (Blake et al., 2003). In our analysis, the sum of C<sub>1</sub>–C<sub>4</sub> alkyl nitrate observations was linearly interpolated to a 1 min time base. Nitric acid was measured using a mist chamber followed by ion chromatography (Talbot et al., 1990). PAN and PPN were measured in situ by the NCAR Gas Chromatography with Electron Capture Detection (GC-ECD) instrument. The PAN and PPN measurements represent 1–3 s samples with a precision of ±5 ppt at 20 ppt, ±3 ppt at 100 ppt, ±5–7 ppt at 500 ppt. The accuracy of the PAN and PPN measurements is 10%. Because the PAN and PPN measurements were made with the same instrument, we assume their uncertainties are correlated, that is, if necessary, both could be brought to the “true” value by multiplying by a single constant. During a five minute interval, two PAN measurements and one of PPN are obtained.

A two-channel thermal dissociation laser-induced fluorescence (TD-LIF) instrument was used for observations of total peroxy nitrates (ΣPNs≡PAN+PPN+HO<sub>2</sub>NO<sub>2</sub>+CH<sub>3</sub>O<sub>2</sub>NO<sub>2</sub>+...) and of NO<sub>2</sub>. TD-LIF is described in detail in Day et al. (2002). The specific instrument configuration used during TOPSE is described in detail by

Thornton (2002). Briefly, TD-LIF relies on a heated inlet (50 ms residence time at 180°C) to dissociate RO<sub>2</sub>NO<sub>2</sub> to yield NO<sub>2</sub> and RO<sub>2</sub>. The resultant NO<sub>2</sub> is quantified along with ambient NO<sub>2</sub> using laser-induced fluorescence (LIF). By operating the heated inlet in parallel with an inlet maintained at ambient temperature, ΣPN mixing ratios can be derived from the difference between the NO<sub>2</sub> signals of the two channels. In addition to acyl and non-acyl peroxy nitrates, N<sub>2</sub>O<sub>5</sub> will also dissociate in the heated inlet, though we expect it was removed through contact with the walls prior to the heated portion of the inlet, and made a negligible contribution to NO<sub>y</sub> in the low NO<sub>x</sub> conditions sampled during TOPSE. NO<sub>y</sub> species such as alkyl nitrates and nitric acid have significantly higher O–NO<sub>2</sub> bond energies than peroxy nitrates and would not have dissociated under the inlet conditions used.

The first third of the campaign was used to test and improve some aspects of instrument performance. High time resolution measurements of NO<sub>2</sub> (channel 1) and ΣPNs (channel 2–channel 1) were obtained simultaneously and continuously during the final nineteen flights of the TOPSE experiment. The precision of the measurements for a 1 min average in each channel under optimal conditions was ±20 ppt which is dominated by uncertainty in the instrument zero. Under some conditions, usually after steep altitude changes, the apparent precision is ±50 ppt. The precision of ΣPNs is given by:

$$\sigma(\Sigma\text{PNs})=[(\sigma_{\text{channel 1}})^2 + (\sigma_{\text{channel 2}})^2]^{1/2} \quad (1)$$

and for a typical scenario  $\sigma(\Sigma\text{PNs})$  is ±28 ppt for 1 min averaging. The accuracy of channel 1 is estimated to be 10% and the accuracy of channel 2 to be 15%. The accuracy of the ΣPNs is estimated to be 15% since the accuracy of the two channels is largely correlated and most of the signal is in channel 2. While TD-LIF NO<sub>2</sub> measurements were used for calculating ΣPN, in the model calculations below we use the NCAR photolysis-chemiluminescence measurements of NO<sub>2</sub> because of their superior precision in the low concentration ranges encountered during TOPSE. TD-LIF measurements were, on average, 20 ppt higher than chemiluminescence measurements of NO<sub>2</sub>, but the ΣPN measurements are the difference between two channels, and observations with the inlet heater turned off confirm that both channels measure the same amount of NO<sub>2</sub>.

Measurements suggest that PAN is the dominant contribution to ΣPNs and that PPN is the only other major acyl peroxy nitrate in the air sampled during TOPSE. In order to infer abundances of non-acyl peroxy nitrates (hereafter referred to as ΔPNs) we subtract speciated measurements of PAN and PPN obtained by the NCAR GC-ECD instrument from the TD-LIF measurements of ΣPNs.

$$\Delta\text{PNs}=\Sigma\text{PNs}-\text{PAN}-\text{PPN} \quad (2)$$

We averaged 1 min of TD-LIF data about each PAN measurement and interpolated PPN to generate a dataset of all species coincident in time at 1 min resolution.

The uncertainty in  $\Delta$ PNs has components associated with both the precision and accuracy of the TD-LIF and GC measurements. In what follows, we do not draw any conclusions based on individual measurements, rather our conclusions are based on averages over a large enough sample that uncertainty in mean quantities is entirely a function of the instruments' accuracies. The techniques are thought to be accurate to 10% (GC) and 15% (LIF) and for both techniques one single multiplicative correction (if it could be known) would bring the observed values to the "true" values (to within the precision uncertainty). The accuracy of these instruments depends on a chain of calibration that connects to NIST traceable reference standards of NO or NO<sub>2</sub>, on the accuracy of flow controllers used to dilute these standards and on titration reactions. None of these factors depend on environmental parameters. Thus the associated accuracy in the average value of a combined quantity like  $\Delta$ PNs adds in quadrature, since the accuracy of the GC and LIF measurements are assumed to be uncorrelated, resulting in a combined accuracy of 18%. The random error associated with an individual  $\Delta$ PNs measurement is obtained by standard propagation of error based on Eq. (2);

$$\sigma(\Delta\text{PNs})=[(\sigma_{\Sigma\text{PNs}})^2 + (\sigma_{\text{PAN}})^2 + (\sigma_{\text{PPN}})^2]^{1/2} \quad (3)$$

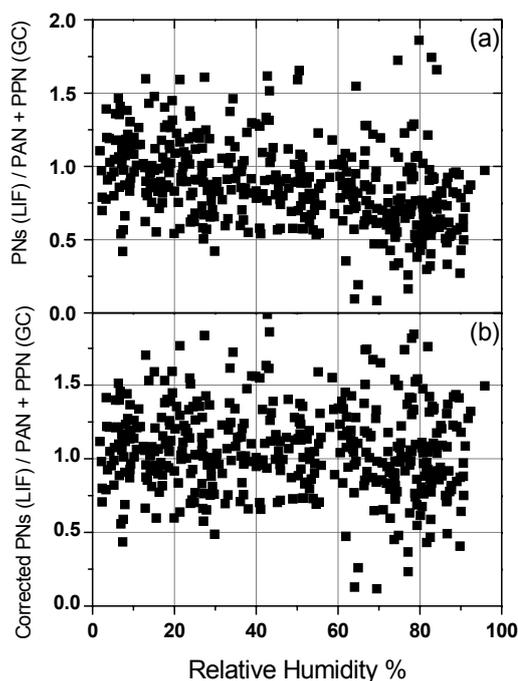
which results in an uncertainty of  $\pm 29$  ppt.

In contrast to the expectations outlined above, Fig. 1a shows that the two techniques differ by 35% at high relative humidity and agree at low humidity. In the top panel of Fig. 1, the ratio of  $\Sigma$ PNs/(PAN+PPN) is plotted versus humidity for data that calculations suggest have negligible amounts of  $\Delta$ PNs ( $\Delta$ PNs less than 10% of PAN). This figure includes more than half the observations in the dataset. The absolute difference is larger than expected and the accuracy is not observed to be independent of environmental parameters. One or both instruments are not accurate to within the 10 or 15% quoted.

Neither technique is known to have a humidity-dependent bias or interference of this magnitude. We examined a wide range of variables and considered many possible sources of instrument error in the effort to understand the calibration difference between the instruments. Humidity provided the clearest correction. Applying a constraint that

$$\Delta\text{PNs} \geq 0 \quad (4)$$

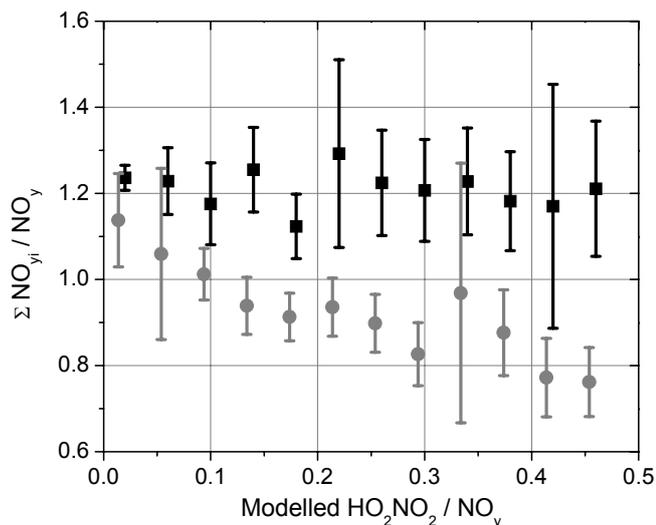
permits the derivation of a constant that implicitly couples the calibration constants for the two instruments and corrects for this difference as a function of humidity. A correction factor,  $C=(1+0.0025*\%RH)$ , was generated that brings the average (PAN+PPN)/ $\Sigma$ PNs near one when  $\Delta$ PNs are insignificant. Since we have no reason to apply the correction to one or the other instrument, the TD-LIF data was multiplied by the correction factor C, and the GC data was divided



**Fig. 1.** (a) Humidity trend in ratio of LIF to GC measurements where HO<sub>2</sub>NO<sub>2</sub> is predicted to be less than 10% of PAN (b) Ratio after the humidity-dependent correction has been applied.

by this factor. This removed the humidity bias (Fig. 1b). Throughout the remainder of this paper we use these adjusted datasets. Applying the factor C to the two data sets alters them by 12% on average (+12%  $\Sigma$ PNs and -12% PAN and PPN). The modelled  $\Delta$ PNs show no trend with relative humidity and the conclusions of this paper would be unchanged if a larger correction had been applied to one or the other instrument. Using Eq. (2) with the corrected datasets provides 1433 1-min measurements of  $\Delta$ PNs, which calculations suggest are predominantly HO<sub>2</sub>NO<sub>2</sub> and CH<sub>3</sub>O<sub>2</sub>NO<sub>2</sub>. We estimate the uncertainty in  $\Delta$ PNs is 25%.

Measurements of NO<sub>y</sub> and comparison to the sum of individual NO<sub>y</sub> compounds ( $\Sigma$ NO<sub>y</sub>) provide another means to evaluate the relative calibration of the GC-ECD, TD-LIF and NO<sub>y</sub> techniques, as well as our ability to infer  $\Delta$ PNs from the adjusted difference of the two sets of measurements. Figure 2 demonstrates the importance of HO<sub>2</sub>NO<sub>2</sub> in the reactive nitrogen budget and the ability of TD-LIF  $\Delta$ PN measurements to account for this compound. The ratio  $\Sigma\text{NO}_{y,i}/\text{NO}_y$  with the above correction applied to each peroxy nitrate dataset, is plotted against fraction of NO<sub>y</sub> that is predicted by a model to be HO<sub>2</sub>NO<sub>2</sub>. The ratio where  $\Sigma\text{NO}_{y,i}=\text{NO}_x+\Sigma\text{ANs}+\text{HNO}_3+\text{PAN}+\text{PPN}$  (gray circle) decreases from a value above 1.1 where  $\Delta$ PNs are insignificant to close to 0.8 where HO<sub>2</sub>NO<sub>2</sub> contributes a substantial fraction of total NO<sub>y</sub>. Conversely, the NO<sub>y</sub> budget using TD-LIF measurements  $\Sigma\text{NO}_{y,i}=\text{NO}_x+\Sigma\text{ANs}+\text{HNO}_3 + \Sigma\text{PNs}$  (black square) is approximately a constant 1.2. This suggests that

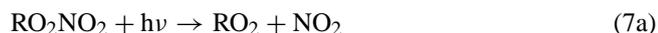
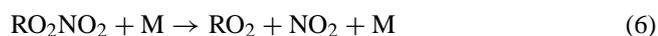
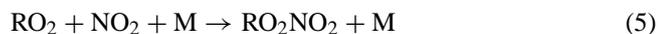


**Fig. 2.**  $\Sigma\text{NO}_{yi}/\text{NO}_y$  vs calculated  $\text{HO}_2\text{NO}_2/\text{NO}_y$ , using  $\Sigma\text{NO}_{yi} = \text{NO}_x + \text{HNO}_3 + \Sigma\text{ANs} + \text{PAN} + \text{PPN}$  (●) and  $\Sigma\text{NO}_{yi} = \text{NO}_x + \text{HNO}_3 + \Sigma\text{ANs} + \Sigma\text{PNs}$  (■). The data were averaged within  $\pm 0.04$  of  $\text{HO}_2\text{NO}_2/\text{NO}_y$  and the error bars represent twice the standard deviation of the mean.

our  $\Sigma\text{PN}$  measurements account for the predicted contribution of  $\text{HO}_2\text{NO}_2$  to the reactive nitrogen budget. If the modelled  $\Delta\text{PNs}$  are added to the PAN and PPN measurements, the average  $\Sigma\text{NO}_{yi}/\text{total NO}_y$  ratio over the whole campaign is 1.2. If the humidity correction is not applied to the data, the  $\Sigma\text{NO}_{yi}/\text{NO}_y$  ratio using the  $\Sigma\text{PN}$  measurements is a constant 1.1, and the ratio using PAN+PPN varies from above 1.2 where  $\Delta\text{PNs}$  are insignificant to 0.8 where  $\Delta\text{PNs}$  are calculated to be 45% of  $\text{NO}_y$ .

### 3 Model description and comparison to observations

Peroxy nitrates are formed when an  $\text{RO}_2$  radical (where  $\text{R}=\text{H}$ , alkyl, or acyl group) reacts with  $\text{NO}_2$  (Reaction 5). In the remote atmosphere,  $\text{HO}_2$  and  $\text{CH}_3\text{O}_2$  make up a large fraction of  $\text{RO}_2$ . Sinks of  $\text{HO}_2\text{NO}_2$  and  $\text{CH}_3\text{O}_2\text{NO}_2$  include thermal decomposition (R6), photolysis (R7), and for  $\text{HO}_2\text{NO}_2$ , reaction with OH (R8). Note that the products given for reaction 8 have not been measured. Models all assume that water is a product of R8 and consequently that R8 is a sink for  $\text{HO}_x$  radicals.



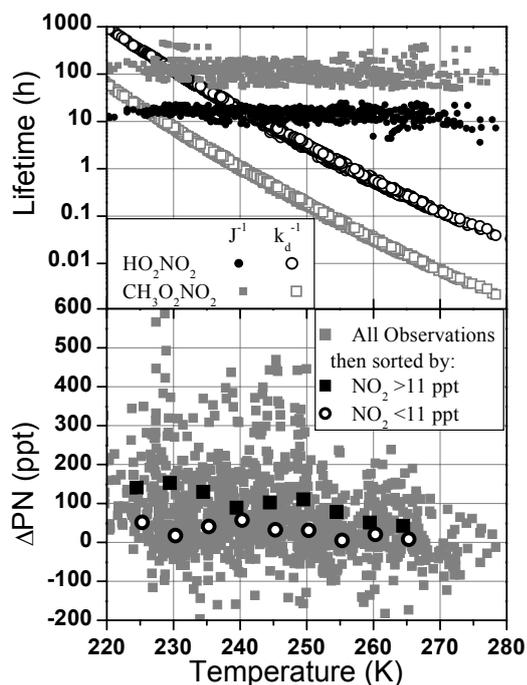
Uncertainties associated with this chemistry are large. For example, for the thermal decomposition of  $\text{HO}_2\text{NO}_2$  the JPL panel recommends an uncertainty factor of 5 at 298 K and of 13 at 230 K (Sander et al., 2003). Recent laboratory measurements of the UV (Knight et al., 2002) and IR (Roehl et al., 2002) cross sections of peroxy nitric acid greatly improve our understanding of its photolysis rate, ( $\text{J} \equiv \text{R7}$ ), although the temperature and pressure dependencies of the quantum yield require further investigation. We know little about the photolysis of  $\text{CH}_3\text{O}_2\text{NO}_2$ .

We use an instantaneous steady state model representing R5–R8 to predict the abundances of  $\text{HO}_2\text{NO}_2$  and  $\text{CH}_3\text{O}_2\text{NO}_2$ .

$$[\text{HO}_2\text{NO}_2]_{\text{SS}} = \frac{k_5[\text{HO}_2][\text{NO}_2][\text{M}]}{k_6[\text{M}] + \text{J7} + k_8[\text{OH}]} \quad (9)$$

$$[\text{CH}_3\text{O}_2\text{NO}_2]_{\text{SS}} = \frac{k_5'[\text{CH}_3\text{O}_2][\text{NO}_2][\text{M}]}{k_6'[\text{M}] + \text{J7}'} \quad (10)$$

Measurements of  $\text{NO}_2$ , the spectrally resolved actinic flux, temperature, and pressure are used in the calculations. As a result of the low mixing ratios of  $\text{NO}_2$  (50% of the observations have  $\text{NO}_2$  below 11 ppt) the precision of the model calculations are roughly proportional to the precision of the  $\text{NO}_2$  measurements, for example  $\pm 40\%$  at 10 ppt  $\text{NO}_2$ . Although OH and  $\text{HO}_2$  were measured during the TOPSE campaign, the observations were too infrequent to use in the model. Steady state concentrations of OH,  $\text{HO}_2$ , and  $\text{CH}_3\text{O}_2$  were calculated using the photochemical model described by Cantrell et al. (2003), which included the steady state equations for  $\text{HO}_2\text{NO}_2$  and  $\text{CH}_3\text{O}_2\text{NO}_2$ . Four individual calculations in which radicals and reservoirs were solved self-consistently were used to investigate the main sources of uncertainty in the kinetics of  $\text{HO}_2\text{NO}_2$ . Rate constants used in the model are from the JPL-2000 recommendations except for the self-reaction of  $\text{HO}_2$  (Christensen et al., 2002) and for the reaction  $\text{HO}_2 + \text{O}_3$  and  $\text{OH} + \text{O}_3$  for which we use JPL-97 recommendations (see Lanzendorf et al., 2001). Photolysis rates were determined using measured actinic flux and made use of the recent molecular data for  $\text{H}_2\text{CO}$  (Smith et al., 2002) and  $\text{HO}_2\text{NO}_2$  (Knight et al., 2002; Roehl et al., 2002). The UV cross section of  $\text{CH}_3\text{O}_2\text{NO}_2$  is assumed to be equal to that of  $\text{HO}_2\text{NO}_2$ . The thermal decomposition of  $\text{CH}_3\text{O}_2\text{NO}_2$  dominates down to 220 K, so we need not consider any potential IR overtone photodissociation from the CH groups present in the molecule. In the first calculation (Model A), the IR photolysis rate of  $\text{HO}_2\text{NO}_2$  is set at  $1 \times 10^{-5} \text{ s}^{-1}$ , slightly higher than the recommendation of  $8.3 \times 10^{-6} \text{ s}^{-1}$  from Roehl et al. (2002), which was given for a system with no albedo. In a second calculation (Model B), the IR photolysis rate for  $\text{HO}_2\text{NO}_2$  was set to zero. In two separate calculations, the rate of thermal decomposition of  $\text{HO}_2\text{NO}_2$  was varied to the maximum (Model C) and minimum (Model D) limits given in JPL-2003. Model A, with standard thermal decomposition and including IR photolysis,

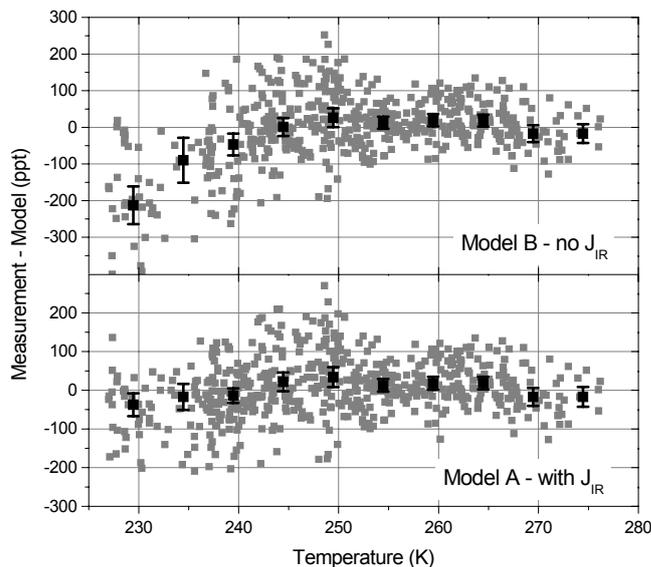


**Fig. 3.** (upper panel) lifetime of HO<sub>2</sub>NO<sub>2</sub> with respect to thermal decomposition (○) and the sum of photolysis and reaction with OH (●) and of CH<sub>3</sub>O<sub>2</sub>NO<sub>2</sub> with respect to thermal decomposition (□) and photolysis (■). (lower panel) ΔPN measurements (■) as a function of temperature, averaged into separate temperature bins for NO<sub>2</sub> < 11 ppt (○) and for NO<sub>2</sub> > 11 ppt (■).

calculates peak HO<sub>2</sub>NO<sub>2</sub> and CH<sub>3</sub>O<sub>2</sub>NO<sub>2</sub> mixing ratios during the last 19 flights of the TOPSE experiment that range as high as 300 ppt and 100 ppt respectively. It predicts HO<sub>2</sub>NO<sub>2</sub> reaching as much as 50% of measured NO<sub>y</sub> and CH<sub>3</sub>O<sub>2</sub>NO<sub>2</sub> as much as 15% of measured NO<sub>y</sub>.

Figure 3 depicts the temperature dependence of the thermal and photochemical sinks of these two peroxy nitrates. The photochemical sinks (R7 and R8) are nearly independent of temperature. HO<sub>2</sub>NO<sub>2</sub> has a slower thermal decomposition rate and a faster photochemical loss than CH<sub>3</sub>O<sub>2</sub>NO<sub>2</sub> because of its large infrared photodissociation cross section and because its reaction with OH also contributes to photochemical loss. For HO<sub>2</sub>NO<sub>2</sub>, thermal decomposition becomes faster than the photochemical sinks above 240 K, while the crossing point for CH<sub>3</sub>O<sub>2</sub>NO<sub>2</sub> is near 220 K. One consequence of this is that the lifetime of HO<sub>2</sub>NO<sub>2</sub> (~12 h in sunlit conditions) is independent of temperature for the colder conditions sampled during TOPSE.

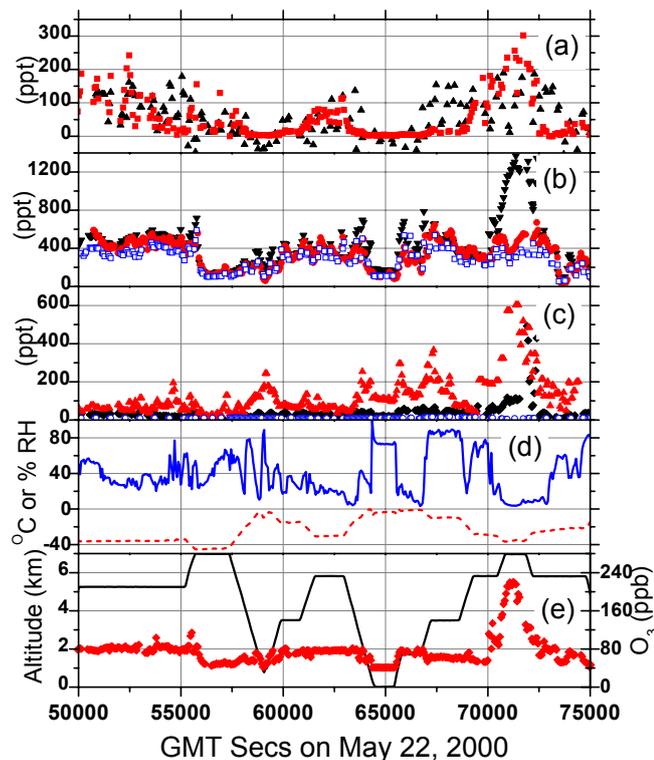
The instantaneous steady state model is valid only when the lifetime of the HO<sub>2</sub>NO<sub>2</sub> or CH<sub>3</sub>O<sub>2</sub>NO<sub>2</sub> is short compared to the rate of change of its sources and sinks. This is not always true for these peroxy nitrates under the coldest conditions sampled during TOPSE. However, many of the data points were collected at high latitudes during the late spring, where the photochemistry has a fairly shallow diur-



**Fig. 4.** Difference between measured and modelled ΔPNs for a model without IR photolysis (upper panel) and a model including IR photolysis for HO<sub>2</sub>NO<sub>2</sub> (lower panel). The black squares represent the median of each 5 K bin and the error bars are twice the standard deviation of the mean.

nal profile, making the model steady state predictions reasonable estimates. To help avoid any bias due to being strongly out of steady state, model results in which the lifetime of either compound exceeded twelve hours were discarded, unless there were more than 20 hours of sunlight per day at that location.

In the lower panel of Fig. 3, the ΔPN concentrations inferred from our observations are displayed versus temperature. The mixing ratios below approximately 250 K are larger than at warmer temperatures. The wide range of concentrations at each temperature derives partly from variation in the abundance of HO<sub>2</sub>, CH<sub>3</sub>O<sub>2</sub> and NO<sub>2</sub> radicals in the airmass. As an example, the large symbols are the mean ΔPNs within a 5 K bin for NO<sub>2</sub> mixing ratios above (black squares) and below (open circles) 11 ppt, which was the median NO<sub>2</sub> during the last 19 flights of TOPSE. On average, higher values of ΔPNs were observed when NO<sub>2</sub> mixing ratios were higher than average and vice versa. In addition to being proportional to NO<sub>2</sub>, below 250 K ΔPNs are calculated to depend strongly on the IR photolysis of HO<sub>2</sub>NO<sub>2</sub>, which has only recently been recognized as large enough to affect its atmospheric mixing ratio. Our data provides direct observational evidence for this term. In the upper panel of Fig. 4 we show the difference between the ΔPN observations and model B (no IR photolysis) and in the lower panel we show the difference between ΔPNs and model A. The relative significance of IR photolysis increases strongly as a function of decreasing temperature and dominates over thermal decomposition as a sink of HO<sub>2</sub>NO<sub>2</sub> below 235 K. At 230 K, the model without IR

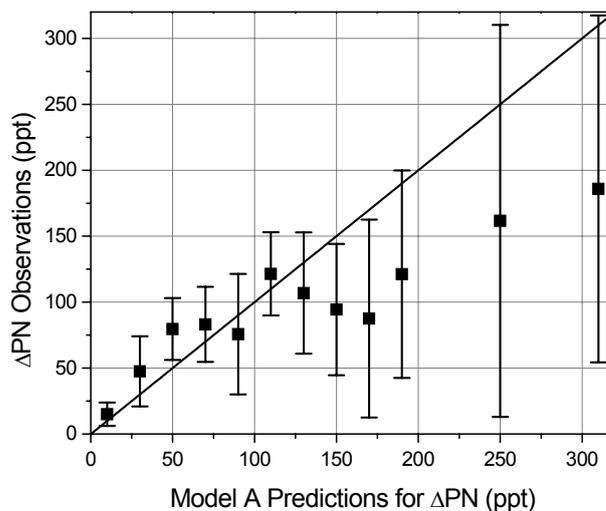


**Fig. 5.** Observations during a flight between Thule and Winnipeg on 22 May 2000 (a)  $\Delta$ PN measurements ( $\blacktriangle$ ) and predictions from Model A ( $\blacksquare$ ) (b)  $\text{NO}_y$  ( $\blacktriangledown$ ), PAN+PPN ( $\square$ ),  $\Sigma$ PN ( $\bullet$ ) (c)  $\text{HNO}_3$  ( $\blacktriangle$ ),  $\text{NO}_x$  ( $\diamond$ ),  $\Sigma$ ANs ( $\circ$ ) (d) temperature (---), % relative humidity (—) (e) altitude (—),  $\text{O}_3$  ( $\diamond$ ).

photolysis has, on average, 200 ppt more HO<sub>2</sub>NO<sub>2</sub> than the observed  $\Delta$ PNs. There are specific events where modeled  $\Delta$ PNs exceed the measurements by 400 ppt without the infrared sink of HO<sub>2</sub>NO<sub>2</sub>.

The model A peroxyxynitrate (HO<sub>2</sub>NO<sub>2</sub>+CH<sub>3</sub>O<sub>2</sub>NO<sub>2</sub>) predictions are compared to  $\Delta$ PN measurements in a time series during a TOPSE flight on May 22 (Fig. 5 upper panel). This flight between Thule and Winnipeg sampled a wide range of tropospheric conditions and encountered air of mixed stratospheric-tropospheric character ( $\text{O}_3 > 100$  ppb) near the end of the flight. HNO<sub>3</sub> and NO<sub>x</sub> make significant contributions to NO<sub>y</sub> in this particular airmass, which nonetheless has quite high PAN mixing ratios. The  $\Delta$ PN measurements are generally scattered around the model predictions and tend to be highest under the coldest conditions as expected based on the chemistry described above. During this flight, NO<sub>x</sub> and  $\Delta$ PNs are nearly equal.

The figures above show that  $\Delta$ PNs vary as expected in response to two of the individual terms in the steady-state equations (J and NO<sub>2</sub>) and vary along a flight track as the steady state calculation suggests they should.



**Fig. 6.** Comparison of average  $\Delta$ PN observations and Model A predictions with the error bars representing twice the standard deviation on the mean and a 1:1 line shown.

Table 1 compiles the median contribution of each species or group to the NO<sub>y</sub> budget during TOPSE for temperatures above and below 240 K. Peroxyxynitrates were the most significant fraction of NO<sub>y</sub> under all temperature regimes sampled during TOPSE. The  $\Delta$ PN predictions of Model A and Model B are shown for reference to the observations inferred by  $\Sigma$ PNs-(PAN+PPN). The significance of  $\Delta$ PNs to NO<sub>y</sub> predicted by Model A and observed agree to within a factor of 2 above 240 K and to within 35% below 240 K. The ratio  $\Sigma \text{NO}_{y_i} / \text{NO}_y$  is between 1.1 and 1.25 using either TD-LIF  $\Sigma$ PNs or GC-ECD PAN+PPN and modelled  $\Delta$ PNs.

Figure 6 shows a direct comparison of calculations of  $\Delta$ PNs and the observations for all flights in the analysis. Within the statistical variance, the observations and model agree. However model predictions exceed the observations at higher mixing ratios and the fact that nearly all calculated concentrations above 150 ppt are higher than observations suggests the effect is statistically reliable. If the steady state approximation is correct, then this could indicate an error in the photochemistry of HO<sub>2</sub>NO<sub>2</sub> or the thermal decomposition of CH<sub>3</sub>O<sub>2</sub>NO<sub>2</sub>. We investigated the factor of 5–15 uncertainty in the HO<sub>2</sub>NO<sub>2</sub> thermal decomposition rate at temperatures in the 220–298 K range. Model calculations (C,D) that incorporated the most extreme values for rates of thermal decomposition predicted  $\Delta$ PN concentrations that differed at most by 100 ppt, with the greatest effect occurring between 235 and 250 K. Both models were less consistent with the observations than Model A, but because HO<sub>2</sub>NO<sub>2</sub> is largest where thermal decomposition is slow compared to photolysis we are unable to define substantially more precise limits on the rate of thermal decomposition than recommended by the JPL panel. We examined other possible effects but found no single explanation that would bring the model-measurement comparison into significantly better agreement.

**Table 1.** NO<sub>y</sub> composition (500–8000 m) above and below 240 K during TOPSE flights between 6 April and 23 May 2000.

NO <sub>yi</sub>	T < 240 K	T > 240 K
	%NO <sub>y</sub>	%NO <sub>y</sub>
∑PNs <sup>a</sup>	90	86
PAN+PPN <sup>b</sup>	73	76
Inferred ΔPNs	17	10
Model A ΔPNs	22	5
Model B ΔPNs	34	5
HNO <sub>3</sub>	11	25
NO <sub>x</sub> <sup>c</sup>	5	8
Alkyl Nitrates	4	4
∑NO <sub>yi</sub>	∑NO <sub>yi</sub> /NO <sub>y</sub>	∑NO <sub>yi</sub> /NO <sub>y</sub>
(NO <sub>x</sub> +∑ANs+HNO <sub>3</sub> +∑PNs)	1.10	1.23
(NO <sub>x</sub> +∑ANs+HNO <sub>3</sub> +PAN+PPN+ModelAΔPNs)	1.15	1.18

<sup>a</sup> TD-LIF measurements with humidity correction applied, <sup>b</sup> GC-ECD measurements with humidity correction applied,

<sup>c</sup> Chemiluminescence measurements

#### 4 Discussion

In the upper troposphere, several studies (Folkins et al., 1997; Jaegle et al., 2000; Jaegle et al., 2001) have described calculations indicating that reaction of OH with HO<sub>2</sub>NO<sub>2</sub> is a dominant sink for HO<sub>x</sub>. Analysis of HO<sub>x</sub> observations by Faloon et al. (2000) suggest that a model in which the HO<sub>2</sub>NO<sub>2</sub> equilibrium constant is reduced by a factor of five, or with HO<sub>2</sub>NO<sub>2</sub> formation suppressed entirely, provides a more accurate representation of upper tropospheric HO<sub>x</sub> observations than the standard model. We estimate that inclusion of the IR photolysis of HO<sub>2</sub>NO<sub>2</sub> should have nearly the same effect on HO<sub>2</sub>NO<sub>2</sub> concentrations at the altitudes where most of the observations described by Faloon et al. (2000) were collected. The main consequence is a decrease in the modelled abundance of HO<sub>2</sub>NO<sub>2</sub>. However, the IR photolysis will have a distinctly different temperature dependence than the suggested change to the equilibrium constant. For the coldest conditions sampled during TOPSE, between 220 K and 240 K, Model A, which includes IR photolysis, predicts ~10% more HO<sub>x</sub> than Model B, and also results in slightly different HO<sub>x</sub> partitioning.

Another interesting aspect of HO<sub>2</sub>NO<sub>2</sub> and CH<sub>3</sub>O<sub>2</sub>NO<sub>2</sub> chemistry is their behavior as a short-term reservoir for HO<sub>x</sub> and NO<sub>x</sub> radicals. Under sunlit conditions, the radicals and alkyl peroxy nitrates should reach steady state, yet once the sun sets, formation diminishes and the only remaining sink is thermal decomposition. During twelve hours of darkness in the upper troposphere at 240 K, all the CH<sub>3</sub>O<sub>2</sub>NO<sub>2</sub> and over half of the HO<sub>2</sub>NO<sub>2</sub> will have thermally dissociated, releasing on the order of tens to hundreds ppt of CH<sub>3</sub>O<sub>2</sub> and HO<sub>2</sub>. The fate of these radicals during the night will depend strongly on the abundance of NO<sub>x</sub> and O<sub>3</sub>. This fact underscores the importance of making measurements at night to challenge our understanding of radical sources and sinks.

#### 5 Conclusions

We describe observations of ΔPNs and demonstrate that they are HO<sub>2</sub>NO<sub>2</sub> and CH<sub>3</sub>O<sub>2</sub>NO<sub>2</sub>. The observations show that during the spring high latitude conditions sampled during the TOPSE experiment, the contribution of ΔPNs to NO<sub>y</sub> is highly temperature dependent, with ΔPNs on average 30% of NO<sub>y</sub> at 230 K and 7% of NO<sub>y</sub> at 250 K. The magnitude and observed temperature dependence of the mixing ratios is consistent with recent laboratory evidence that the *J* value for HO<sub>2</sub>NO<sub>2</sub> has a large IR component. Prior analyses of the NO<sub>y</sub> budget in the upper troposphere that did not take into account HO<sub>2</sub>NO<sub>2</sub> or the new *J* value should be revisited.

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