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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Measurements of the sum of HO_2NO_2 and $CH_3O_2NO_2$ in the remote troposphere" *by* J. G. Murphy et al.

Anonymous Referee #2

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General Comments

This manuscript presents new measurements of peroxynitrates, which are used to infer the concentrations of HO2NO2 and CH3O2NO2. These measurements confirm the important role of HO2NO2 and CH3O2NO2 under the cold conditions of the upper troposphere at mid- and polar latitudes. The measurements also provide evidence for infrared photolysis in shortening the lifetime of HO2NO2. The paper present significant new results and is generally well written. The authors combine many different measurements (total peroxynitrates, PAN, PPN, HNO3, NO2, NOy). Despite the large uncertainties and some unexplained problems in the observations, it seems that the results are robust, as they focus on averaging a large number of observations and examining trends with temperature and other variables. The bulk of my comments below address issues with the lack of specificity in parts of the text, which should be easily

addressed by the authors.

Specific Comments

1) Abstract. The abstract remains very vague in its description of the results. More quantitative statements would be valuable: what are the levels of observed Σ PN and inferred Δ PN? To what extent does photochemistry agree with observations (50%? 100%? 200%?)?

2) In the text, as in the abstract, the authors rarely quantify their results. All the numbers are in the Figures, but the text lacks some synthesis of the figures. One suggestion would be to include a table summarizing the observed (and model calculated) partitioning of NOy species for different temperature regimes for TOPSE (for example above and below 240 K).

3) A brief description of TOPSE would be useful to the reader. When and where did the experiments take place? What altitudes/latitude/temperature ranges were sampled?

4) Figure 1a. More information on how the humidity-dependent factor is derived and its impact on later calculations would be useful. What fraction of the data is plotted on Figure 1a? What are the temperature/altitude ranges used for this figure? To the naked eye, it seems that there is no bias for measurements below 60% RH, but that there is a systematic difference at higher RH. Are the points for RH>60% representative of specific conditions or are they present for all altitudes/latitudes/season? Another concern is whether and why the humidity-dependent correction factor applies to conditions where HO2NO2 and CH3O2NO2 are the dominant component of Σ PNs, as these conditions have been excluded from Figure 1.

5) Figure 2. The authors do not explain the systematic 20% difference between NOy and Σ NOyi.

6) Page 5698. ligne 12. The authors claim that ẗhe wide range of concentrations at each temperature derives partly from variations in the abundance of HO2, CH3O2,

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Interactive Comment

and NO2 radicals in the airmass ÷ However, the comparison between model A and observations also shows a very large scatter. The wide variations in HO2 and NO2 are supposedly taken into account the model, but a scatter of 100-200 pptv persists. This scatter is similar to what is shown in Figure 3. This would suggest that uncertainties in the observations (not environmental conditions) are responsible for most of the large scatter on Figure 3.

7) The authors emphasize the disagreement between modeled and observed Δ PN seen at high values on Figure 6. Is this discrepancy statistically significant? What fraction of the observations fall in the category Δ PN>200 pptv. Where most of the disagreement seems to be? In keeping with the rest of the paper, I would suggest that the authors show the full scatter of individual observations Ű not just the binned data.

Technical Comments

1) P. 5693, ligne 10. The authors use the NCAR photolysis-chemiluminescence NO2 measurement instead of their own because of their superior precision at the low levels observed. It would be worthwhile discussing whether the two measurements agree or not.

2) Page 5695, ligne 3. What fraction of the observations do these 1433 measurements represent? Are these 1-minute average data?

3) In Figure 2, are Total NOy (in Σ NOyi/total NOy) and Measured NOy (in Modeled HO2NO2/measured NOy) the same quantities?

4) Figure 3. Should the legend with black spares NO2<11 ppt read NO2>11 ppt?

5) It is unclear whether the observations and model calculations shown on Figure 6 are from the May 22 flight discussed, or all of the data. Please clarify.

Interactive comment on Atmos. Chem. Phys. Discuss., 3, 5689, 2003.