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Atmospheric
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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 #1

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General Comments

This manuscript describes measurements of two peroxynitrate compounds, HO_2NO_2 and $CH_3O_2NO_2$, that are important to nitrogen oxide chemistry in clean regions. The abundance of HO_2NO_2 has largely been inferred from models and indirectly from the abundances of HO_x and NO_x compounds in the past with only one previous measurement. The lack of experimental data shows that observation of these compounds is quite difficult. Although the measurement scheme described in this manuscript appears to be far from perfect, it is a step in the direction of characterizing peroxynitrate chemistry. The approach is to infer the concentrations of the two compounds from the difference in the NO_2 signal in a heated and a non-heated inlet, where the heated inlet induces thermal dissociation of the peroxynitrates. There are several interferences (e.g., PAN and PPN) that must be accounted for in the difference, making the signal of interest a small difference between large signals. As a result, the scheme seems prone to systematic uncertainties and potential interferences. The authors make a convincing case, however, that the technique does measure the compounds of interest, and they do a reasonable job of dealing with uncertainties. Furthermore, if their arguments are correct, the contribution of the peroxynitrates is very important to the NO_y budget in remote regions.

Specific comments

1.Page 4, top. The instrument reference given for the specific configuration of the TD-LIF system during TOPSE (Thornton, 2002) is a PhD thesis, which is rather difficult to access. Consequently, a few extra details of the PN measurements should be given in this manuscript, including the temperature and residence time in the heated inlet required to thermally dissociate PN to NO_2, and the possible interferences that could arise from this method, such as the fraction of any other components of NO_y that would be likely to dissociate at under these conditions to give NO_2. Even if potential interferences are estimated to be small, a short (even one sentence) discussion of their importance here would be useful.

2. Page 5, bottom. The correction of the relative humidity dependence of the instrument response to PN seems rather arbitrary and not well justified. It brings up several questions. First, if there is no reason to suspect an RH dependence, how did the authors arrive at this parameter for correction? Are there any potential interferences that could have an RH dependence? Also, the correction is applied evenly to both the TD LIF NO_2 instrument and the PAN instrument, although the artifact is surely in one or the other since they are based on very different techniques. Does splitting the difference of the suspected error between the two instruments have any consequences for the conclusions reached later on?

3. Page 6 and Figure 2. The figure is not quite as convincing as the discussion would indicate. The ratio of the sum of speciated compounds to NO_y does not appear to be

1.2 at small values of caculated PN. It is almost unity to within the error bar and has a value closer to 1.1 than 1.2. On the right side of the graph where the calculations show 40-50% of NO_y as ΔPN, the ratio of speciated compounds to NO_y is near 80%. Is the NO_y measurement likely to be systematically 20% wrong to account for this difference? Given the arbitrary scaling of the RH response of the system with a 24% average increase in the ΔPN concentration, this conclusion appears a bit suspicious.

4. Page 8. The conclusions regarding the importance of overtone photodissociation of HO_2NO_2 are interesting. Although no near IR photolysis of $CH_3O_2NO_2$ has been inferred because it lacks an OH group, C-H stretch overtones in this compound could give it a similar IR degradation pathway.

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

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