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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Airborne observations of total $RONO_2$: new constraints on the yield and lifetime of isoprene nitrates" *by* A. E. Perring et al.

A. E. Perring et al.

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We thank the reviewer for the constructive comments on our manuscript. We have tried to answer all of the comments and questions and to pay attention to the reviewer request for additional discussion of uncertainties, data selection and the assumptions used in our analysis. Both reviewers discussed our lack of attention to isoprene AN correlations. We have added a section in the manuscript explaining that isoprene and ANs should not be correlated. We address specific comments as outlined below.

Reviewer Comment: 1) 12318, line 26. I do not recall if the LIF instrument has ever been used to measure isoprene nitrates from chamber studies, but it would be good to reference that if so. It also seems to me that some statement about the response of multifunctional nitrates are equivalent if the thermal degradation characteristics are equivalent (this may not be the case).

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Response: While we have not previously reported such measurements, bond energies for multifunctional nitrates are not significantly (in terms of our measurement) different from monofunctional compounds. We have reported field observations of the thermal decomposition of ambient samples expected to have significant isoprene nitrate influence and shown a correspondence between predicted and observed temperature dependence. (Day et al, 2002, Murphy et al, 2006) In addition, two papers are in preparation discussing LIF measurements of isoprene nitrates in smog chambers and comparison to other measurements. In one of the manuscripts we describe sampling pure isoprene nitrates (synthesized by wet chemical methods in the laboratory) in air, where the signals in the non-nitrate channels of the TD-LIF were zero (indicating that the nitrates are not dissociating in the other temperature channels) and the magnitude of the signal matched both the calculated concentration and a PTR-MS measurement to within 10%. (Perring et al, in preparation)

Reviewer Comment: Also, if the RONO2 form into a nitrate aerosol phase upon continued oxidation, as has been measured, is the LIF thermal degradation response the same?

Response: Our TD-LIF measurement of HNO3 has been shown to be the sum of aerosol and gas-phase HNO3 (Fountoukis et al, ACPD, 7, 2007) and we expect organic nitrates in the aerosol to behave similarly. Text will be added to the revised manuscript to address these issues.

Reviewer Comment: 2) Methods section: I would like to better understand the uncertainty of the Total AN measurement. There is a lot of scatter in the data that seems to be about -+100-150 pptv. Can the authors provide some more quantitative estimate of the uncertainty in the determination, and how it may depend on the magnitude of NOy in the other channels? Also, why was it decided to report no ANs from above 4km?

Response: During INTEXA, the 200C (NO2+PNs) and 380C (NO2+PNs+ANs) channel were sampled sequentially. To calculate an ANs concentration, the signal in the 200C

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channel was interpolated across the 20s interval when the 380C channel was sampled. The uncertainty of the ANs measurement is therefore more strongly affected by the variability in NO2 and PNs than are some of our other measurements. ANs were not reported above 4km because above that point the ANs were on order of 10% of the underlying NO2+PNs signal and could not reliably be distinguished from the temporal variation between subsequent measurements of the 200C channel. A discussion of the sampling strategy and the uncertainties of the ANs measurements will be added to the revised manuscript.

Reviewer Comment: 3) Reference for formaldehyde data? There were 2 measurements of formaldehyde on the aircraft. From the data set, it looks like the URI data are about 35% lower than the NCAR data. Which data set was used? Has there been any resolution to the discrepancy?

Response: The discrepancy between the two formaldehyde measurements has not been resolved. In the first draft of this paper we used the NCAR data because there was better coverage in that dataset. (NCAR reported data for 77% and URI for 41% of points below 1km) The correlation between the two measurements is very good, however, so for the revised paper we will average the two measurements where both are available, scale the NCAR data down by 17% where it alone is available and scale the URI data up by 17% where it alone is available. We will add discussion of the additional uncertainty introduced by this discrepancy.

Reviewer Comment: 4) It is unclear to me how the data were selected into the high isoprene profile. (It is also unclear to me why a vertical profile of these data is relevant, at all.) But if it is, then there should be some clarification how the points are selected. Perhaps a comparison that shows the high isoprene set versus non-high isoprene would be better than high isoprene vs all. Does it make a difference that the isoprene data are collected on a different time base than the CH2O and AN?

Response: Isoprene oxidation by OH is expected to result in production of ANs when

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NO is abundant but not to produce ANs when NO is absent. Since isoprene has a short lifetime, isoprene concentrations are not a quantitative marker for emissions. In this analysis we attempted to derive a filter identifying data with high isoprene exposure as a qualitative test to see whether the data does segregate (i.e. if ANs are a more important component of NOy when isoprene influence is high) which supports the conjecture that production of ANs is closely associated with isoprene. In the revised version we will clarify these issues and our methods for data selection.

Reviewer Comment: 5) The bottom line of the manuscript seems to be that isoprene nitrates are the bulk of the total AN in most of the continental BL (perhaps not in urban centers). If this is the case, then why even make the distinction of high isoprene points vs all points? This distinction disappears in al subsequent analysis (the entire BL data set is used for the analysis).

Response: Due to the complications of attributing formaldehyde sources we will be amending the manuscript so that the high isoprene points are more clearly identified. In the revised manuscript we will maintain the distinction between high isoprene and other data in the plots that show all continental boundary layer points by using different symbols for the two subsets.

Reviewer Comment: 6) How does isoprene nitrate formation via NO3 oxidation factor in to this analysis, if at all? The Horowitz 2007 reference suggests that about 50% of isoprene nitrates may come from this route. Shouldnt this be factored in to the data analysis?

Response: Because of the short lifetime (5-10 hours) we expect nighttime formation of nitrates from NO3 + isoprene to impact the daytime concentrations only minimally. We will include added discussion to this effect in the revised paper.

Reviewer Comment: 7) Figure 1 shows the relationship on which the estimates are made. I have to wonder about the scatter in this data and what it means to the analysis. I would like to see some error analysis applied to this correlation. Also, what is the

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relationship of AN to isoprene?

Response: We believe the reviewer is referring to Figure 3 (which shows the ANs-CH2O correlation) rather than Figure 1 (which shows isoprene oxidation products and yields). We analyzed the uncertainty in this figure later in the paper via Figure 7 and associated discussions but we will make this more explicit and place at least part of the discussion earlier in the paper. The relationship of both ANs and formaldehyde to isoprene is complicated by the different lifetimes of the parent (isoprene) and the product molecules (ANs and CH2O). The proposed figure does not have sufficient statistics for us to be satisfied that it is meaningful but we have added discussion to the revised manuscript to discuss the relationship between both ANs and isoprene and CH2O and isoprene. Generally, some of the high ANs and CH2O points also coincide with high isoprene but ANs and CH2O are often both high when isoprene was at the detection limit. We interpret this to imply that we were in an isoprene-impacted region where all of the isoprene had reacted away but the products remained for a more sustained period of time. This interpretation could also explain the discrepancy between modeled and measured CH2O at low isoprene (see Fried et al, 2008).

Reviewer Comment: 8) Figure 4. While I would not disagree with the conclusion that isoprene nitrates are significant, it seems to me that the role of terpenes is underestimated. There is a high yield of nitrates from terpene oxidation, and only 2 terpenes are reported in the INTEX data. Comparisons of canister data with total terpenes (e.g. from PTRMS) suggest that the canister data will underestimate total terpenes (esp if not all terpenes are reported). While it may not be possible to quantify the contribution of terpenes, some mention of the uncertainty in this source seems justified.

Response: We thank the reviewer for noting this omission. We will add a brief discussion of this systematic bias in the revised manuscript.

Reviewer Comment: 9) In the calculation of NMHC reactivity and RONO2 sources, how were the data below detection treated?

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Response: The data below detection were assumed to be 0. We will amend the manuscript to state this more explicitly. We have rerun our calculations assuming concentrations equal to the lower limit of detection (5 ppt for most compounds) and it does not significantly change our conclusions.

Reviewer Comment: 10) The lifetime calculation suggests a total oxidative lifetime of about 32 minutes. As noted this depends on the composition of the isoprene nitrates and the individual rates. However, the reaction rate with ozone was suggested by Giacopelli (2005) to be too high in his model, so the true lifetime would more likely be more like the one hour rate from OH oxidation. Also, calculating the total lifetime by using the individual rates reported by Giacopelli results in slightly different lifetimes compared to the weighted average used by the authors. Not sure why this is, but it doesnt make a big difference.

Response: We have recalculated the OH+IN and O3+IN rate constants based on the percentage yields and hypothetical rate constants and have amended our OH+IN from 6.92*10ˆ-11 to 6.9*10ˆ-11 molecs/cmˆ2/s and our O3+IN from 2.18*10ˆ-16 to 2.17*10ˆ-16. The discrepancy was due to rounding of the percentage yields. We currently estimate an uncertainty of a factor of 2 the for both the O3 and OH rate constants with INs. We will add discussion specifically about the O3+IN rate constant, to indicate more clearly that it is likely too high and to discuss the implications of this.

Reviewer Comment: 11) Table 1. Patchen et al. 2007 (Int. J. Chem Kinetics) also reported yields of isoprene nitrates (but at reduced pressure). [Direct kinetics study of the product-forming channels of the reaction of isoprene-derived hydroperoxy radicals with NO, International Journal of Chemical Kinetics, Volume 39, Issue 6, Date: June 2007, Pages: 353-361]

Response: We will add Patchen et al to our table and thank the reviewer for noting our omission.

Reviewer Comment: 12) Can the authors include an analysis of the relationship of IN

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directly to the precursor, isoprene? I plotted the total AN vs isoprene data and can see something of a relationship between total AN and isoprene, but a large fraction of high AN points at very low levels of isoprene. I could understand the observation of high isoprene and low AN during periods of low photochemical activity, but this doesn’t seem to be the case. If lifetimes of AN are really comparable to the parent, then there shouldnt be cases where AN continue to be high when isoprene is low. If the recycling leads to longer lived products measured by the LIF instrument, then the relationship would make more sense. Or, a contrarian view, these high AN are not isoprene nitrates at all. This is just a first impression, and the authors may have considered this in more detail. Some additional comment or analysis of this relationship would be illuminating.

Response: It is important in this context to keep in mind that the N-containing products of AN oxidation can be either more highly functionalized ANs, NO2 or HNO3. Our best guess of the AN lifetime from the correlation of ANs with CH2O indicates that they are at least an order of magnitude more long-lived than is isoprene itself and we interpret this to mean that many of them maintain their nitrate functionality through at least one additional oxidation. As noted above, we include more detailed discussion of the relationship of ANs and CH2O to isoprene itself and the issues of relative lifetimes.

Reviewer Comment: 13) Figure 7. Solid line should be labeled 12% BR, 90 min LT (as in caption). Also, shouldnt there be some correction to the yields to account for the fact that really all of the nitrates are not from isoprene?

Response: The typo has been corrected and we will add discussion of this issue in the revised text. The magnitude of the effect of additional nitrates on the slope of the correlation is much smaller than the slope difference as calculated from the two different formaldehyde measurements or the differences in expected slopes resulting from the range of published branching ratios.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 12313, 2008.