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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Isoprene nitrates: preparation, separation, identification, yields, and atmospheric chemistry" *by* A. L. Lockwood et al.

Anonymous Referee #2

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Lockwood et al synthesize and characterize the chemistry of several of the isoprene hydroxy nitrates produced in the OH oxidation of isoprene in the presence of NO. This is a very nice study that will be of great interest to atmospheric chemists. The yield and fate of the isoprene nitrates is perhaps one of the largest sources of uncertainty in the gas-phase chemistry of the atmosphere (and the tropics, in particular). The measured reaction rate of ozone with the isoprene nitrates are very fast and will be of substantial importance in the atmosphere. I only wish we knew what the products of these reactions are (in particular how much NOx is recycled)! The manuscript should be published in ACP after the following issues are addressed.

Point 1. Retention and loss of the INs.

More detail is needed on the authors' understanding of the transfer of the INs from the reactor to the GC-ECD. It is noted that: “The GC-ECD inlet, sample loop, and column were conditioned with a large gas phase concentration of the synthesized isoprene nitrates to alleviate adsorptive losses of the INs during experiments.” What model do the authors have for this conditioning? Does an approach to equilibrium mean that irreversible adsorption to the surface and subsequent reaction/decomposition ends? Or is it that an equilibrium is set up with surfaces under the high ‘conditioning’ concentrations (with some decomposition constant), and then is re-established when the Ins are sampled at lower conditions? Also, given the 100C temperature or the sample loop, is any nitrate loss anticipated? If so, does the abundance of nitrate detected depend on the time spent in the sample loop? Was this ever investigated?

Point 2. Why is there such high variability in the measured sensitivity?

The variability in the sensitivities (SIN/SIBN = 1.21 (±0.53,1 sigma) determined under high concentrations (10’s ppbv) is surprisingly large considering the stated detection limit (3 pptv). Do you have any idea why? I believe this uncertainty is not currently propagated through to reported IN yields? If not, why not? I would also like to see a calibration curve to understand how linear the system is.

Point 3. IN yields and uncertainty.

It is stated: “However, given our previous experience of the potential for losses, and given the calibration uncertainty, we report a conservative asymmetric uncertainty for the total yield as 0.070 (+0.025/–0.015).”

I appreciate the challenge here given the difficulty of accounting for known and unknown losses of the hydroxynitrates. Nevertheless, it isn’t clear why this should be considered a “conservative” estimate as it does not appear to have a basis in the data or experiments as reported. Perhaps some experiments such as varying sampling residence time, surface area, were done but not reported? In any case, it would be helpful to better describe the basis for the uncertainly estimate. Perhaps the estimate is just the upperbound of the data illustrated Fig 6 (and would this necessarily include the cal-

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ibration uncertainty)? Is one possible model that the data shown in Figure 6 represent something like a lower limit to the yield and that the variability reflects variable loss?

Point 3: "We note that while we observe that the (1,2)-IN is 31% of the total IN yield, Chen et al. (1998) observed that this peak was 45–65% of the total IN yield. In contrast, Paulot et al. (2009b) assume that the (1,2)-IN is 24% of the total IN yield, a bit smaller than our measured value."

This information could be interpreted as: 1) IN (1,2) = 24% total IN Yield (based on theoretical calculations) is in error. 2) Other IN isomers are differentially lost during sampling (or in the GC), and the measured 31% (and earlier 45-65%) yields reflects these differential losses.

Comment?

Point 4. The dipole moments reported in Table 1 are quite different than those calculated by Paulot et al. Are the differences understood? Are the differences material for understanding the elution times of the nitrates?

Point 5. It isn't clear how is the IN yields were corrected for OH loss (mean of 12%). Was a single number used or were each of the IN treated separately (using Giacopelli rates?). It seems that there are really two classes of reactivity – the 1,4 and 4,1 being very fast and so these will be most influenced by this reactivity.

Point 6. It is really surprising how small the yields of the 1,4 and 4,1 nitrates are. These are the nitrates with the fastest reactivity towards OH. I am concerned that the low yield of these products may reflect differential loss in the sampling or GC.

In summary, very nice and challenging experiment of significant importance. Error analysis needs further development.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 10625, 2010.