Comments/Changes, Reviewer #1

1. The Abstract now refers to the INs as isoprene hydroxy nitrates, and then defines those as "isoprene nitrates".

2. The abstract now says "Three isomers, representing nitrates resulting from OH addition to a terminal carbon, represent 90% of the total IN yield." This avoids our shorthand nomenclature, and yet is sufficiently succinct for an Abstract.

3. We prefer to not provide a figure, as there are so many isomers each with many potential mechanisms. We believe that the revised manuscript makes the point adequately as follows: "For example, a likely product of O_3 oxidation of the (1,2)-IN is $HOCH_2C(CH_3)(ONO_2)COOH$, which would likely have a large deposition velocity." This statement gives a useful example, without adding too much to the length of the paper.

4. The Experimental Section now states that "Isoprene concentrations were determined...", as suggested by the reviewer.

5. Because of the structure of 2-methyl-2-vinyl oxirane, when the oxirane ring opens, the -OH group can end up only on Carbons 1 or 2. Thus, this synthesis can only produce 3 INs, as stated in the second sentence of the Isoprene Nitrate Identification section. We have edited that sentence to make it clearer in the revision. However, we note that, as stated, the (2,1)-IN is indeed produced, and this aided in its identification.

6. We now use the word "unresolved" instead of "unseparated", as suggested by the reviewer.

7. We agree with Reviewer #1 that that sentence was confusing given its location in the manuscript, and it was unnecessary, so we have removed it from the revision.

8. The revised manuscript now states that "The earlier peaks are light contaminants, perfluorocarbons from the bag, and secondary products from oxidation of species such as methyl vinyl ketone and methacrolein." We do not believe that any decomposition of INs in the column would produce any peaks as such. If there were any decomposition, it would be more continuous, increasing as the column temperature increased. However, given the known thermal decomposition kinetics of organic nitrates, there should not be any significant amount of IN decomposition in the column, for the temperatures that applied to the separation.

9. The revised manuscript now states more clearly that "Each of the individual IN concentrations were corrected for IN consumption by OH, as described in Atkinson et al. (1982b), using the k_{OH} values reported in Giacopelli et al. (2005). The average correction factor for all the INs was 1.12 (± 0.10). Given the small correction factor, uncertainties in the calculated rate constants should have a negligible effect on the yield results.

10. The revision now states "These rate constants are very large..."

11. We find that Table 1 is very crowded, and that what is new is the $k(O_3)$ values, while the k(OH) values are already published previously by Giacopelli et al. From those data, those

interested can calculate the "lifetimes", which are of course dependent on the chosen values for [OH] and [O_3]. So, in the revision, we have made the following amendment/addition: "Assuming that [OH] = 1 x 10^6, and using the values for k_{OH} presented in Giacopelli et al. (2005), and assuming [O_3] = 1 x 10^{12} molecules cm^{-3}, the lifetimes for the isomers vary from 45 min. for the (2,1)-IN to two hours for the (1,2)-IN, as shown in Table 1. The lifetimes are mostly impacted by ozonolysis. For example, for the (1,2)-IN, the lifetime against OH loss is 8.1 hrs. (k=$3.4x10^{-11}$ $cm^3molecule^{-1}s^{-1}$), while for the O_3 reaction, it is 2.6 hrs. (k=$1.06x10^{-16}$ $cm^3molecule^{-1}s^{-1}$)."

Comments/Changes, Reviewer #2

1. The "conditioning" for INs is essentially the same as described in detail in Muthuramu et al., 1993. We now cite that paper in the sentence referring to conditioning. We believe that conditioning involves occupying active sites with the INs or similar compounds, at which irreversible adsorption (perhaps chemisorption) takes place. Once those sites are occupied, minimal loss takes place for subsequent injections. That is the observation discussed in the Muthuramu paper. The revised manuscript now states that "We found that blanks following these samples were free of INs, indicating that the uptake of the INs from "conditioning" samples was irreversible." Regarding the potential for decomposition in the loop, the Experimental Section now states "These temperatures are much too low for any thermal degradation of the nitrates."

2. We apologize, the original submission reported that uncertainty in error. The revised manuscript states the correct uncertainty in the relative sensitivities as 1.21(±0.12, 1s). As suggested by the reviewer, and to clarify the quality of the calibration with a pure IN standard, we have provided the calibration curves for IBN and the (1,2)-IN in the revision as Figure 3.

3. We appreciate this question. Given our previous experience in handling these compounds, we are indeed cautious about this uncertainty estimate. The revised manuscript answers and clarifies as follows: "The minimum in the uncertainty estimate derives from the propagated uncertainties, and the maximum represents the approximate upper limit of the data plotted in Figure 7."

4. It is conceivable that in the Chen et al. work there were differential losses of the other INs that made the relative yield for that isomer appear larger. We believe that the current measurements are superior to the Chen et al. measurements in part because we have conditioned the column and injection system with actual IN samples. Our measurement of the (1,2)-IN yield is a more direct measurement, so it is difficult to know how to interpret the difference between our measurement and the number reported in Paulot et al.

5. It is curious why our dipole moments are so different from the Paulot et al values. While we do not expect the absolute values to be accurate, the relative values between isomers should be, and it is that information that we use. While Paulot et al. predict a relatively small dipole moment for the (1,2)-IN, we find it to be the most polar, and we indeed find that it elutes last (among the three that we synthesized) from the polar HPLC column, where that isomer was identified by from the mass spectrum. The only other place we might have used the dipole

moments for identification would be to reverse the assignments for peaks 1 and 3, the two (4,1)-INs. However, in the revision, at the end of Section 3.1 on isomer identification, we now clarify with "The remaining 2 IN peaks, peaks 1 and 3 in Fig. 6, are assigned to the Z- and E-(4,1)-IN isomers, respectively. The two calculated dipole moments are not distinguishable, but the relative yields are consistent with the results from Paulot et al. (2009b) regarding the prevalence of the Z-isomer."

6. See point #9 above in response to Reviewer #1, regarding the corrections for OH loss.

7. We can only comment that we did our best to ensure that the system was well-conditioned. We also did not see evidence for substantially greater variability for the (1,4) and (4,1)-INs (as you might expect for greater differential losses), beyond what one might expect for lower concentration products.

We are grateful for the comments provided by the two reviewers and believe that addressing them has now made for a considerably improved manuscript.