

## ***Interactive comment on “Measurement of isoprene nitrates by GCMS” by Graham P. Mills et al.***

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This paper describes analytical methods for separating and measuring several organic nitrates which can be formed in during the oxidation of isoprene in Earth's atmosphere. Methods are put forward to allow measurement of these species in air, and demonstrated by analyzing products formed from photo-chemical reactions in a synthetic reactor with isoprene, air, NO<sub>x</sub>, and sunlight.

This paper is well-written and very appropriate for publication in the AMT journal after consideration of the comments listed below. This work taken together with the companion work published in Bew, et al, 2016, represents an important step forward for making progress in our understanding of isoprene chemistry in our atmosphere.

General comments:

1) The authors state that there were problems for the isoprene hydroxynitrate trans-

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mission with longer columns (and warmer elution temperatures). Then it is stated the analyses were run on 30m instead of 60m columns, but it is not demonstrated that this completely eliminated the problem of hydroxynitrate decomposition or conversion. It is suggested here that the authors continue reducing their column length until results are reproducible. Additionally, I note that in our experience the 1-OH-2-ONO<sub>2</sub> ISOPN isomer continues to suffer decomposition/isomerization problems in a metal-free low pressure GC-CIMS setup even on a 4-meter 0.53 megabore RTX-1701 column, with head-pressure at ~150 mbar and tail pressure ~40 mbar, under which it elutes at ~60C. Additionally, and not without significant effort, we have not been able to trap the 1,2- externally and then transfer this quantitatively to the column without significant losses. Thus, our preferred method is to trap these compounds directly on the column phase at ~ -15C. Care must be taken not to also condense water, as co-condensation of water and 1,2-ISOPN results in rapid hydrolysis of the 1,2-ISOPN.

2) Order of elution for the hydroxynitrate isomers. In addition to the results published in Lee, et al, 2014, we now have NMR-supported identification of the 1,2-, c-4,1-, and t-4,1- ISOPN isomers. We find the elution order on RTX-1701 column to be 1,2-, 4,3-, c4,1-, (t4,1 and c1,4 together), and finally t1,4. These chromatograms from isoprene oxidation experiments are shown in Nguyen, et al., 2014, and the elution order for the five primary isoprene hydroxyl nitrates identified here is in agreement. In addition, Xiong, et al 2015, using I- CIMS shows a chromatogram from an OH+isoprene experiment, with a similar chromatographic technique. One primary problem that has remained through the years with the analysis of isoprene hydroxyl nitrates appears to be the very high instability of the 1,2-ISOPN. It appears to be thermally unstable, decomposing and isomerizing to t1,4 isomer even at temperatures as low as 60C. Given the structural similarity of the 2,1-ISOPN to the 1,2-ISOPN and the general elution relationship for 1,2 vs 2,1 hydroxynitrates for a series of alkenes (Teng, et al, 2015). I would suggest that the 2,1-ISOPN isomer should elute even before the 1,2-ISOPN. Based on this, I suggest that the late-eluting species reported in this work arises from something other than (or a conversion product of) the 2,1-ISOPN species.

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3) The 1,2-ISOPN has a very fast hydrolysis rate. We've constrained (unpublished) its lifetime to be <5 seconds in D2O using NMR experiments. It is likely it also reacts rapidly in the condensed phase with other species, including itself. While, on a clean Teflon surface minimal H2O is adsorbed, it is possible that on a dirty Teflon surface, other low volatility hydrophilic material could be present, allowing for uptake of water, and thus allowing for a fast hydrolysis rate in a humid bag. I suggest that these experiments be tried with very dry air in a clean bag, using a GC method akin to those described in the references below (short column (2-4m), 8 sccm gas flow, sub-ambient pressure, such that 4,3-ISOPN elutes at <65C, no metal in sampling system or GC-system (PEEK/PTFE/PFA seem okay), trap analytes directly on column at reduced temperatures (-15C)), and see if the same results are achieved.

Specific comments:

Working from print version:

P4 L5: Can the authors describe the energetics of the chemical (NI and PI) ionization schemes?

P5 L24-26: Suggest writing the isoprene and nitrite amounts as a mixing ratio, as this will be more useful to the reader (~20ppmv, each). P7 L19: Define MSD acronym.

P8 L29: Where did the NO2 come from? IN decomposition?

Section 5.1: It seem to me that important inherent assumptions in this method of calibration include: a) decomposition of IN to NO2 in the cold quartz tube (or entire CL system) is small; b) reaction of IN with luminal is small. It would be useful to discuss the validity of these assumptions in more detail. It would be useful to include a figure of a CL experiment in the SI so the reader can get a feel for the time constants inherent with this method. What is the typical 'cold' CL signal compared to the IN signal?

Section 5.2: Is it proper to interpret this procedure as contents of the cube were 'directly' sampled to the MS through a short piece of heated column? It would be natural

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then to compare the sensitivities determined in this manner to sensitivities determined in a similar manner with the Tenax trapping using the same CL reference, as this is needed to show that the transmission of the trapping method is high, and suitable for field samples.

P11 L26, 31: It is stated here that the IN's discussed in this manuscript are stable on Tenax stored at -25C. This statement could use further support.

P12 L25-28: The 1,2-IN could also be lost through hydrolysis in the humid bag.

P13 L13-16: Is it not also possible this peak could be caused by a decomposition product from some other (e.g., 2,1-IN) precursor occurring during the analysis?

P18 L5: Unclear what is meant by signal/noise? It seems to me the natural unit here would be integrated signal (over Gaussian peak) per unit mol fraction for compound X divided by integrated signal (over Gaussian peak) per unit mol fraction?

P22 L3,4: 'Fig 4' should be 'Fig 3'?

Fig 6: These samples were collected trapped on Tenax? Perhaps include this information the caption.

SI:

P7 Caption L1: (3,4)-IN should be (4,3)-IN?

References:

Crounse, J. D., Teng, A., and Wennberg, P. O.: Experimental constraints on the distribution and fate of peroxy radicals formed in reactions of isoprene + OH + O<sub>2</sub>, presented at Atmospheric Chemical Mechanisms: Simple Models – Real World Complexities, University of California, Davis, USA, 10–12 December 2014.

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biogenic compounds, Atmos. Chem. Phys., 14, 13531-13549, doi:10.5194/acp-14-13531-2014, 2014.

Schwantes, et al., J. Phys. Chem. A, 2015, 119 (40), pp 10158–10171.

Teng, A. P., Crounse, J. D., Lee, L., St. Clair, J. M., Cohen, R. C., and Wennberg, P. O.: Hydroxy nitrate production in the OH-initiated oxidation of alkenes, Atmos. Chem. Phys., 15, 4297-4316, doi:10.5194/acp-15-4297-2015, 2015.

Xiong, F., et al : Observation of isoprene hydroxynitrates in the southeastern United States and implications for the fate of NO<sub>x</sub>, Atmos. Chem. Phys., 15, 11257-11272, doi:10.5194/acp-15-11257-2015, 2015.

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