

***Interactive comment on “Peroxyacetyl nitrate (PAN) and peroxyacetic acid (PAA) measurements by iodide chemical ionisation mass spectrometry: first analysis of results in the boreal forest and implications for the measurement of PAN fluxes” by G. J. Phillips et al.***

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This paper describes observations of peroxyacetic acid with the same iodide ion CIMS that is used for acyl peroxy nitrates. This paper could be a very important addition to the literature and presents some results that the atmospheric measurements community will do well to pay attention to and address in future research. The research as presented brings up a number of questions, and the paper contains some errors and

C7605

omissions that need to be dealt with. As you will see below, I think a healthy sense of skepticism is in order here, since there are contravening studies that did not observe a PAA effect, but should have, based on this paper's assessment of how and when there is significant PAA. Assuming the comments and questions are taken care of, this paper should be acceptable for publication. A list of general and specific question and comments follow.

General comments;

The naming convention for PANs used in this paper is not consistent, and is something of a hybrid between the method that seems to be favored by Europeans: acyl peroxy nitrates (e.g. acetyl peroxy nitrate) and the method that names them as anhydrides of two acids: e.g. peroxyacetic nitric anhydride. Either is fine as they both lead to the correct structure, but the term used in the introduction “Acyl peroxy nitric anhydrides” is clearly not correct, and really peroxyacetyl nitrate isn't correct either. I would urge the authors to pick from one of the correct ones. This shouldn't be too big a problem since the acronym PAN can be used for the bulk of the paper. There are a number of studies that compare PANs measurements that were not addressed in this paper, and those studies show no evidence of a significant PAA signal. The first paper in that regard is the original Slusher et al., 2004 [Slusher et al., 2004] who showed intercomparisons with the NCAR GC/ECD instrument, and found no evidence of spurious signals that could be due to PAA. It should be noted that these measurements were not a part of a comprehensive study, so we don't know the corresponding NO<sub>x</sub> levels etc., and were made at the NCAR Mesa Lab, hence had some urban impact. The second is a more comprehensive summary of PANs measurements by Wooldridge et al., that covers a number of field studies in which the PAN TD-CIMS has been used, compared with several different methods, although the paper focuses on the TD-LIF method for total PANs. Again, there is no evidence of a significant PAA effect. A third set of PANs measurements were conducted for the very purpose of comparing the various techniques in use by the community at that time: the PAN Intercomparison Experiment, PIE, con-

C7606

ducted in Boulder CO., in 2005. Some of the data from that appear in Wooldridge et al., [Wooldridge et al., 2010] and the data have been presented in a poster at AGU [Tyn-dall et al., 2005], but unfortunately they have never been written-up in publication form. That experiment was in summer, on a mesa at the edge of the city, and so had a range of conditions in which one would think PAA would be formed. Again, there was no evidence of a PAA signal in the CIMS data. Since I know the authors to be careful and accomplished experimentalists and I believe their observations, this brings up an interesting conundrum; why is this PAA signal present in their instrument at their site, when it has not been apparent in other studies? Could the answer be in the ion chemistry and the particular instrumental conditions used? The ion chemistry that is proposed as the reason PAA is detected as acetate;  $\text{CH}_3\text{C}(\text{O})\text{OOH} + \text{I}^- \Rightarrow \text{CH}_3\text{C}(\text{O})\text{O}^- + \text{HOI}$  (R1) does appear to be exothermic (although I got a slightly different answer than the authors), however the mechanism is a bit more complicated than for  $\text{CH}_3\text{C}(\text{O})\text{OO} + \text{I}^- \Rightarrow \text{CH}_3\text{C}(\text{O})\text{O}^- + \text{IO}$  (R2). Could there be an activation energy to R1 that would make the relative detection of PAA and PA radical dependent on instrumental conditions? Here I'm thinking of the kinetic energy of collisions in the collisional dissociation chamber and their role in providing that activation energy. In that regard, it seems crucial that details about that part of the instrument be provided (see below) in order to assess that effect. Another possible reason for the apparent interference of PPA is if the instrument in this study was operated in a way that caused much larger losses of PA radical between the TD zone and ion flow tube. Again, more details on the operating conditions, but more importantly the resulting signals, e.g. reagent ion counts, net PAN sensitivities, will help in addressing those questions.

Specific Comments;

Abstract – Page 20182, Line 8:  $\text{CH}_3\text{C}(\text{O})\text{O}_2^-$  should be  $\text{CH}_3\text{C}(\text{O})\text{O}^-$  Lines 10 and line 15: there should be some numbers attached to the statements “high temperature and low  $\text{NO}_x$ ” and “the range of mixing ratios of  $\text{NO}_x$ ”. Line 17: It is not clear if the  $\text{HO}_2$  being talked about here is measured or modeled (assumed).

C7607

Introduction – Page 20182, Line 21: The PAN naming system needs to be fixed at this point, and made consistent throughout the paper. Page 20183, Line 22:  $\text{CH}_3\text{C}(\text{O})\text{O}$  is not an alkoxy radical, that would be  $\text{RO}$ , it is more properly termed a carboxyl radical. Page 20184, Line 4: It should read  $k_4$  not  $k_3$ . Page 20184, Line 24-28: It would be nice to have a summary of the levels of PAA that have been observed in other places.

Page 20185 Line 10 or so: This is a good place to mention the intercomparisons of the TD-CIMS with other methods.

Instrumentation – Pages 20186-20189, This is where it would help to have a lot more details on the experiment. What is the diameter of the TD tube, and what is the flow rate into the instrument? What material is the inlet orifice made of? What are the typical reagent ion ( $\text{I}^-$ ) counts produced by the ion source. What are the dimensions of the IMR and is the IMR voltage biased relative to ground? What are the conditions in the CDC, voltages, pressure?

Does the zeroing method also destroy PAA?

The PAN photosource discussion needs more details. This system undoubtedly produces PAA, probably a lot of it since these systems are set up to have an over abundance of radicals, so that  $\text{NO}$  is converted to  $\text{NO}_2$  and the PAN formation reaction is the major fate of  $\text{NO}_2$ . Also, this source has been widely used by a number of groups measuring PANs and so could serve as the first means to check for PAA interferences. It would be very informative to know what the level of signal from the photosource was through the cold inlet, and if there was any data for the photosource running without  $\text{NO}$ .

Page 20187. Line 25-29. It is interesting the instrument gives a signal for acetic acid since the reaction;  $\text{CH}_3\text{C}(\text{O})\text{OH} + \text{I}^- \Rightarrow \text{CH}_3\text{C}(\text{O})\text{O}^- + \text{HI}$  is endothermic by about 34 kcal/mole. So only a tiny fraction of the cluster  $\text{CH}_3\text{C}(\text{O})\text{OHI}^-$  should break part to make acetate if everything is at room temperature. Could this be a clue as to why this system seems more sensitive to PAA than others? What is the sensitivity to acetate?

C7608

Page 20188. Line 1. Should be 'the raw data were.'

Page 20188. Line 27. Do the authors mean CH<sub>3</sub>C(O)OO<sup>-</sup> or CH<sub>3</sub>C(O)O<sup>-</sup> here? Is CH<sub>3</sub>C(O)OO<sup>-</sup> ever observed in the system. The reaction of PAA with I<sup>-</sup> will be even more endothermic than for acetic acid, based on aqueous-phase pK<sub>a</sub>s.

Page 20188-20189. Here we need to know what the reagent ion counts were in order to put the PAA sensitivity into perspective. If PA radical is lost through the inlet doesn't this mean the k<sub>6</sub>/k<sub>7</sub> is larger than 2.5? Isn't this loss one area that may explain why other studies have not seen an effect that could be due to PAA?

Page 20189, Line 6. One thing to keep in mind when dealing with m/z 85 (MPAN) is that CF<sub>3</sub>O<sup>-</sup> appears at the same mass and probably comes from CF<sub>3</sub>OH, which seems to be present in many samples of PFA tubing. It shouldn't proton-transfer with I<sup>-</sup>, but will with acetate.

Page 20189, Lines 15-25. The effect of acetate is due to proton transfer reactions with the corresponding carboxylic acid as discussed by Veres et al., [Veres et al., 2008], and will depend on the levels of acetate, relative to those of iodide. It would be good to have a sense of what those levels were, so we could compare to observations in other CIMS systems.

Page 20190, Line 5. Should be 'hydroxyphenyl'.

Page 20190, Line 18. It would be good to put these PAA measurements in context. Are they higher than other sites?

Page 20192-20193. Steady state model. This is a useful way to look at the chemistry, and the authors note the limitations of assuming, for example one number for HO<sub>2</sub> (30 pptv – which seems high to me). It would be good to note that the time to reach steady state for this system can be fairly long, and will be temperature dependent due to reaction 2.

Page 20192, Line 3. Don't you mean the production terms in reactions 1 and 4?

C7609

Page 20192, Line 15. The IUPAC page has a fairly certain number for this branching ratio (0.41±0.2) so I'm not sure why this statement is here, perhaps they are referring to the temperature dependence? Also, the authors should tell us what number they used for their calculation – it seems like it was 0.4 for the case I checked. Also, we need to know the OH that was used in the calculation.

Page 20193, Line 12. Wasn't HO<sub>2</sub> measured at the site?

Page 20193, Line 24. What is EC? It needs to be defined at first use.

Page 20195, Line 15. The discussion of the results presented by Min et al., of the PANs and total peroxy nitrates fluxes should note that the above-canopy comparison of the two methods was excellent, implying little or no sensitivity to peroxyacids in the CIMS. These data were not included in the Wooldridge paper. Also, it is not clear from the text which method showed larger fluxes, from context (and reading Min et al.) it was the CIMS measurement, but this should be phrased more clearly here.

#### References

Slusher, D. L., L. G. Huey, D. J. Tanner, F. M. Flocke, and J. M. Roberts (2004), A thermal dissociation-chemical ionization mass spectrometry (TD-CIMS) technique for the simultaneous measurement of peroxyacyl nitrates and dinitrogen pentoxide, *J. Geophys. Res.*, 109(D19), D19315, doi:10.1029/2004JD004670.

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C7610

acids in the atmosphere, *Int. J. Mass Spectrom.*, 274, 48-55.

Wooldridge, P. J., et al. (2010), Total peroxy nitrates ( $\Sigma$ PN) in the atmosphere: The thermal dissociation-laser induced fluorescence (TD-LIF) technique and comparisons to speciated PAN measurements, *Atmos. Meas. Tech.*, 3, 593-607.

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C7611