

Interactive comment on “Efficient photochemical generation of peroxycarboxylic nitric anhydrides with ultraviolet light emitting diodes” by N. D. Rider et al.

Anonymous Referee #1

Received and published: 5 February 2015

The authors describe the use of UV-LEDs instead of a low-pressure Hg Lamp with Phosphor coating for generation of PAN and similar compounds. There are some slight advantages to be gained by using LEDs (e.g. less impurities are generated), though, in the end the yield of PAN is, within errors, indistinguishable from that obtained by using a Hg-lamp, which is the considerably cheaper solution.

The main deficit of this manuscript is a complete lack of chemical equations describing what the authors are actually doing. This is compounded by the excessive use of acronyms instead of chemical formula or names. The listing on 18 pages of SI-text of the MCM output does not help in the least. Indeed, use of the MCM in this study

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is overkill. The authors need to understand what reactions are important and which (of the hundreds listed) are not. A large, chemically complex (but still not complete) scheme does not provide any insight whatsoever into what is going on in their reactor. Considering that the MCM does not treat two of the ketones used as precursors properly, uses estimated (not measured) photolysis rates and cannot deal with e.g. wall losses of radicals in a small quartz reactor makes it incomprehensible to me why one would want to use it for this particular task. I do not regard its use here as validating the conclusions presented apart from in a purely qualitative manner. A reaction scheme presenting a selection of the most important reactions needs to be incorporated into the manuscript.

Specific comments below:

P908 L6: “In addition, some users have noted that the 285nm light output of phosphor-coated Hg lamps can change over time (either through scratches or ageing of the phosphor coating) and that the source performance, i.e., the NO to PAN conversion efficiency, then degrades unbeknownst to the operator (J. M. Roberts, personal communication, 2014).”

This is non-quantitative and the reference (a personal communication) not helpful. Who are “some users” ? Can change over what period of time ? Can change by how much ? How can an internal phosphor coating be scratched ?

P908 L16 desired not desirable

P910 L 14. Residence times of up to 44 mins. Put this in context: What is the thermal lifetime of PAN at the reactor temperature ?

P910 L16 “to ensure that the reactions go to completion” What reactions are implicated here (all of those listed in the MCM output ?). What is the residence time in the tubing compared to the quartz reactor ?

P911 L26. The substantial offsets in the CRDS signals need to be discussed here.

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I suggest moving the text of section 4.3 to this place and identifying the di-ketones responsible here. The authors should also estimate what percentage of the ketones used are in the form of (other) di-ketones. Were the d-ketones and their photolysis also simulated in the MCM ?

P914 L25 A small fraction of NO was oxidised in the dark to NO₂. This is actually about 14 % (i.e. not small). The authors suggest it is likely to be due to reaction of NO with O₂. The rate constants are known. Do the calculation and confirm or disprove your own hypothesis.

P915 L 9. The response of the signals is very slow, which results from the slow flow rates through the reactor and its large volume. Some PAN reactors have volumes of 50mL rather than 500mL. Why is this one so large ? Is this a consequence of having to place large arrays of LED around the reactor rather than inserting the thin pen ray lamp ?

P915 L 26 "slightly larger". Be quantitative.

P917 L 1. Here, OH is mentioned. However, as we have seen no chemical equations in the entire manuscript, we do not know where OH comes from. Again, a reaction scheme presenting a selection of the most important reactions needs to be incorporated into the manuscript.

P930 2nd-last word in the caption of Figure 3. Perhaps "systematically" is better than "deliberately".

Interactive comment on Atmos. Meas. Tech. Discuss., 8, 905, 2015.