

AMTD 8, 905-934, 2015 " Efficient photochemical generation of peroxyacetic nitric anhydrides with ultraviolet light emitting diodes" - Author final response

We thank both reviewers for their constructive comments, which are given below in *italic* font. Our responses are in regular font. Changes to the manuscript text are shown in red underlined font. Line numbers refer to the revised word document with tracked changes visible.

### **Anonymous Referee #1**

*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.*

...

*A reaction scheme presenting a selection of the most important reactions needs to be incorporated into the manuscript.*

The reaction scheme that the reviewer is asking for has appeared in numerous publications in the literature (e.g., Meyrahn et al., 1987;Warneck and Zerbach, 1992; Volz-Thomas et al., 2002; Flocke et al., 2005; Furgeson et al., 2011) and we had judged this chemistry to be common knowledge in the atmospheric chemistry and physics community, but were perhaps mistaken. We agree with the reviewer that stating the important reactions would improve the clarity of the manuscript and have added the main reaction sequence to the introduction:

"Most commonly, the PAN species most abundant in the atmosphere, peroxyacetic nitric anhydride (PAN), is produced from irradiation of acetone in its  $n \rightarrow \pi^*$  band in the presence of a calibrated amount of NO in excess  $O_2$  (Meyrahn et al., 1987;Warneck and Zerbach, 1992) by the following reaction sequence (for acetone,  $R = CH_3$ ):



Additional reactions were added in response to questions further below.

*This is compounded by the excessive use of acronyms instead of chemical formula or names.*

The majority of the acronyms in this manuscript (PAN, PPN, PiBN, PnBN, TD-CIMS, TD-CRDS, SPN, CL, NOy, MCM, UV-LED, sccm, slpm, MFC) are commonly used by experts in the field and have all been defined when first used. The only unusual acronyms are the names of the ketones: diethyl, diisopropyl, di-n-propyl ketone, and ethyl isopropyl ketone which were abbreviated as DIEK, DIPK, DNPk, and EIPK. We chose to abbreviate these as we often refer to them in the text. As the reviewer's concern is purely an editorial one, and

we don't feel that the above list is an excessive use of acronyms, we have not amended the manuscript in response to the reviewer's remark.

*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 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.*

The main reason for using the MCM was stated in the discussion in section 4.2: Our experimental results contradict published results by Volz-Thomas et al. (2002), who had stated that diethyl ketone photolysis produces ethyl nitrate in high yield (~50%) and would not be a suitable precursor for PPN. The point of the MCM simulation was to investigate if ethyl nitrate could be formed in such high yield. To make this point more clearly, a phrase was inserted on line 192:

"A box model was constructed from a subset of the MCM V3.2 obtained from <http://mcm.leeds.ac.uk/MCM> and run using the Atchem on-line tool V1.5 (Jenkin et al., 1997;Saunders et al., 2003;Jenkin et al., 2012) to simulate the production of PAN, PPN, and PiBN and side products, such as ethyl nitrate when DIEK is used (Volz-Thomas et al., 2002), in the photochemical source."

Our experimental AND modeling results are in agreement that ethyl nitrate is NOT produced in high yield. We hence disagree with the blanket statement that "*A large, chemically complex (but still not complete) scheme does not provide any insight whatsoever*" as we use this comprehensive mechanism to disprove published work.

We do not agree with the reviewer that the use of the MCM is "overkill" as only a subset of pertinent reactions was in fact used (which were given in the supplemental). We agree with the reviewer that the box model simulation and the MCM are not perfect and that a mechanism smaller than the subset of the MCM used here could, perhaps, have been used to achieve the same (or similar) results and conclusions. However, if we had used a smaller mechanism, reactions might have been omitted that increase the rates of formation of side products (for example, the many radical reactions in the MCM, which individually unlikely amount to much, but on aggregate have the potential for significant secondary radical chemistry). As the computational expense to run models nowadays is a minor consideration, the desire to truncate the model (and potentially compromise accuracy) is unwarranted.

The reviewer states, correctly, that wall losses were not included in the model simulation. These could have been incorporated as pseudo-first order losses. However, since the species most affected by radical losses are reactive radicals such as OH and the acids HONO and HNO<sub>3</sub>, and not the desired peroxyacyl radicals, which are remarkably resilient in this regard, the inclusion of wall losses would have led to a purer source output. We have added a sentence on line 208:

"Heterogeneous reactions and wall losses of reactive radical species (i.e., OH) and acids (i.e., HONO and HNO<sub>3</sub>) were not accounted for in this mechanism."

The reviewer states that *the MCM does not treat two of the ketones used as precursors properly*. We have stated how the MCM was modified in the text (and included the revised mechanism as a listing in the appendix) such that the simulation treats ketone photolysis exactly as the MCM does. In light of the reviewer's

comments questioning the photolysis process, though, we did perform another literature search and were reminded of a minor channel during ketone photolysis (which is not included in the MCM), namely the generation of OH during the reaction of alkionyl radicals with molecular oxygen O<sub>2</sub>. We have added the following sentences on line 220:

"The MCM does not include a side channel of the reaction of alkionyl radicals (RC(O)) with molecular oxygen which generates OH and is a minor pathway at atmospheric pressure and 293 K (Blitz et al., 2002;Romero et al., 2005). An additional set of model simulations was performed that included this side channel (with OH yields of ~3.5% for CH<sub>3</sub>C(O) + O<sub>2</sub> and ~5.3% for C<sub>2</sub>H<sub>5</sub>C(O) + O<sub>2</sub> and i-C<sub>3</sub>H<sub>7</sub>C(O) + O<sub>2</sub>, respectively) and was compared to the simulations described above."

The results of these simulations have been added to Table 1. A sentence was added on line 351:

"When the OH production rate is increased by including OH production from RC(O) + O<sub>2</sub> (Table 1, columns labeled with MCM\*), the yields of the desired PAN products are marginally lowered, and the yield of alkyl nitrates decreases as well."

The reviewer also states that the photolysis rates were *only estimated*. In fact, photolysis frequencies were calculated using the known cross-sections and quantum yields of acetone and hydroxyacetone, which was chosen because the MCM uses the photolysis frequency of hydroxyacetone for DIEK photolysis. These frequencies were multiplied by ketone concentrations, which were estimated based on relative vapor pressures and FTIR observations [Furgeson et al., 2011]. Indeed, the radical production rate from ketone photolysis is hence somewhat uncertain, but we don't believe that this has a significant impact on the result as the radicals are in excess relative to the NO added.

*Specific comments below:*

*P908 L6: "In addition, some users have noted that the 285nm light output of phosphorcoated 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?*

We agree with the reviewer's concerns and have removed the sentence from the manuscript.

*P908 L16 desired not desirable*

We thank the reviewer for catching this grammatical error and have corrected the manuscript as suggested.

*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?*

At 293 K, the thermal lifetime of PANs is greater than 1 hr (e.g., Kabir et al., 2014). As such, dissociation of PAN is not important because the back reaction is very fast, considering that PA radicals are in excess and are being produced continuously in the reactor. We have hence not altered the text in response to the reviewer's comment.

*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?*

The internal volume of this tubing was ~ 50 sccm, so that the residence time in this tubing was between 1 and 5 min. As stated above, there is an excess of peroxyradical species generated in the source. The function of the extra tubing is to allow this radical pool to deplete, and it is short enough so that thermal decomposition (see earlier question) is not an issue. We have modified the sentence in question as follows:

"The gas mixture exiting the reaction chamber was passed through a 1 m long section of coiled 0.25" o.d. Teflon tube to ensure that the ~~reactions go to completion~~ source output contains a minimal amount of free radicals."

*P911 L26. The substantial offsets in the CRDS signals need to be discussed here. I suggest moving the text of section 4.3 to this place and identifying the di-ketones responsible here.*

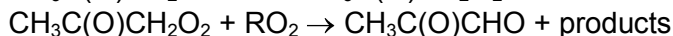
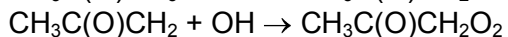
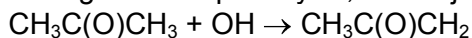
It is good practice to keep facts (experimental/results) separate from interpretation (discussion) to the greatest extent possible and have therefore not altered the sequence of the manuscript as suggested by the reviewer. We did insert a phrase on line 185

"This offset was larger than had been observed in the earlier experiments by Furgeson et al. (2011) and could be lowered to ~0.2 ppbv by cooling the trap in an ice-water bath and partially bypassing the oxygen flow, indicating that the offset was due to an impurity in the reagent."

*The authors should also estimate what percentage of the ketones used are in the form of (other) di-ketones. Were the di-ketones and their photolysis also simulated in the MCM?*

We thank the reviewer for this suggestion. The MCM subset of course included all major known products, including the dicarbonyls glyoxal (glyox in MCM code), methylglyoxal (mglyox), HCOCO<sub>2</sub>H, 2,3-pentadione (COC23C5 in MCM code) and their degradation pathways.

During acetone photolysis, the major  $\alpha,\beta$ -dicarbonyl product is methyl glyoxal, produced mainly by the pathway



During diethyl ketone photolysis, the major  $\alpha,\beta$ -dicarbonyl product produced is 2,3-pentadione produced by a similar pathway as above.

We have added a Table (Table 3) listing the major dicarbonyls produced in each scenario and have added the following text on line 363:

"The box model simulations also yield  $\alpha,\beta$ -dicarbonyls, which interfere with the quantification of  $\text{NO}_2$  by optical absorption in the TD-CRDS (Table 3). Acetone and diethyl ketone photolysis produce 244 pptv of methylglyoxal and 36 pptv of 2,3-pentadione, respectively, which increases to 440 pptv and 192 pptv, respectively, after the OH generation from alkonyl radical plus molecular oxygen is included. The  $\alpha,\beta$ -dicarbonyls are produced by abstraction of a hydrogen atom on the carbon adjacent to the carbonyl, for example, for DIEK:



This radical converts to the peroxyradical by adding molecular oxygen (reaction 3), which in turn reacts with NO to generate the alkoxy radical (reaction 5). Subsequent H-abstraction produces the dicarbonyl:



Negligible amounts of  $\alpha,\beta$ -dicarbonyls are produced from DIPK photolysis, likely because reaction 9 is sterically hindered."

and have expanded the discussion (now: section 4.2) as indicated below:

"The use of the photochemical sources gives rise to offsets in the CRDS absorption signals (Furgeson et al., 2011) which need to be taken into account when reducing the data. The species causing this offset mostly originate outside of the photochemical source, as the offset is there before the lights are turned on. Simple ketones do not significantly absorb at 405 nm (Martinez et al., 1992), but  $\alpha,\beta$ -dicarbonyls do (Fuchs et al., 2009). We speculate that the interfering species are dialkyl diketones, generated mainly from dimerization of acyl radicals which are produced during ketone photolysis, and that these species are generated slowly in the reagent solutions. We were able to reduce, but not completely eliminate, these offsets by lowering the concentrations of the ketone and the impurities emitted with the aid of an ice bath. The MCM model simulations show that acetone and diethyl ketone photolysis produce several 100 pptv of methyl glyoxal (when acetone is used) and 2,3-pentadione (with DIEK), respectively. The 405 nm absorption cross-sections of  $\alpha,\beta$ -dicarbonyls produced in the MCM simulations are each approximately an order of magnitude less than that of  $\text{NO}_2$  (Szabo et al., 2011; Horowitz et al., 2001; Staffelbach et al., 1995). The observed offsets (Table 3, last row) are consistent with what was observed for acetone, but higher than predicted for DIEK and DIPK, for reasons that are unclear. The higher offsets suggest that either more than simulated OH was produced and/or that the yields of dicarbonyls in the MCM are underestimated. Fortunately, since  $\Sigma\text{PN}$  and NO were both determined by difference and the offset appeared to affect all CRDS channels equally, these offsets were of no further consequence in this work."

*P914 L25 A small fraction of NO was oxidised in the dark to  $\text{NO}_2$ . This is actually about 14 % (i.e. not small). The authors suggest it is likely to be due to reaction of NO with  $\text{O}_2$ . The rate constants are known. Do the calculation and confirm or disprove your own hypothesis.*

The rate constants are known, but the extent of contamination with oxygen is not. One can expect that the reaction  $\text{NO} + \text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$ , which is one of the few 3<sup>rd</sup> order gas-phase reactions known, will have consumed most of the molecular oxygen that has leaked into the system. The amount of  $\text{NO}_2$  will reflect the amount of oxygen contamination, which is not known.

No changes were made to the manuscript in response to the reviewer's comment.

*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?*

The 500 mL size was the size of the quartz reactor we had on hand. We chose to not optimize this volume as the construction of several quartz chambers would have been expensive and in our opinion was not necessary as the main point of the paper (that UV-LEDs can be used to generate PANs in high purity) could be made with the existing design. We discuss on lines 485-492 that the chamber geometry can be altered to suit one's needs.

No changes were made to the manuscript in response to the reviewer's comment.

*P915 L 26 "slightly larger". Be quantitative.*

We have reworded to entire paragraph in question (see the response to a related comment by reviewer #2) and the phrase has been removed.

*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.*

The model produces O<sub>3</sub> (by NO<sub>2</sub> photolysis and subsequent reaction of atomic oxygen with molecular oxygen) which in turn photodissociates to O(<sup>1</sup>D) which reacts with water to make a OH. There are also indirect pathways via HO<sub>2</sub>, generated, for example, by photolysis of HCHO (which is a by-product of acetone photodecomposition). HO<sub>2</sub> is cycled to OH by either reaction with NO or by other channels, for example, reaction between peroxyacyl and hydroperoxy radicals.

We have also added the pathway that generates OH from alkionyl radical plus molecular oxygen to the mechanism as stated above.

In response to the reviewer's comment, we have expanded the section in question as follows:

"Stable side products include the expected alkyl nitrates CH<sub>3</sub>ONO<sub>2</sub>, C<sub>2</sub>H<sub>5</sub>ONO<sub>2</sub> and i-C<sub>3</sub>H<sub>7</sub>ONO<sub>2</sub> in 0.32%, 0.23%, and 1.14% yield, respectively. Alkyl nitrates are produced in the minor channel of the reaction between alkylperoxy radicals (RO<sub>2</sub>) with NO:



The time series indicates that this reaction occurs mainly in the initial phase before the NO has been oxidized (Figure 6). The branching ratio of reaction 5b relative to 5a+5b increases with the number of carbons in the organic fragment R (Lightfoot et al., 1992;Perring et al., 2013); consequently, the yield of isopropyl nitrate (1.1%) is greater than that of ethyl (0.2%) and methyl nitrate (0.3% - see Table 1). The latter is likely an upper limit because the relatively high yield by Williams et al. (2014) was used in the simulation."

and have also added the major reactions to the subsequent sections:

"With DIEK and DIPK, C<sub>2</sub>H<sub>5</sub>C(O)CH<sub>2</sub>CH<sub>2</sub>ONO<sub>2</sub> and C<sub>3</sub>H<sub>7</sub>C(O)CH(CH<sub>3</sub>)CH<sub>2</sub>ONO<sub>2</sub> are formed from reaction of DIEK or DIPK with OH (and subsequent reaction with NO<sub>2</sub>) in 0.52% and 0.66% yield, respectively. The latter alkyl nitrates are not expected to elute on the time scale of the chromatograms shown in Figure 2. The reaction sequence for this chemistry (shown for DIEK below) starts with abstraction of the terminal hydrogen of the ketone by OH followed by (rapid) production of the peroxy radical, which produces the alkyl nitrate via reaction (5b).



"The OH radical comes from multiple sources, including photolysis of O<sub>3</sub> (produced from NO<sub>2</sub> photolysis and subsequent combination of the atomic with molecular oxygen) to O<sup>1</sup>D and subsequent reaction with H<sub>2</sub>O as well radical cycling with HO<sub>2</sub>, produced, for example, from the reaction of alkoxy radicals (generated in reaction 5a) with molecular oxygen."

"In the case of DIEK and DIPK, the model predicts formation of hydroxyl group bearing PANs (yield 2.74% and 2.23% relatively to NO<sub>γ</sub>). These would likely elute well after PPN and PIBN and hence not interfere with the PAN-GC, but would systematically bias ΣPN high. They are produced from the peroxy radical produced in reaction 7, which can convert to the alcohol in a minor channel when reacting with RO<sub>2</sub>:



The alcohol is subject to photolysis and produces the hydroxygroup bearing PAN via reactions 1-2 and 6."

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

We have changed the caption as suggested by the reviewer and inserted a statement describing how the NO was varied:

"(B) Time series in which the amount of NO added was ~~deliberately~~systematically varied as indicated by the black trace."

## Anonymous Referee #2

*This work presents an updated method for the production of acetyl peroxyxynitrate species including PAN, PPN, PiBN, and PnBN. The novelty of this work lies in the authors use of UV-LEDs as the light source in place of the standard Hg lamps used in the photo-production via ketones. As a member of the field I fully appreciate the advantages of UV-LED over HG lamps in terms of lower power consumption and heat loadings. However, the paper fails to fully convince the reader with significant hard evidence of the other benefits of this method the authors claim. Particularly, the section in which GC chromatograms are compared to show (1) UV-LEDs are more efficient at forming APNs and (2) less side products are formed using UV-LED methods. In both cases only a single comparison is given with no statistical analysis showing that the small differences observed are significant and repeatable. As this is the heart of the paper, more focus in terms of actual laboratory evidence should be placed on the comparison of the two methods.*

We agree with the reviewer that the experimental results in this manuscript show essentially the same performance of the Hg lamp and UV-LED setups. This is in part because a lot of effort has gone into optimizing the Hg lamp source described by Furgeson et al. [2011] and the comparison was performed under conditions at which the Hg lamp source was performing optimally, that is, in above 90% yield. In other words, there is a narrow margin for improvement, and it has been difficult to demonstrate an improvement over a well-performing method. We also had a closer look at repetitive runs and concluded that the data show an equal (statistically indistinguishable) performance of both sources under these conditions.

In light of this, we have changed part of the narrative of the paper.

in the last sentence of the abstract:

"The ~~use of present work demonstrates that~~ UV-LED arrays ~~are a viable alternative to current Hg lamp setups~~ offers many advantages over conventional Hg lamp setups, including greater light output over a narrower wavelength range, lower power consumption, and minimal generation of heat."

in section 3.3:

"The performance of the UV-LED photochemical source was ~~directly~~ compared to the photochemical source containing a phosphor-coated Hg lamp described by Furgeson et al. (2011). A comparison of PPN and PiBN production is shown in Fig. 4. Both sources convert approximately the same amount of NO to PPN or PiBN, with ~~a slightly higher yield when the UV-LED setup was used, especially after the Hg setup was operated for some time and had warmed up. For both compounds, there were slightly larger impurity peaks when the Hg lamp source was used. no statistically significant difference in yield and impurity peak areas.~~"

and in section 4.1 (which was moved to the end of the discussion as section 4.3 as requested by the reviewer further below).

"4.1-3 Utility of UV-LEDs: ~~Comparison with vs.~~ Hg lamps

The ~~present work shows that the~~ UV-LED photochemical source is ~~a viable alternative to the commonly used an improvement over its~~ Hg lamp predecessor in several regards ~~setup. Perhaps most importantly, it~~ While the performance of the new UV-LED and the (previously optimized) Hg setups demonstrated in this manuscript were equal (Fig. 4), we found it easier to generate greater concentrations while maintaining a higher purity ~~and cleaner~~ output than ~~we were able to achieve our experiences have been~~ with the Hg setup (Fig. 4). There are multiple reasons for this, including a greater light output over a narrower wavelength range and minimal generation of heat."



*The paper in general is well written, and presents a very thorough discussion of the theoretical yields from these reactions, a very nice supplementary discussion to the laboratory work. I would recommend this for publication following minor additions and changes to the manuscript as described below.*

We thank the reviewer for these kind comments.

*Specific Comments:*

*P907, line 10: This sentence [Photochemical sources that generate PANs in situ are an attractive alternative as they remove the need to transport, store, and dispose of toxic chemicals and more readily provide a stable output.] is not entirely true as some of the chemicals that you are using would be considered hazardous waste. Relative to synthesizing PAN using wet chemical techniques the synthesis methods described in this work are safer, but not entirely without hazard.*

The chemicals that are used in the photochemical sources (NO in N<sub>2</sub>, and ketones in oxygen or air) are sufficiently dilute that they do not require special hazmat labeling during transport (other than the compressed gas label). A more important issue is the output of the photochemical sources, as chemicals that are considered quite unhealthy such as aldehydes, including formaldehyde, are co-emitted with the PANs, which of course pose their own sets of hazards. We have modified the sentence in question as follows:

"Photochemical sources that generate PANs in situ are an attractive alternative as they remove the need to transport, store, and dispose of liquid toxic chemicals and more readily provide a stable output."

*P907, line 26: Why make such a statement here [Recently, Furgeson et al. demonstrated that PPN and peroxyisobutyric nitric anhydride (PiBN) can be generated from either NO or NO<sub>2</sub> and diethyl ketone (DIEK) and diisopropyl ketone (DIPK), respectively, with yields in the 70–90% range (Furgeson et al., 2011) but they did not assess this new pathway by the most commonly used PAN measurement technique, PAN-GC.] , this sounds like a critique of this previous work. Unless there is a reason for mentioning this lack of GC work you should remove this statement, or choose to elaborate as to why this matters.*

We agree with the reviewer that this point needs more explaining. It was suggested by one of the reviewers of the Furgeson et al. [2011] paper that PPN generation from DIEK wouldn't be useful for the majority of the community who are primarily relying on PAN-GC to quantify PANs because of what had been reported by Volz-Thomas et al. [2002]. We have reworded this paragraph as follows:

"Recently, Furgeson et al. demonstrated that PPN and peroxyisobutyric nitric anhydride (PiBN) can be generated from either NO or NO<sub>2</sub> and diethyl ketone (DIEK) and diisopropyl ketone (DIPK), respectively, with yields in the 70% - 90% range (Furgeson et al., 2011). However, it has remained unclear if this method is suitable for calibration of the most commonly used PAN measurement technique, PAN-GC, in part because Volz-Thomas et al. (2002) had concluded it was not, but also because Furgeson et al. (2011) did not have access to a PAN-GC to show otherwise."

*P909, line 18: There is no Figure S1 in the supplement, Figure A1?*

This has been corrected.

*P910: There are a lot of details on the manufacturer of components and it makes this section extremely choppy and difficult to read. Many of these details are unnecessary (e.g. MFC types, data acquisition boards) as any given company or model could be used in place. I suggest only putting in details for products that are essential to this particular set up, such as the LEDs.*

We have removed some of this information as requested by the reviewer.

*P911, line 15: Peroxycarboxylic nitric anhydrides? Of do you actually mean “nitric anhydrates nitrates”*

We are following the naming convention introduced by Roberts [1990], who, on page 245 of his review has written a monograph arguing for this convention. We have therefore not altered the manuscript in response to the reviewer's comment.

*P911, line 21: Perhaps add the Wild et al. 2014 ES&T citation that is about this exact type of cavity ringdown instrument using O3 addition.*

Since our group has developed the  $\Sigma$ PAN TD-CRDS measurement technique [Paul and Osthoff, Anal Chem 82, 6695, 2010; Paul, Furgeson and Osthoff, Rev. Sci. Instrum. 80, 114101, 2009] and the Wild et al. 2014 ES&T paper describes a much later developed, non-specific NO<sub>y</sub> measurement, we prefer to cite our own work and have not altered the manuscript in response to the reviewer's comment.

*P911, line 23: e.g. means “for example” thus you should delete “because of”*

We have changed the order of the words here as there are several reasons why the response differs between CRDS channels.

*P912, line 1: What is this effect due to? Direct interference by DIPK or DNPk? I realize you attempt to answer this in the discussions section but I think this belongs here instead*

It's mainly interference from other  $\alpha,\beta$ -dicarbonyls (see our response to reviewer 1). Even though reviewer 1 has suggested a similar restructuring, we have decided to leave the structure as is because the interpretation of this effect makes use of the modeling results, and we prefer to have the interpretation (discussion) separate from facts (experimental /results).

*P913, line 17-22: Is this discussion [DIEK, DIPK, and DNPk eluted as negative peaks at 95, 190, and 426 s, respectively. In addition, the chromatogram of DIEK contained two impurity peaks at 90 and 102 s, that of DIPK an impurity eluting at 84 s, and that of DNPk a second negative peak at 302 s. These peaks were more pronounced when the bypass of the glass trap was closed and a larger ketone concentration was delivered (data not shown).] necessary? If you are going to describe this then you should comment on the impurities.*

In this section, the appearance of the chromatograms is described. We are unable to identify all of these peaks, but comment on most of the impurity peaks in the discussion (section 4.2). We have therefore decided to leave the experimental section as is and not to expand the discussion as it would be too speculative.

*P914, line 6: How do you know the remainder is NO<sub>2</sub>?*

NO<sub>2</sub> is the dominant absorber at 405 nm, with an absorption cross-section of  $6.1 \times 10^{19}$  molecules cm<sup>-2</sup> [Paul and Osthoff, 2010] that is an order of magnitude larger than those of the  $\alpha,\beta$ -dicarbonyls generated in the photosource. In response to a comment by reviewer 1, we have added a table with the concentrations (and interferences) predicted by the box model and expanded the discussion in section 4.3 as indicated above.

*P915, line 23-26: The difference for PPN in 4a is very small. Is this difference significant or is this an ideal result that shows the difference? How reproducible is this? This is a weak point in the work. Convince the reader this difference is reproducible and significant.*

Please see our response above.

*P916, line 5: "varied to vary", this is awkward*

We have changed the wording to "varied to change".

*P917, line 18: Respectively to what?*

We are not sure what the reviewer is referring to - the sentence on p 917 line 18 reads "In contrast to results reported by Volz-Thomas et al. (2002), less ethyl nitrate is produced as the temperature is increased.", which implies that more ethyl nitrate is produced at a colder temperature than at a warmer. No changes were made the manuscript in response to the reviewer's comment.

*P917, line 24: Figure 4 fails to convince me of this. The differences in peak areas are so small that without a proper error analysis I am not convinced that this difference is statistically significant. Also, I do not see the additional impurities that the authors are referring to. These are some significant point the authors use to suggest that the LED system is advantageous, and therefore need to be shown in a more convincing manner.*

Please see our response above.

*P919, line 22: Once again I do not think that you have thoroughly illustrated this.*

Please see our response above.

*P920, line 6-7: What is negligibly small in this case. If you are presenting these sources as a method of calibration that can be analyzed using the theoretical calculation of concentrations rather than an actual secondary calibration for validation, then you need to show the absolute potential error in this synthesis method.*

Please see our response above.  
The absolute errors are shown in Table 1.

*Section 4.1: This should be moved to the very end of this manuscript. Ultimately showing that this method of synthesis, using the LEDs, is the novel part of this manuscript.*

We have reorganized the manuscript as suggested.

*You need to do a better job of convincing the reader that, other than the improvement in power consumption, this is an improvement on other techniques.*

Please see our response above.

*Section 4.2 and 4.3: This is information that can be useful presented earlier in the manuscript, such as when you are initially speaking of the interferences and secondary products in the sources. Overall I think this work could use quite a bit of reorganization to improve the flow and readability of the manuscript.*

We have reorganized the manuscript as suggested.

*Figure 1: While this picture is nice, it does not illustrate how the LEDs are oriented on the photolysis cell, which is the heart of this manuscript. This should be made clearer here or in an inset diagram.*

We have marked the position of the LEDs with red arrows and modified the figure caption accordingly.

*Figure 2: This figure could be improved if you include the precursor compound in the legend or description.*

We have modified the figure as requested.

*Figure 3: Why are the GC units not in concentrations, but in Figure 2 they are in concentrations?*

The GC units are in V (peak height) in Figure 2 and in  $V \times s$  (peak area) in Figure 3. The mixing ratios given are from the TD-CRDS in both cases. No changes were made.

*The calculated NO trace should be indicated that it is presented on the left axis.*

We have modified the axis title to "Mixing ratio (ppbv)" and adjusted the caption also.

*The black NO trace is nearly identical to the zero line. Please modify the zero line to be dashed or color the NO to better separate them.*

Done.

*Figure 4: Perhaps shade either the red or blue curves to better illustrate the area since the lines overlap.*

We have modified the figure as requested.

*I would prefer to see an average chromatogram with standard deviations presented here to inform the reader whether or not these differences are significant.*

We show an example of reproducibility as Figure 3A. In the case shown, the fluctuations are due to the slight changes in the amount of the limiting reagent, and averaging those would be misleading. Averaging chromatograms would also widen the peaks (as retention times slightly fluctuate). Since we have concluded that there is no statistically significant difference, we decided to only present single chromatograms.

*Figure 5: It was not clear in the text why two different GC systems were used. It is mentioned in a single sentence that the Varian was used for some samples. Why? This needs to be made clearer in the text. Otherwise I am asking myself why you didn't run the PPN on the varian or the PnBN on the HP.*

We have added an explanation to the manuscript on line 166:

"Some experiments were replicated using the group's Varian PAN-GC whose construction and operation have been described by Tokarek et al. (2014) because the HP-GC had been modified for unrelated experiments."

*Figure 6: Please increase the font size on the legends. Also please retain the order of the legends, e.g. list the PAN species first or NO first in all panels.*

We have increased the font size by 20% and changed the order of the legend as requested.

*Figure A1: Please increase the font size on all of the labels, or this will be extremely difficult to read.*

Done.

*Also is this a commercial design or is it something that you have made in your lab? Please indicate this better.*

We state in the text (line 121) that the arrays were designed and constructed in-house, and as a result we have not modified the manuscript in response to the reviewer's question.

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