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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Measured solid state and sub-cooled liquid vapour pressures of nitroaromatics using Knudsen effusion mass spectrometry" *by* Petroc D. Shelley et al.

Anonymous Referee #1

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Organic nitrates in general and aromatic organic nitrates are important atmospheric compounds that contribute to SOA formation. From this point of view it is important to have saturation vapor pressures and suited prediction methods at hand, that will aid mechanistic understanding and modelling of SOA formation from this class of compounds.

It is known, that GCM can strongly overestimate the vapor pressures of organic nitrates and of multiple functionalized organic molecules, in general. One reason is that the GCM are based on not-suited or too small training sets. From this point of view the manuscript is absolutely timely and it addresses an important aspect in atmospheric

physical chemistry.

Essentially, the authors provide vapor pressures and thermodynamic data for 20 functionalized aromatic nitrates, grouped into Nitro-phenols, Nitro-benzaldehydes, Nitrobenzoic acids. The measured vapor pressures measured over the solid compounds were converted to vapor pressure over subcooled liquids for more general use.

In addition the authors investigated the role of the calibration standards in their KEMS and corroborated their findings by comparison to selected EDB results. The authors try to systematize their results in concepts of inductive and mesomeric effects of aromatic substituents and in terms of H bond donor strength or dipole moments. The material presented in the manuscript is very good and useful. However, I identify some weakness in the presentation of the material. Especially, the result section 4.1 is difficult to follow and it is mixing results and discussion. Related to that, I also suggest to support the textual description by more graphics/diagrams (see comments below).

The manuscript should be published in ACP, but needs major revisions along the lines below.

Major comments

Why do you consider the comparison to GCM EVAPORATION at all, if it should not be used for aromatic compounds? I suggest to leave out the parts regarding EVAPORATION.

The Results section contains results and discussions. Either results and discussions must be separated into two independent section. Or the type of section should be indicated by "Result and Discussion".

Line 243-260: Why do you put so much emphasize on the methoxy phenols? This has not much to do with your work and the concepts of inductive, mesomeric and H-bond effects are so general that you don't have to introduce it by this specific example. In any case, it is not your result and therefore misplaced in a Result section. Moreover, I don't

understand what is supposed to be learned from Figure 3, it is not showing the overall importance of the H-bond (line 244). The methoxy phenols could help the discussion of your findings, though, if you could relate their vapor pressures to their H-bond abilities.

I suggest to omitting whole part with the methoxy phenols and Figure 3 and Table 4 should be skipped (In Table 4, something happened to the table header). That would make some space for my next suggestion to put more illustrations to section 4.1.

line 261-312: Here you present and discuss your findings for the nitro phenols. It is very difficult to follow your description and interpretations based only on the text and on the tables, because you present many numbers in combination with similar looking compound names.

I understand that the authors have access to MOPAC2016 and were able to calculate by themselves the partial charges on the carbon which carries the phenol group and estimate H bond strength as well as calculate dipole moments. I suggest to present all used helping quantities, i.e. (relative) strength of I- and M-effect, partial charge on phenolic C, dipole moments, in an extra table or add it to the Table 5. The authors then should try to plot the vapor pressures as function of (some of) these quantities in addition to table(s) and text.

I know, it may be challenging to clearly arrange that information in a graphical way. However, it would help the readability of the manuscript a lot. E.g. “outliers” could be used as start for your discussion of secondary effects like steric effects, or intramolecular H-bonding (as presented in the current text).

line 313-326: In the same sense as before: do you have dipole moments of the nitrobenzaldhydes? Could you add this information to Table 6, make a graphics and discuss the results in similar terms as the phenols?

line 327-329: Why don’t you show that relation in a plot.

line 330-348: In the similar sense as commented above: try to find a good graphical

presentation of your findings. Using partial charge on the carboxylic C, would that enable comparison of the acids to the phenols, in terms of H-bond donor strength?

line 349-362: Summary, yes, it this very informative. I argue again, it would be great to have the proposed diagrams in the previous sections, which show the trends and the exceptions, highlighting the statements in this summary.

Minor comments

line 114 – line 118: I understand that you only used PEG-3 and PEG-4 to calibrate your KEMS? I feel, the discussion of the PEG series is distracting and confusing (me) here. It is covered by the Krieger et al. (2018) reference. If you feel the need to discuss PEG in such detail, I suggest to move it to the supplement.

line 118f: You mentioned the PEG-4 is a suited standard, but you obviously used also PEG-3. What is the quality of the KEMS for PEG-3 measurements?

line 268f: I suggest to take the sentence to the previous paragraph and make the new paragraph after the sentence.

Section 4.5: I suggest to move some details of the EDB measurements to the EDB section 2.3 and to focus here on the comparison itself.

line 560: I would suggest to slightly reformulate. “in non-protic systems the dipole moment. . .”

Figure 9: I think there is space to show all data discussed and given in Tables 11 and 12, also some are less complete.

In general: check your literature input: e.g. McFiggans, O’Meara

If you quote authors directly, the format should be: “As mentioned by Bilde et al. (2015) . . .”

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