

Atmos. Chem. Phys. Discuss., referee comment RC2
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Comment on acp-2021-775

Anonymous Referee #2

Referee comment on "Comparison of saturation vapor pressures of α -pinene + O₃ oxidation products derived from COSMO-RS computations and thermal desorption experiments" by Noora Hyttinen et al., Atmos. Chem. Phys. Discuss.,
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The data displayed in Figure 1 are interpreted by the authors as primarily indicating a large discrepancy between COSMOtherm-predicted vapour pressures and those obtained from the FIGAERO-CIMS technique for compounds with small molecular mass. However, an alternative reading of that plot would be that the two methods for obtaining vapor pressure indicate very different dependence of the vapour pressure on molecular mass. COSMOtherm suggests that with an increase in molecular mass by ~ 40 g/mol the vapor pressure decreases on average by ~ 1 order of magnitude. For the FIGAERO data that dependence is less than half as pronounced, whereby a three-fold increase in the molecular mass (from 130 to 390 g/mol) only lowers the vapor pressure from 10^{-7} Pa to 10^{-10} Pa. I note that the calibration involving PEGs (Table S1, Figure S1) indicates that an increase in the molecular mass of the PEGs by 88 g/mol leads to a 2.5 order of magnitude decrease in volatility, which is very comparable to what COSMOtherm suggests.

In other words, the discrepancy between the two techniques is also quite large for the heaviest molecules – agreement is only apparent for molecules between 200 to 300 g/mol. The most likely explanation for the discrepancy is a limitation of the FIGAERO technique and not of the COSMOtherm estimation method. The authors themselves offer an explanation on lines 224-226: "It is also possible that saturation vapor pressures of dimers with the lowest volatilities ($p_{\text{sat}} < 10^{-11}$ Pa) cannot be measured using thermal desorption, as the molecules would thermally decompose before evaporating from the sample (Yang et al., 2021)."

At the root of the failure of the FIGAERO technique as applied here may be the extrapolation to volatilities that fall far outside of the calibration. The calibration only involves the molecular mass range from 282 to 370 g/mol and $\log p_{\text{sat}}$ from -5 to -7, but it is applied to a mass range from 130 to 390 g/mol and a vapour range of more than 10 orders of magnitude.

I suggest some rephrasing of formulations in abstract and manuscript text would be called for, e.g. line 4 to 5: "We found a good agreement between experimental and

computational saturation vapor pressures for molecules with molar masses around 190 g mol⁻¹ and higher." Maybe the thrust of the paper could be shifted towards highlighting how the calibration procedure AND thermal decomposition limits the FIGAERO technique to a estimating the volatility to certain set of compounds and that there is both an upper and a lower volatility limit to this technique. I even wonder whether it is really appropriate to refer to the values obtain by the FIGAERO technique as "experimental saturation vapour pressures" (as done in the title of the manuscript). This is a rather indirect inference based on a number of assumptions that may not be all that valid. Maybe formulating as "vapour pressure values inferred from regressions with desorption temperatures" would be more cautious.

Line 24: Just because the SOA community has been using saturation vapour pressure does not mean that "it is essential to have reliable methods to estimate the saturation vapor pressures of complex organic molecules formed in the atmosphere". What really is required is the equilibrium partitioning ratio between the SOA and the gas phase. The saturation vapour pressure is simply commonly used to estimate that partitioning ratio (together with an activity coefficient of the compound in the SOA). A better formulation would be therefore: "it is essential to have reliable methods to estimate the volatility of complex organic molecules formed in the atmosphere."

Line 43ff.: The thermodynamic property controlling the rate or timing of desorption would only be the saturation vapour pressure, if the molecule were to desorb from its own pure (liquid) phase. This doesn't appear to be the case in the method referred to here. As such, this method does not "measure" the saturation vapour pressure, but the equilibrium partitioning ratio. Would it then not be better to calibrate the method using compounds with known equilibrium partitioning ratios in order to find the correlation between equilibrium partitioning ratios and desorption temperature? After all, it is the equilibrium partitioning ratios that you are interested in in the first place.

Line 149ff.: I appreciate that you refer to the earlier study by Kurten et al., 2018 to justify the selection of conformers containing no intramolecular H-bonds, but I think some sort of explanation would still be required here. There doesn't seem to be any compelling reason why the ozonolysis of a-pinene should preferentially lead to oxidation products that do not contain intramolecular H-bonds. Furthermore, one of the advantages of a method such as COSMOtherm is precisely the fact that it should be able to account for the effect of intramolecular H-bonding on solvation. The rationale provided, namely "This method has been shown to provide more reliable saturation vapor pressure estimates for multifunctional oxygenated organic compounds", seems not very convincing as it could simply be coincidence.

Line 96ff.: Doesn't that procedure lead to a bias in the comparison of measured and estimated saturation vapour pressure?

Line 15: "grouped [...] **into**"

Line 23: "the role [...] **in** SOA formation"

Line 44: "estimated **from** the desorption temperatures"

Line 131: "**for** the smallest" "**for** the largest"