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Atmospheric Chemistry and Physics
Discussions

Interactive comment on “Formation of secondary organic aerosols from the ozonolysis of dihydrofurans” *by* Yolanda Díaz de Mera et al.

Anonymous Referee #2

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This paper represents a new chemical mechanism potentially relevant for NPF, but the experimental data does not fully prove the proposed mechanism. Lack of experimental support is compensated by theoretical arguments and I guess this paper could be published once the problems pointed out by referee #1 and my concerns below are addressed.

Reviever #1 already provided an extensive and complete review and I avoid repeating that but I still want to express my major concerns despite the overlap. My main concern is that authors quite vaguely exclude the SO3 channel and the role of sulphuric acid in observed NPF. Proper exclusion of SO3 channel is critical since authors are providing a new chemical mechanism arising from SO3 exclusion and explaining NPF in their system with previously unrecognised pathways. I cannot judge myself, if the proposed mechanism with SO2 catalyzing Criegee conversion to organic acids or aldehydes is

relevant or not, but I do question a) the absence of sulphuric acid in the system and b) the atmospheric relevance of the proposed mechanism even if correct and relevant in chamber conditions.

Authors state that reaction of SO3 with water vapour cannot be related to NPF since there is no water. Water is omnipresent even in authors’ chamber and the reaction of SO3 with water is fast and unlikely seriously limited by the availability of water even in “dry” conditions. Water can come from the walls, and even through the Teflon wall, with trace gases and from the synthetic air bottle. Even if the lack of water would slow down the SO3 conversion to sulphuric acid, vast amounts of SO3 can be produced from sCI+SO2 or OH+SO2 and minute water concentrations could be enough for sufficient sulphuric acid formation. What are the yields of OH from ozonolysis of these DHFs?

OH scavenging was >95%. Still, with very high concentrations of furan and ozone, the OH production could potentially be high enough that the residual <5% reacting with SO2 (High concentrations up to 0.5ppm!) can be a significant source of SO3 and subsequently sulphuric acid under assumption that water residuals are present. More is required to show that not enough sulphuric acid can be formed via sCI+SO2/OH+SO2 -> SO3 (+H2O) -> H2SO4. (Even though the presented theoretical analyzis suggests SO3 is not released from the reaction of sCI and SO2, previous literature shows that’s unlikely the case with most alkenes). With some assessment of water vapour concentration upper limit and with known or approximated reaction rates and yields authors could maybe get at least an idea about maximum sulphuric acid concentrations in the chamber.

The statement that SO2 remained constant (p6., l7.) is not supported by data shown. Was it measured? And if it was measured, with 0.5 ppm SO2, there’s 1e13 molecules of it in a cm-3. If one per-mille of that is converted to H2SO4, that would be sufficient (concentration up to some 1e10 molec cm-3) to drive NPF with unavoidable background contaminants (e.g. ammonia or amines) or with some products from DHF oxidation and produce the observed NPF rate of maybe 1000 #/s. And a 1 per-mil drop in SO2 may be tricky to observe. So what is really the experimental evidence for the SO2 recycling?

All in all, before publishing this paper, I would like to see more results and discussion to exclude the SO3 channel and sulphuric acid produced via that channel either purely from OH or with an assumption that theoretical prediction of no SO3 formation from sCI was incorrect. If, from experimental data, the presence of sulphuric acid cannot be excluded, the paper should be written in a manner that accounts for that deficiency.

I also have some doubts that any organic acids formed from these relatively small alkenes would have sufficiently low vapour pressures that they could homogeneously nucleate. (There are also methods to estimate the vapour pressure of such compounds, see e.g. Donahue et al. Atmos Chem Phys 11, 3303–3318, 2011; Pankow et al., Atmos Chem Phys 8, 2773–2796, 2008). These acids may be partitioning between particle/wall and gas phase, but that they underwent homogeneous nucleation with high nucleation rates is more questionable. If authors suggest nucleation is driven by proposed compounds, some more data or discussion would be appreciated.

On the other hand, the concentrations in the chamber system are vastly above the atmospheric ones (ozone, DHF and SO2 are 100-100 times higher than typical for the atmosphere), meaning that at least the atmospheric relevance of such acids, even if they were nucleating in the chamber, is more than questionable and against the present understanding on atmospheric nucleation processes.

Intro: Authors largely exclude the discussion related to extremely low volatile organics formed in auto-oxidation reactions from alkene ozonolysis (Ehn et al., Nature, 506, 476-, Nature; and many subsequent publications) considered to be one of the main pathways to atmospheric NPF and SOA. Since the title and motivation of this paper is SOA, the major progress on that field should be shortly discussed in the introduction.

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