

Interactive comment on “Secondary organic aerosol formation from photooxidation of furan: effects of NO_x level and humidity” by Xiaotong Jiang et al.

Anonymous Referee #1

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In this work, the authors studied the photooxidation of furan and the resulting secondary organic aerosol formation. In particular they investigated the effect of NO_x level and relative humidity on the yields and chemical composition of SOA. The experiments were conducted with a laboratory chamber and measurements by SMPS, FTIR, and ESI-MS formed the basis for the main experimental results. The topic is of interest to ACP's audience and fits within the scope of ACP. However, the results are too general and inconclusive and there are a few issues with experimental design. I do not recommend publication in ACP at this point.

Major comments:

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First of all, it is unclear what the insights are from the presented set of results. The manuscript presents trends in yields with NO_x/humidity, but there is no experimental investigation that would elucidate the “why”. For example, the increase in yields with increasing NO_x is consistent with isoprene photooxidation studied by Kroll et al. (2006). That is true only for high VOC/NO_x ratio. In all other studies, NO tends to suppress yields. So why for furan at these VOC/NO_x ratios, the trend is positive with NO_x? What is special about furan? What is NO, or NO₂, or NO_x doing that would change the volatility of the products? A similar set of questions would also be raised regarding RH. What are the reactions that are affected by water, and would affect yields? The measurements of composition and yields are not sufficiently tied together to present a holistic story. Without these mechanistic insights, it is hard to generalize the findings and NO_x/RH effects to make this an impactful study. The lack of any proposed or cited mechanisms in the main body of the manuscript make the results seem like an isolated set of findings and therefore do not advance the knowledge of SOA formation.

Another weakness of this paper is the lack of context. Based on the introduction and discussion, it seems that furan is being studied because it can be a direct emission or a secondary product. It is not clear if direct emissions of furan are important. The authors seem to group furan together with aromatic compounds such as toluene and m-xylene, but they are quite different (e.g. the SOA yields of furans are an order of magnitude lower than single-ring aromatics). The secondary products from alkane oxidation are dihydrofurans, and are different from furan studied here. The discussion of results does not draw any linkages to these other compounds. So, again, it is not advancing the knowledge of oxidation of alkanes, or aromatic compounds.

I am also concerned about the use of NaCl as a seed. It seems that there may be secondary reactions that the authors are not considering. From the IC results, it seems there is a significant amount of NaNO₃. Assuming the only cations are Na⁺ and H⁺, this would mean some of the chloride from NaCl became HCl, which can volatilize and photolyze in the gas phase to give chlorine atoms, a strong oxidant. In fact, the

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presence of 1,2-dichloroethane suggests that Cl is reactive and participating in some reactions. Therefore, this photooxidation system is actually quite complicated, with OH, O₃ and Cl reactions all being potential sources of SOA.

Other comments:

Page 4, line 1: the neutralizer is not used to remove charge completely. Rather it is meant to remove excess charge from the atomized solution and bring it closer to charge equilibrium

Page 5, line 1: NaCl is cubic when dry. Is there correction using the shape factor in obtaining size distribution and volume concentrations?

Page 5, line 19: what is the potential for organic-bound water being removed from the dryer (leading to overestimation of ALW)?

Page 5, line 30: there is no prior separation for the ESI-MS. Is there any evidence of matrix effects for quantification?

Page 5, Page 33: what is the resolution of the mass analyzer?

Page 6, line 25 – 26: why is it assumed coagulation is the dominant reason for decrease in number? At a particle concentration of 10⁴ cm⁻³, the homogenous coagulation timescale is on the order of days. Heterogeneous coagulation is likely very fast and would have been completed.

Section 3.2: there is extensive discussion of O₃ formation, but this paper is supposed to focus on SOA formation. It is unclear whether such an extensive discussion of O₃ is warranted. It would be great if the authors can tie the O₃ trends to oxidation mechanisms. In fact, the large differences in O₃ may complicate the interpretation, because the relative fractions of OH and O₃ oxidation (rather than NO_x itself) may be driving some of the trends.

Page 7, line 16: it seems to me that the difference in rate of O₃ increase is within

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experimental uncertainty. Perhaps error bars should be shown in Figure 3.

Page 9, line 5-6: awkward phrase “equally relevant”?

Section 3.3: all the FTIR results are presented in absolute abundance, i.e. total abundance of each functional group. It is likely more insightful to look at relative abundance, normalized by SOA amount to infer changes in reaction mechanisms. As presented now, it is difficult to see the changes because all functional groups are increasing.

Page 10, line 29: I expect N₂O₅ to be quite low under photooxidation conditions.

Figure 1: Why is 1.4 used as density? Is there literature data that suggest density should be 1.4? Density is likely a function of O/C ratio. Perhaps the authors can justify the use of 1.4 by comparing to literature density data for SOA with similar O/C?

Figure 1, y-axis for number concentration: Is it really just a few particle per cm³? Is there a missing exponent (maybe multiplied by 10⁴?)

Figure 3: SOA yield should be unitless, or in percent.

Table 1: there are too many significant digits, especially in the SOA yields

Figures 5 and 6 and redundant, same with 7 and 8. In each case, only 1 of the 2 is needed for show changes in functional groups.

Figure 9: It will be useful to highlight the ion peaks described in Table 3. In Table 3, it is difficult to infer trends if the peak abundances are normalized to the highest peak in each spectrum.

Table 2: where would CH₂, CH₃ come from? Furan does not contain any CH₂ or CH₃ groups and I do not expect oxidation to produce any.

Table 3: Is the mass resolution high enough to calculate exact elemental formula? If so, the exact mass should also be shown to justify elemental formula.

It should also be noted that there are far too many grammatical errors in this manuscript

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for me to point out. In many cases, these mistakes seriously hinder a reader's ability to understand the science. The manuscript needs to be carefully edited for clarity.

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