



Comment on acp-2021-29

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Community comment on "Formation kinetics and mechanisms of ozone and secondary organic aerosols from photochemical oxidation of different aromatic hydrocarbons: dependence on NO_x and organic substituents" by Hao Luo et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-29-CC1>, 2021

This manuscript describes a chamber study on ozone and SOA formation in oxidation of a few aromatic benzenes. Concentration of O₃ and intermediate products were monitored with respect to the reaction time, and the effect of alkyl substitution on benzene ring was discussed. But the measurements here did not offer too much new insight into the formation mechanism of O₃ and SOA in these reactions. The mechanism shown in Figure 7 was nothing new, and can be easily obtained from MCM or many previous papers working on mechanism. Oligomerization of Gly and MGly to form SOA was also well known.

General Comments:

(1) The PTR measurements provided some information on the reaction intermediates, but the PTR-MS data were hardly discussed in this manuscript. Simple description on concentration changes for products and peak concentrations of O₃ is NOT directly relevant to O₃ or SOA formation. No discussion on the formation mechanism of acetaldehyde, formic acid, and acetic acid which were not usually observed in previous studies. Effort might be required to work out how these compounds are formed by referring to previous publications or suggesting new formation pathways.

(2) The chamber studies here used rather high concentrations of AHs (~1000 ppbv or higher) and initial NO_x (~100 ppbv or higher). Unfortunately, NO_x concentrations were not reported in the course of reactions. Both [AH] and [NO_x] are considerably higher than values in usual atmosphere.

Specific Comments:

(3) Product identification by PTR-MS: (a) Line 118/233/254: m/z 85 should be "2-butenedial", m/z 87 might be "butanedione". (b) Line 230: Why was m/z 111 assigned to "hexene diketone"? I am not sure what "hexane diketone" means. I suppose it be CH₃C(O)CH=CHC(O)CH₃, and its cation C₆H₉O₂⁺ after PTR has m/z 113.

(4) We notice the experiments were carried out in a 2 m³ chamber. Was the wall effect corrected? Aerosol and O₃ can also lose on the reactor wall on long reaction time.

(5) How was OH radical generated? Particularly for NO_x-free experiments. This should be

important in understanding O_3 formation under NO_x -free conditions.

(6) Figures: All O₃ formation curves are presented as [O₃] vs Time. Different aromatic benzenes have different reactivity towards OH radical. Besides, the initial [AH] concentrations are different. Therefore plotting "[O₃] vs Time" does not provide too much insight on the progress of the reaction. It is probably more proper to present "[O₃] vs D[AH]", which might give information on O₃ formation potential. Similarly for concentrations of other products. Besides, on shortening of O₃ peak appearance when increasing AH concentrations (Line 146-154, Figure 3a) might also be rationalized in terms of AH consumption.

(7) Section 3.1 The First Paragraph: The rate coefficients of AHs with OH radical were well-known. No need to confirm their reactivity.

(8) Section 3.1 "... without NOx": I am surprised to see O₃ formation under NOx-free conditions (Figure 1a). The O₃ concentration is quite substantial, up to 25 ppbv with a consumption of ~50 ppbv in toluene. Quite high yields here. Our current understanding of O₃ formation is based on photolysis of NO₂. The authors stated "The possible contributors of these O₃ might be intermediates such as carbonyl compounds" but offered no details. Could the authors be more specific and give possible reactions leading to ozone formation? This is really important if the measurements are correct here!

(9) Line 139: "... AHs ... reduce the consumption of O₃". This is NOT correct. In the oxidation of VOCs, the increased O₃ formation is due to the addition conversion of NO to NO₂ by RO₂/HO₂ radicals.

(10) Figure 1: Specify "NO free" in figure caption. Figure 2: It might be necessary to plot the concentrations of AH on the same plot.

(11) Line 155: I am not sure the purpose to compare O₃ peak concentrations. I believe what we really care is the yield, instead of peak concentrations under some particular reaction conditions (VOC concentration, or VOC/NOx ratios, ...).

(12) Line 250-251: Yields of Gly and MGly in benzene are lower than those in substituted benzenes. Then what does "inhibited" mean?

(13) Line 253: "... resulting in the inhibition of ring-opening reaction". Any evidence for this claim? As far as I know, ring-opening of the bicyclic alkoxy radical is faster when alkyl-substitution is available.

(14) Line 263-265: "However, ... Kamens, 2001)." The sentence gives an impression that oligomerization occurs before partitioning into particles. The fact is that dicarbonyls are uptaken by particles first and then dimerize in particles.

(15) Line 274-276: Formation of m/z 87 and m/z 111 depends more strongly on the pattern of methyl substitution, but only on the number of methyl substitution. m/z 87 from neighboring methyl substitutions (o-Xylene and 1,2,3-TMB), while m/z 111 from meta-methyl pairs (m-Xylene and 1,3,5-TMB). Again Fig 23S was plotted as "concentration vs time". High concentration does NOT necessarily means high yield, and discussions on them unlikely lead to reliable conclusion.