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Interactive comment on "Degradation Kinetics and Secondary Organic Aerosol Formation from Eugenol by Hydroxyl Radicals" *by* Changgeng Liu et al.

Anonymous Referee #2

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This study investigated the OH reaction rate of pure eugenol compound and its SOA yield with a custom-built oxidation flow reactor (OFR). The impact of NO2 and SO2 influence on SOA formation was also investigated. The results of the study might be very interesting to many, yet quite a few items need to be clarified before it can be accepted for publication.

Experiment design: The manuscript mainly deals with two topics: the rate constant of Eugenol-OH reaction and SOA yield of Eugenol. As for the 6 experiments listed in the Table 1, apart form the Eugenol, how about the combination of other species such like m-xylene/1,3,5-TMB/SO2/NO2. For experiments determines the rate constant for the

reaction with OH, were SO2/NO2 added? And for SOA yield studies, what was the reference compound to derive OH? It seemed that here SO2/m-xylene/1,3,5-TMB are all not appropriate to sever as the reference compound since m-xylene/1,3,5-TMB they themselves are also SOA precursors and SO2 instead influence the SOA yield. It is quite confusing. The authors need to clarify in Table 1 what combinations (including reference compound for deriving OH) of species are prepared for obtaining the rate constant, and what combinations instead are for studying the SOA yield.

From the study only the overall rate constant for reaction with OH was obtained. It seemed that not so much degradation kinetics are presented as indicated by the title.

Line 28: The enhancement values need not to have 4 significant figures. Lines 77-84: What's the overall concentration of eugenol in ambient air? How important does this precursor compared with other Methoxyphenols. Line 105: The [O3] was in the range of 0.94-9.11 ppmv while you want to explore the reaction between OH radical and eugenol. Can you clarify whether such high level of O3 was just used to generate OH radical in the mixing tube, or they indeed existed in the flow tube? If it is the latter case as your supplement material shows, then an evaluation of the interference from the O3 is needed. Lines 109-110: This is not acceptable. The OH reactivity applied in this experiment is at least 80 s-1 to 380 s-1 with only Eugenol accounted (using OH reaction rate calculated in section 3.1), not mentioned the SO2 (0-198ppb) and NO2 (0-109ppb in line 27) added in the later experiment. It suggested the calculated OH exposure should be at least several times lower than the OH exposure calculated without considering the external OH reactivity (=0 s-1 assumed in original calculation) (Peng et al., 2015) Lines 116-117: Better add the assumed average [OH] and the reference as well. Lines 124-125: How do the authors calibrate their aerodynamic size distribution in AMS? If the authors consider the chemical-composition based particle density (Kuwata et al., 2012; Salcedo et al., 2006), how about it when compared to the effective aerosol density applied here? The aerosol size distribution of each experiment should be considered separately. The 100% full cut size of AMS lens is around 600

nm in mobility size (Nault et al., 2018). The effective density calculation from dva/dm could be biased if the aerosol in OFR grow beyond the AMS lens cut. Lines 152-153: The decay of SO2 was used to calculate [OH], so why was SO2 not used as the reference compound in the relative rate method? As mentioned above, the reader should be informed in Table 1 what were initially added and what are the reference compound. Lines 135-137ïijŽThis is confusing. Did the authors examine a full cycle of UV light applied in the experiment? Lines 140-141: What is the photon flux of 254 nm in OFR. How do the authors determine 254 exposure/OH exposure ratio? Lines 163-164: Is it possible that the difference between your measurement and the theory was caused by the O3 reaction? Lines 164-167: Have the authors considered the potential wall loss of three species, which could result in different species decay ratios. Thus extra uncertainty on OH reaction rate coefficient of Eugenol could be introduced. Lines 181-183: How about those reaction rate coefficients estimated from experiment when compared to those from the SAR method? Line 207: The decrease have also been reported in references of (Palm et al., 2016; Palm et al., 2018) Line 211: Should be larger than 30% based on Fig. S4 in (Peng et al., 2015). Please show the detailed calculation results. Line 227: How about the wall loss of aerosols in the flow tube. The authors could examine the wall loss by directly injecting aerosols into the OFR. Line 263: Have the author consider the NH4NO3→CO2 effect, which could influence fCO2 and thus O/C and H/C ratio substantially. This bias could be larger especially in the later NO2+ Eugenol experiment. Line 284-286: For saying this, OH exposure should be compared. Line 294-296: We cannot definitely conclude that the decrease is due to the fragmented molecules formed through the oxidation of gas-phase species. So better add "probably" or "possibly" before "due to". Line 311: Can the formed SO4 be fully explained by the SO2 decay in SO2+ Eugenol experiment? Line 323: Why does the eugenol can partition quickly under acidic aerosol condition? Lines 360-362: In the paper of Finewax et al. (2018), it is phenoxy radical rather than OH-aromatic adducts that react with NO2 or O2. In fact, the formations of phenoxy radical and OH-aromatic adduct from phenols are totally different in reaction pathways. Lines 366-367: Still,

the reaction pathway through the NO2 addition on the phenoxy radical was neglected by the author. Line 375: The authors could still specify the NO3 exposure compared to OH exposure by assuming thermo-steady state of NO2 and O3. Line 391: In this method, if the NO and NO2+ ions from organonitrate were missed, the organic nitrate calculation was underestimated (Farmer et al., 2010). The authors can use the real-time NO+/NO2+, and NO+/NO2+ ratio from NH4NO3 and organonitrate (a factor of 2.25) (Fry et al., 2018) to calculate -ONO2 group concentration for organonitrates. Line 839: "ratioas" should be "ratio as".

References: Salcedo, D., Onasch, T. B., Dzepina, K., Canagaratna, M. R., Zhang, Q., Huffman, J. A., DeCarlo, P. F., Jayne, J. T., Mortimer, P., Worsnop, D. R., Kolb, C. E., Johnson, K. S., Zuberi, B., Marr, L. C., Volkamer, R., Molina, L. T., Molina, M. J., Cardenas, B., Bernabe, R. M., Marquez, C., Gaffney, J. S., Marley, N. A., Laskin, A., Shutthanandan, V., Xie, Y., Brune, W., Lesher, R., Shirley, T., and Jimenez, J. L.: Characterization of ambient aerosols in Mexico City during the MCMA-2003 campaign with Aerosol Mass Spectrometry: results from the CENICA Supersite, Atmos Chem Phys, 6, 925-946, 2006. Farmer, D. K., Matsunaga, A., Docherty, K. S., Surratt, J. D., Seinfeld, J. H., Ziemann, P. J., and Jimenez, J. L.: Response of an aerosol mass spectrometer to organonitrates and organosulfates and implications for atmospheric chemistry, P Natl Acad Sci USA, 107, 6670-6675, DOI 10.1073/pnas.0912340107, 2010. Kuwata, M., Zorn, S. R., and Martin, S. T.: Using Elemental Ratios to Predict the Density of Organic Material Composed of Carbon, Hydrogen, and Oxygen, Environ Sci Technol, 46, 787–794, 10.1021/es202525q, 2012. Peng, Z., Day, D. A., Stark, H., Li, R., Lee-Taylor, J., Palm, B. B., Brune, W. H., and Jimenez, J. L.: HOx radical chemistry in oxidation flow reactors with low-pressure mercury lamps systematically examined by modeling, Atmos. Meas. Tech., 8, 4863-4890, 10.5194/amt-8-4863-2015, 2015. Palm, B. B., Campuzano-Jost, P., Ortega, A. M., Day, D. A., Kaser, L., Jud, W., Karl, T., Hansel, A., Hunter, J. F., Cross, E. S., Kroll, J. H., Peng, Z., Brune, W. H., and Jimenez, J. L.: In situ secondary organic aerosol formation from ambient pine forest air using an oxidation flow reactor, Atmos. Chem. Phys., 16, 2943-2970, 10.5194/acp-16-2943-

2016, 2016. Fry, J. L., Brown, S. S., Middlebrook, A. M., Edwards, P. M., Campuzano-Jost, P., Day, D. A., Jimenez, J. L., Allen, H. M., Ryerson, T. B., Pollack, I., Graus, M., Warneke, C., de Gouw, J. A., Brock, C. A., Gilman, J., Lerner, B. M., Dubé, W. P., Liao, J., and Welti, A.: Secondary organic aerosol (SOA) yields from NO3 radical + isoprene based on nighttime aircraft power plant plume transects, Atmos. Chem. Phys., 18, 11663-11682, 10.5194/acp-18-11663-2018, 2018. Nault, B. A., Campuzano-Jost, P., Day, D. A., Schroder, J. C., Anderson, B., Beyersdorf, A. J., Blake, D. R., Brune, W. H., Choi, Y., Corr, C. A., de Gouw, J. A., Dibb, J., DiGangi, J. P., Diskin, G. S., Fried, A., Huey, L. G., Kim, M. J., Knote, C. J., Lamb, K. D., Lee, T., Park, T., Pusede, S. E., Scheuer, E., Thornhill, K. L., Woo, J. H., and Jimenez, J. L.: Secondary Organic Aerosol Production from Local Emissions Dominates the Organic Aerosol Budget over Seoul, South Korea, during KORUS-AQ, Atmos. Chem. Phys. Discuss., 2018, 1-69, 10.5194/acp-2018-838, 2018. Palm, B. B., de Sá, S. S., Day, D. A., Campuzano-Jost, P., Hu, W., Seco, R., Sjostedt, S. J., Park, J. H., Guenther, A. B., Kim, S., Brito, J., Wurm, F., Artaxo, P., Thalman, R., Wang, J., Yee, L. D., Wernis, R., Isaacman-VanWertz, G., Goldstein, A. H., Liu, Y., Springston, S. R., Souza, R., Newburn, M. K., Alexander, M. L., Martin, S. T., and Jimenez, J. L.: Secondary organic aerosol formation from ambient air in an oxidation flow reactor in central Amazonia, Atmos. Chem. Phys., 18, 467-493, 10.5194/acp-18-467-2018, 2018.