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

Anonymous Referee #1

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Formation of secondary organic aerosols from the ozonolysis of dihydrofurans. Diaz de Mera, et al.

The manuscript's focus is to show nucleation of particles from the ozonolysis of 2,3-dihydrofuran and 2,5-dihydrofuran. Production of condensable gases is suggested to involve formation of organic acids from Criegee intermediates (CI) via catalysis by SO2. This mechanism is mainly supported by the fact that increasing water vapor reduced the observed nucleation. The authors suggest that higher water vapor concentrations compete for reaction with CI, reducing the fraction of CI that reacts with SO2. The authors' main argument is that CI are available to react with SO2 via a new mechanism that does not involve oxidation of SO2 to form sulfuric acid in the presence of water vapor. Notably, the proposed mechanisms appear to have an intermediate that involves SO3 (TS1.1, TS2.1, TS3.1). While it is stated that SO2 is not depleted, no data is

shown to support this statement. Previously SO2 has been shown to be oxidized by a number of CI, derived from different precursors, whether di-iodo species or from ozonolysis of alkenes.[1–5] To propose a new mechanism of reaction requires clearer evidence, particularly when measuring nucleation. Direct measurements of SO2 must be presented and it must be shown that the mass lost to particle formation would be easily detectable and above signal to noise of the SO2 detector. Although efforts were taken to remove water from the system and particle nucleation was still observed, low levels of residual water, from chamber walls perhaps, could provide water vapor. No direct measurement of humidity or water vapor was presented. Table 1 does not indicate which experiments included water.

The explanation of reaction of stabilized Criegee intermediates (SCI) with SO2 is problematic because the alkene reacted is small and cyclic, making it inherently unstable. Existing studies suggest that for such a small CI, stabilization will be negligible.[3,6–9] The energy released from the ozonolysis reaction will be in the range of 45 kCal/mol, all of this energy will remain in the resulting CI. Unimolecular decomposition should be the dominant pathway for these compounds. Studies showing reaction with SO2 used either a different route to SCI formation (di-iodo photolysis) or in fact detect oxidation of SO2. A seven member cyclic alkene, larger than the dihydrofurans by 2 carbons, showed yields of organic acids that were not strongly dependent on RH and were very low, less than a few percent.[10] While the proposed mechanism may occur, more information on its feasibility, in terms of the unimolecular reactions of the CI must be addressed. The energy of the transition state en route to the primary ozonide, or at least the primary ozonide itself, which indicate the reaction exothermicity, must be considered. Formation of SOA from oxidation is a complicated, multiphase process that is yet more complex due to deposition of condensable vapors and particles to the chamber walls, particularly for a the reactor used here, which has a low surface area to volume ratio.[11–13] For these reasons, inferring rate constants, even a ratio of rate constants, for the reactions leading to SOA formation is not reasonable without having any gas phase measurements. Data is not available for the decay of the furan or the

increase in condensable products. It is agreed that you observe increased humidity decreases SOA formation, but it data does not clearly explain the origin of this effect. Extrapolation of SOA formation data to rate constants of the oxidation reactions formation condensable products is not warranted. Those measurements are difficult enough to make, even when directly measuring the gas phase, without the complications of partition, both to particles and the chamber walls. If this analysis is to be used, more rigorous modeling of SOA formation and wall loss must be included.

The authors present clear indications of an interesting process leading to SOA formation from ozonolysis of compounds that have not had much study, but require somewhat speculative explanations in terms of the mechanism, particularly because the presented mechanism is at odds with existing knowledge of ozonolysis of small, cyclic alkenes. The observations and explanations may well be fully valid, but sufficient evidence, particularly concentrations of SO2 and some composition information on either the gas or particle phase, to support the mechanistic claims is not presented. Major revisions are required, including presentation of the SO2 concentrations and some rationalization of the formation of SCI from this dihydrofurans.

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