

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

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Answer to referee #2. We sincerely thank the comments of the referee. Additional information is now included together with data from new experiments carried out during these few weeks in line with the requirements of the referee. The mechanism for sCl reaction with SO₂ to generate organic acids and SO₂ is not really new. Other studies have found the formation of an acid and the release of SO₂ from the secondary ozonide as the most energetically favourable reaction channel for even smaller sCl (Jiang, 2010; Kurten, 2011; Vereecken, 2012). The experimental results obtained in this study are consistent with the isomerisation channel proposed in these previous theoretical works. a) “Absence of sulphuric acid in the system”. From the literature-available data for ice, passing the synthetic air through the LN₂ trap, the vapour pressure is expected to fall well below 10⁻⁷Pa (Murphy and Koop, 2005) and thus the expected concentration in

C1

the dried synthetic air is below 1×10⁷ molecule cm⁻³. Since residual concentrations could be higher, we have conducted a series of experiments to test the possibility of SO₃–water reaction in the reactor and to estimate the water concentration. We have used a degassed sample of solid sulfur trioxide (99.5%, stabilized, Aldrich) contained in a glass flask to obtain different SO₃ concentrations in the reactor (as it was done in previous studies (Jayne, 1997). Freshly dried synthetic air was mixed with SO₃ in the teflon reactor and the mixture was continuously monitored by the CPC for 40 minutes. The figure shows the results for experiments with SO₃ concentration in the range 1 to 12ppb. No particles could be observed for experiments with low initial SO₃ concentrations. On the other hand, NPF was observed for the experiments with SO₃ in the range 6 to 12 ppb. Under these experimental conditions, nucleation is attributed to the formation of H₂SO₄ from the reaction of SO₃ and the residual H₂O. The overall gas-phase reaction $\text{H}_2\text{O} + \text{SO}_3 \rightarrow \text{H}_2\text{SO}_4$ exhibits a second-order dependence on water vapor concentration, the first-order rate coefficient for the SO₃ loss being $k = 3.90 \times 10^{-41} \exp(6830.6/T) [\text{H}_2\text{O}]^2$ (Jayne, 1997). Taking into account that the approximate H₂SO₄ gas phase concentration able to nucleate is around 5×10⁶ molecule cm⁻³ (Metzger, 2010), the concentration of water in the reactor may be obtained by simulating the SO₃ and H₂SO₄ profiles for different guessed H₂O profiles. Thus for example, since no NPF was observed for the experiment with 2ppb of SO₃, the water concentration must be below 15ppb. On the other hand from the experiment with 6ppb of SO₃, a 20ppb water concentration is required to reproduce the observed nucleation. From all the experiments carried out, we estimate that water concentration in the reactor is 20±10ppb. To check for permeation through the reactor wall, some experiments have been also carried out with dry air after 1 hour in the reactor. The results were similar to those carried out with freshly dried air. Figure 1

This figure and the related discussion has been included in the supporting information.

According to the SO₂ comments, direct measurements of SO₂ are included in this reply and in the revised manuscript. We have carried out new experiments with lower

C2

SO₂ concentrations in the range 10-20ppb. In all cases the profile of SO₂ remained neatly constant. For example it was 10.0±0.2ppb during the whole experiment for the experiments with 10ppb of SO₂. A first order loss rate constant may be derived from the SO₂ profile: $k = 8.5 \times 10^{-6} \text{ s}^{-1}$. Thus, SO₂ losses (if they occur) are very low. See the figure. Figure 2

To check the possibility of SO₃ production, we can assume a simple mechanism where any lost SO₂ molecule would be converted exclusively into SO₃: $\text{SO}_2 \rightarrow \text{SO}_3$ $k = 8.5 \times 10^{-6} \text{ s}^{-1}$ [SO₂]₀ = 10ppb And then SO₃ would exclusively react with water to produce H₂SO₄: $\text{H}_2\text{O} + \text{SO}_3 \rightarrow \text{H}_2\text{SO}_4$ $k = 3.90 \times 10^{-41} \exp(6830.6/T) [\text{H}_2\text{O}]^2$ (Jayne, 1997)

Simulating the SO₂, SO₃ and H₂O profiles for a 20ppb water concentration and for 10ppb initial SO₂ concentration, it would require more than 1 hour to generate $5 \times 10^6 \text{ molecule cm}^{-3}$ of H₂SO₄, which is the approximate concentration able to nucleate (Metzger, 2010). For 20ppb initial SO₂ concentration it would require 28 minutes. Nevertheless, for these experiment nucleation was visible at 2minutes (almost instantaneous if we take away the mixing time of reactants). Relatively high levels of OH would deplete SO₂ if SO₂ concentration were very low. In this sense, the experiments with high dihydrofurans and ozone concentrations (for example 0.5 and 1.0 ppm, respectively) and low SO₂ concentration (in the range of 10ppb) show that residual OH concentration must be negligible in the system since the experimental SO₂ concentration remained constant during the experiments. Thus, considering the low levels of water vapour in the reactor and the observation of nearly constant SO₂ for the experiments with lower SO₂ concentrations, the contribution of SO₃-H₂SO₄ pathway to NPF seems to be minor and unable to lead to nucleation by itself. In this sense the catalytic pathway releasing SO₂, which is thermodynamic-favourable, may be the key to NPF. For higher SO₂ concentrations (in the range of 0.5 ppm) small changes at the level of the uncertainty of the SO₂ measurements can not be completely excluded as a possible source of SO₃.

C3

b) Atmospheric relevance. We have carried out experiments at lower concentrations. Thus, for example, for 2,5-DHF no particles were detected for 0.02, 0.04 and 0.02ppm concentrations of 2,5-DHF, ozone and SO₂, respectively. For 0.05, 0.1 and 0.05 ppm concentrations (2,5-DHF, ozone and SO₂) NPF could be observed but particle number concentration, particle size diameter and particle mass concentration were very low and noisy and could not be measured accurately. To assess the effects of water, SO₂ and ozone, the concentrations had to be increased. Although the concentrations of reactants in this study are higher than average concentrations in the atmosphere and nucleation from the ozonolysis of only DHFs is not expected, this work shows that these reaction lead to condensable species that could contribute to NPF or particle growing in the atmosphere. Furthermore this study reports theoretical and experimental data that points the catalytic role of SO₂ in the oxidation of SCIs.

Vapour pressure. From the work of Donahue et al (2011) a saturation mass concentration around 100 microgram.m⁻³ is expected for C₄ chemicals with a 1:1 oxygenation ratio (O:C). It is the high degree of oxygenation which leads to a low volatility value, $5 \times 10^{11} \text{ molecules cm}^{-3}$. For the range of initial reactant concentrations in the laboratory experiments this range of product concentration could be reached. A comment has been introduced in the manuscript as suggested by the referee. Ehn 2014 reference has been included in the introduction as suggested by the referee.

Main changes in the manuscript. Page 1, line 14. It has been rewritten. Water presence at ppb-ppm concentration may have an effect on SOA production. Nevertheless, for higher concentrations, no effect was found. Page 1, line 18. SO₃ role is not overall ruled out. SO₂ catalysed reactions are suggested as an additional pathway to NPF. Page 1, line 18. SO₃ is not excluded as a possible intermediate to produce SOA. Page 3, line 31. The term "completely dry conditions" has been removed. Page 4, line 4. The estimated water concentration inside the reactor is stated. Page 4, line 22. The experiments carried out with the ozone analyser are introduced. Page 6. Line 9. New data and discussion about SO₂, SO₃ and sulfuric acid is introduced. Page 7, line 21.

C4

New data and discussion about SO₂, SO₃ and sulfuric acid is introduced. Page 9, line 29. The energy of the first step of the ozonolysis is introduced. Page 10, line 18. From the results of this study, (R4) is suggested as the probable pathway to NPF. Page 10, line 24. Vapour pressure estimates are given. Page 11, line 14. SO₃ role is not overall ruled out. The statements concerning SO₂ are restricted to low SO₂ concentration conditions. Table 2. The optimized energies of the reactants and first ozonides are included in the table. Figure 2 includes experimental gas-phase profiles for SO₂ and O₃. Figure 3 includes the O₃ experimental profile. Figure 5a. Reactants and the first ozonides have been included in the mechanism scheme. New figures, S1 and S3, have been introduced in the supporting information.

References: Jayne, J. T., Po1schl, U., Chen, Y., Dai, D., Molina, L.T., Worsnop, D.R., Kolb, C.E., Molina, M. J.: Pressure and Temperature Dependence of the Gas-Phase Reaction of SO₃ with H₂O and the Heterogeneous Reaction of SO₃ with H₂O/H₂SO₄ Surfaces. *J. Phys. Chem. A*, 101, 10000-10011, 1997. Kurtén, T., Lane, J. R., Jørgensen, S., Kjaergaard, H. G.: A Computational Study of the Oxidation of SO₂ to SO₃ by Gas-Phase Organic Oxidants. *J. Phys. Chem. A*, 116, 6823-6830, 2011. Metzger, A., Verheggen, B., Dommen, J., Duplissy, J., Prevota, A. S. H., Weingartner, E., Riipinen, I., Kulmala, M., Spracklend, D. V., Carslaw, K. S., Baltensperger, U.: Evidence for the role of organics in aerosol particle formation under atmospheric conditions. *PNAS*. 107, 6646-6651, 2010. Murphy, D., M. and Koop, T.: Review of the vapour pressures of ice and supercooled water for atmospheric applications, *Quart. J. Royal Meteorol. Soc.*, 131, 1539–1565, 2005. Vereecken, L., Harder, H., Novelli, A.: The reaction of Criegee intermediates with NO, RO₂, and SO₂, and their fate in the atmosphere, *Phys. Chem. Chem. Phys.*, 14, 14682–14695, 2012.

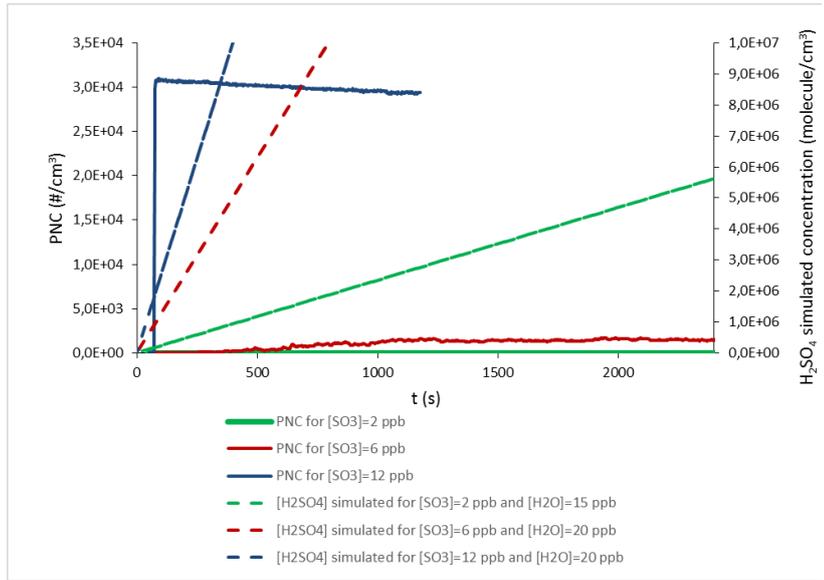
Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/acp-2016-891/acp-2016-891-AC2-supplement.pdf>

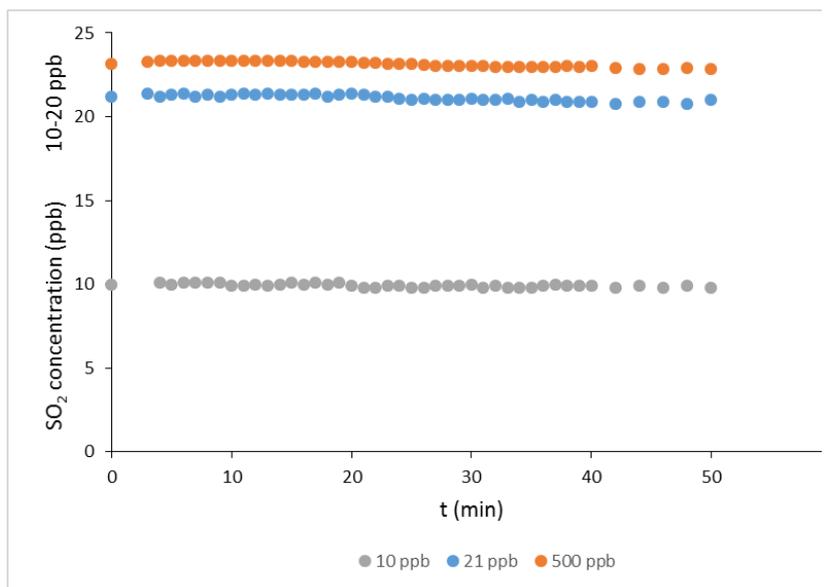
C5

Interactive comment on *Atmos. Chem. Phys. Discuss.*, doi:10.5194/acp-2016-891, 2016.

C6



C7



C8