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Atmospheric Chemistry and Physics Discussions

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 sCI 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 sCI (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 the dried synthetic air is below 1x107molecule 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 H2O + SO3 → H2SO4 exhibits a second-order dependence on water vapor concentration, the first-order rate coefficient for the SO3 loss being k= 3.90x10-41exp(6830.6/T)[H2O]2 (Jayne, 1997). Taking into account that the approximate H2SO4 gas phase concentration able to nucleate is around 5x106molecule 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 20ïĆś10ppb. 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

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= 8.5x10-6s-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: SO2 → SO3 k= 8.5x10-6s-1 [SO2]o = 10ppb And then SO3 would exclusively react with water to produce H2SO4: H2O + SO3 → H2SO4 k= 3.90x10-41exp(6830.6/T)[H2O]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 5x106molecule 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.

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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, 5x1011molecules 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.

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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.

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Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/acp-2016-891/acp-2016-891-AC2-supplement.pdf

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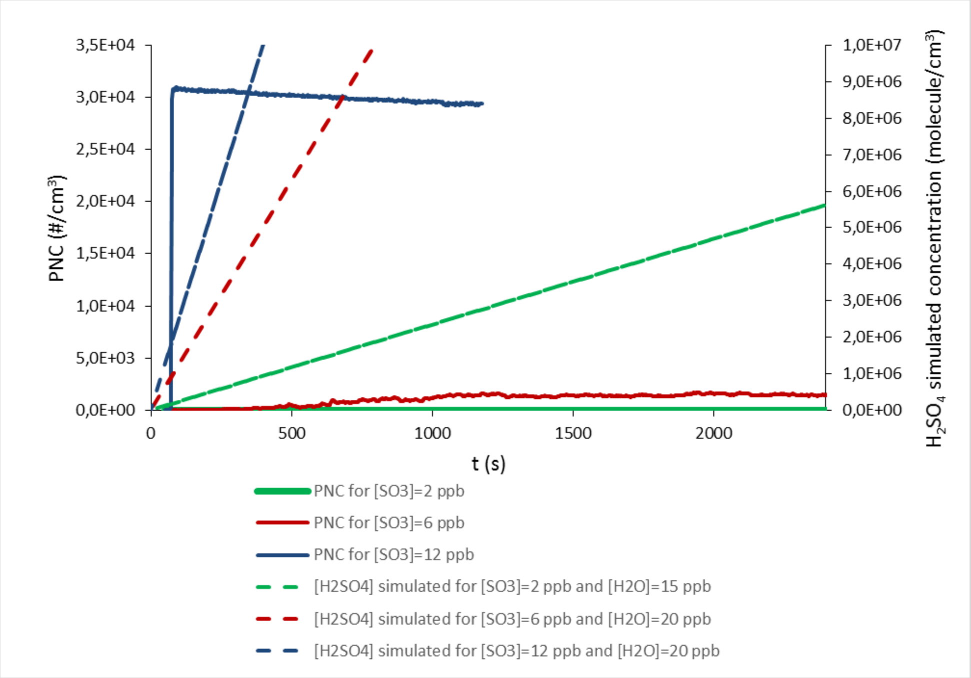

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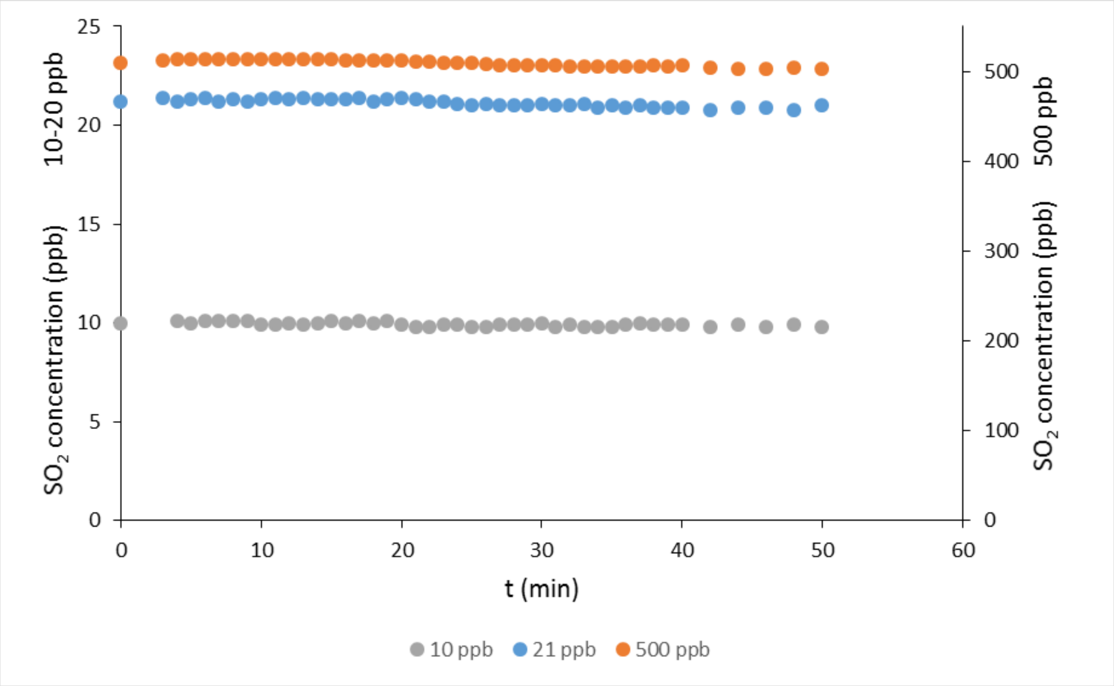
25
20
15
10
5
0
10-20 ppb
SO$_2$ concentration (ppb)
500
400
300
200
100
0
500 ppb
SO$_2$ concentration (ppb)
0
10
20
30
40
50
60
t (min)
● 10 ppb
● 21 ppb
● 500 ppb