

We thank the Referee for the very insightful comments. We have revised our manuscript according to the suggestions of the Referee's comments and our responses to the comments are as follows. Referee's comments are in black, authors' responses are in blue, and changes to the manuscript are in red color text.

This paper presents results from a series of simulation chamber experiments on the formation of secondary organic aerosol (SOA) from the photooxidation of furan. SOA yield was found to vary with both VOC/NO_x ratio and relative humidity. Some information on the chemical composition of the SOA is presented, along with possible chemical mechanisms for the generation of several of the identified species. The experiments appear to have been conducted appropriately, however there are some aspects of the data interpretation that need to be clarified and/or improved prior to publication.

1. The effect of relative humidity in increasing SOA yield seems to be very similar to that reported for p-xylene by Healy et al. (2009), who proposed that the increase in relative humidity results in higher levels of HONO formation in the chamber which leads to increased OH concentration, a faster p-xylene decay rate, and higher aerosol mass yields. Could the same effect be happening here? Was there a change in the rate of decay of furan as the relative humidity was increased through experiments 6-12?

Author reply:

According to the Referee's suggestions, we have added a figure of relationships between relative humidity and OH concentration as well as the degradation profile of furan under different RH conditions. The effects of RH conditions on OH concentration and SOA formation found in the present study are similar to those reported by Healy et al. An increasing trend of OH concentration and a faster decay rate of furan were observed as RH increased, as shown in Fig. S3. It is possible that the faster rate of gas phase oxidation under higher OH concentrations would lead to

the generation of less volatile compounds as presented previously (Chan et al., 2007). This part has been revised on page 9 and page 13.

Page 9, line 28:

“It is worth note that under high RH conditions, as shown in Fig. 1, the NO₂ hydrolysis (reaction (R11)) can generate nitrous acid (HONO), which has been considered as a major source of OH. As indicated in Fig. 4, the SOA yields obtained in the present work clearly show a gradual increase with RH. Also shown in Fig. S3 is the dependence of OH and furan concentrations on RH during the experiments determined from the decay of furan using a reaction rate coefficient of $k(\text{OH}+\text{furan}) = 4.01 \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ (Atkinson et al., 1983). It is therefore probable that the increase of RH results in high levels of HONO formation in the chamber, which leads to an increase in OH concentration, a faster furan decay rate, and higher aerosol mass yields. This result is in reasonable good agreement with previous studies, which proposed that the amount of products that can partition into the particle phase increases with the increasing rate of hydrocarbon oxidation (Healy et al., 2009; Chan et al., 2007). Moreover, the increasing RH might also enhance the SOA formation due to the fact that the functionalized gas phase components were more favoured to condense on the surface of wet particles (Liu et al., 2019).”

Page 14, line 8:

“As shown in Fig. S3, an increase in RH leads to higher OH concentrations resulting from higher HONO levels generated by the reaction of NO₂ with H₂O. Previously, Anglada et al. confirmed, using quantum mechanical calculations, that the water component could increase the OH production (Anglada et al., 2011). The positive correlation between initial water vapour concentration and OH concentration has also been previously observed experimentally (Healy et al., 2009; Tillmann et al., 2010). Additionally, Healy et al. have also reported that increasing OH concentration promoted the decay of VOC and enhanced SOA formation (Healy et al., 2009). Similarly, in the present work, a faster decay rate of furan was also observed as RH

increased, as shown in Fig. S3. It is possible that the faster rate of gas phase oxidation under higher OH concentrations will lead to the generation of less volatile compounds as presented previously (Chan et al., 2007). A higher OH concentration promotes oxidation reactions, influences the distribution of organic products, and facilitates the SOA formation (Sarrafzadeh et al., 2016).”

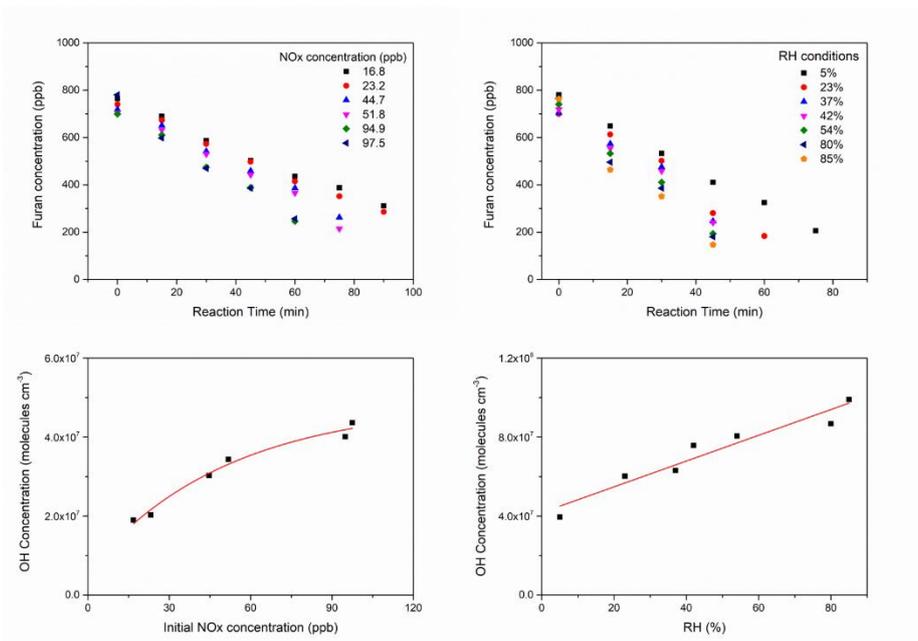


Figure S3: Relationship between relative NOx concentrations, humidity, and steady OH concentration in the furan photooxidation experiments performed under different NOx levels and RH conditions. The OH concentration was calculated based on $[OH] = \ln \frac{[furan]_0}{[furan]_t} / kt$, $k = 4.01 \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ (Atkinson et al., 1983).

2. A similar kinetic effect may also be occurring in experiments 1-5 where the VOC/NOx ratio was varied. Nitrous acid (HONO) is the main source of OH produced by heterogeneous reaction of nitrogen dioxide with water at the walls of the reactor. When NOx is increased, it is mainly in the form of NO₂ and this may result in more OH formation, faster furan oxidation and more SOA formation. The authors should check the rate of furan decay in this subset of experiments and report/interpret accordingly.

Author reply:

As suggested by the Referee, the relationship between NO_x level and OH concentration as well as the degradation profile of furan have been added in Fig. S3. Experiments conducted under different NO_x levels indicate that the OH concentration was controlled by the NO_x level if there were no additional OH precursors added before the experiment. As shown in Fig. S3, the OH concentration exhibits a gradual increase with the increase of NO_x concentration and there appears to be a correlation between NO_x concentration, OH concentration and SOA yield. Therefore, the increase of SOA yield was attributed to an increase of OH concentration, which was affected by OH recycling (reaction (R6), Fig. 1) and thus contributed to the enhancement of SOA formation.

Page 9, line 8:

“the concentration of OH radicals produced *in situ* in the present study before additional source of OH was insufficient to produce a considerable amount of SOA under low-NO_x conditions. As shown in Fig. S3, the OH concentration exhibits a gradual increase with NO_x concentration and there appears to be a correlation between NO_x concentration, OH concentration and SOA yield. Therefore, at low-NO_x conditions, the increase of SOA yield was attributed to an increase of OH concentration, which was affected by OH recycling following reaction (R6) (see Fig. 1) and contributed to the enhancement of SOA formation. This result is consistent with a previous study concerning the impact of NO_x and OH on SOA formation from β-pinene photooxidation, which has proved that the positive correlation between SOA yield and NO_x levels ($[VOC]_0/[NO_x]_0 > 10$ ppbC/ppb) was caused by the NO_x-induced increase of OH concentration (Sarrafzadeh et al., 2016b).”

Page 13, line 24:

“Experiments conducted under different NO_x levels indicate that the OH concentration is controlled by the NO_x level if there is no additional OH precursor added before the start of the experiment. As shown in Fig. S3, an increase in NO_x

level results in more OH generation and a faster furan decay rate. This justifies the observed higher SOA mass concentration and higher SOA yield.”

Minor Comments:

1. The abstract is written in a generic manner and should be re-written to contain information specific to this work. For example, it is stated that the reaction conditions affected SOA yields. But it should state something like “varying VOC/NO_x ratios over the range 48 to 8 cause SOA yields to increase from 0.04% to 0.5% under dry conditions”. Some similar statements should be used to report the influence of relative humidity.

Author reply:

We thank the Referee for this suggestion. We have re-written this section as:

“Atmospheric furan is a primary and secondary pollutant in the atmosphere, and its emission contributes to the formation of ultrafine particles. We investigate the effects of NO_x level and humidity on the formation of secondary organic aerosol (SOA) generated from the photooxidation of furan in the presence of NaCl seed particles. SOA mass concentration and yield were determined under different NO_x and humidity levels. A significant difference is observed both in the variation of SOA mass concentration and SOA yield with the initial experimental conditions. Varying VOC/NO_x ratios over the range 48.1 to 8.2 contributes to the effective formation of SOA in the presence of NaCl seed particles, with the SOA mass concentration and SOA yield ranging from 0.96 μg m⁻³ to 23.46 μg m⁻³ and from 0.04 % to 1.01 %, respectively. We found that there was a favourable relationship between the SOA yields and NO_x concentration. Especially, the increase of SOA yield with increasing NO_x concentration was continuously observed at high NO_x levels owing to a corresponding increase of the amount of low-volatility hydroxyl nitrates and dihydroxyl dinitrates that can partition into particle phase. In addition, varying RH from 5% to 88% increased the SOA yield from 1.01% to 5.03%. The enhanced SOA

formation from humid conditions may result from the high OH concentration, rapid furan decay rate, enhanced carbonyl-rich products condensation, and the aqueous-phase reactions. Using hybrid quadrupole-orbitrap mass spectrometer equipped with electrospray ionization (HESI-Q Exactive-Orbitrap MS), three carbonyl-rich products and three kinds of organonitrates were identified in the collected SOA. Based on the MS analysis and FTIR spectra, the reaction mechanism of furan photooxidation was proposed. This study demonstrates the effects of NO_x and humidity on SOA formation during the furan-NO_x-NaCl photooxidation, and provides new insights into the oxidation regime and SOA composition in furan photooxidation. The results also illustrate the importance of studying SOA formation over a comprehensive range of environmental conditions. Only such evaluations can induce meaningful SOA mechanisms to be implemented in air quality models.”

2. On page 2 (line 27), it is mentioned that several studies have previously investigated SOA formation from furan, but they appear to focus only on kinetic and mechanistic aspects.

Author reply:

We have revised this sentence as follows:

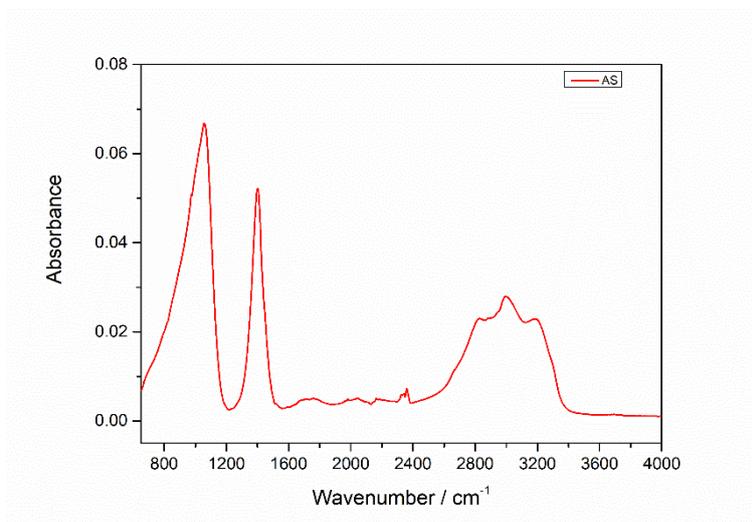
“Although the determination of kinetics and products of furan oxidation has been performed (Cabanas et al., 2004; Liljegren and Stevens, 2013; Tapia et al., 2011), the influence of several factors including NO_x level and relative humidity on SOA formation from furan has not been well examined.”

3. On page 3 (line 26), it is mentioned that sea salt particles are the second most abundant particles in the atmosphere. This statement is seemingly used to justify the use of NaCl as seed particles, while it is more common to use ammonium sulfate as seeds in SOA formation experiments. Given that furan is a product of biomass burning and is also more likely to be released in urban environments than marine

environments, the use of NaCl as seeds seems rather odd. The authors should provide some more reasons why NaCl particles were used as seeds.

Author reply:

We agree that ammonium sulfate is more commonly used as seeds in smog chamber simulations compared to NaCl. But concerning the strong absorption of ammonium sulfate in mid-infrared region, the addition of ammonium sulfate would interfere the assignment of the functional groups in the FTIR spectra. Specifically, the following figure shows the characteristic peaks of ammonium sulfate: the stretching modes of the SO_4^{2-} ion are at 1089 and 975 cm^{-1} ; the broad band between 3400 and 2800 cm^{-1} is assigned to NH_4^+ stretching. However, NaCl does not have the absorption band in mid-infrared region. Consequently, we decided to choose NaCl as seeds in the present experiment. To remove any confusion regarding the use of NaCl seed particles, the statement has been modified as:



“All the experiments were conducted in the presence of NaCl seed particles, which acted as the nuclei and provided sufficient seed surface area at the beginning of the reaction to suppress the effects of vapour wall losses of semi/low-volatility species.”

References

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