

## ***Interactive comment on “Effect of relative humidity on SOA formation from isoprene/NO photooxidation: role of particle-phase esterification under dry conditions” by H. Zhang et al.***

### **Anonymous Referee #2**

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This manuscript presents a study of the effect of relative humidity (RH) on the mass of Secondary Organic Aerosols (SOA) produced by isoprene, performed in an outdoor smog chamber. In a way, this study is the next step to the study of Surratt et al. (2010) where, in addition to identifying the products involved in SOA formation, the SOA mass is considered. This study is therefore very relevant for atmospheric chemistry currently. But while the experimental work presented is generally of good quality, I have some serious concerns about the very limited number of experiments performed (4 in total). In comparison, other studies of the same topic (Dommen et al., 2006)

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have involved 17 experiments ! It is not clear that a discussion or conclusion can be based on such a limited dataset and therefore that this work is publishable. Perhaps the only way to compensate for the limited dataset would be to compare the results with those of previous works to confirm the trends observed here (see below). In addition, the discussion of the mechanisms is at odd with some basic facts of inorganic and organic chemistry. Thus, the title of this paper could be unfortunate, as esterifications are unlikely to explain the observations. Finally, some works directly relevant to this study (effect of RH on SOA yield), which have not been quoted, must absolutely be discussed. In conclusion, the editor would have to decide if this paper is publishable in view of the limited dataset. But, should it be the case, it is essential that the issues addressed below are completely answered before publication can be considered.

Detailed comments:

1) Insufficient dataset and comparison with Dommen et al., 2006

The main concern about this work is the small number of experiments. While a trend between the SOA mass produced and RH can be seen, it is rather small (less than a factor 2) and borderline from being significant. The concentrations of isoprene and NO have almost the same effect on SOA mass than RH, which add some uncertainties in the results. Moreover, no detail is given on how the SOA mass is determined (see comment below), but it is also likely to include large uncertainties. The discussion - and the entire paper - being based on these 4 experiments, it is not clear that this work is publishable.

At the very least this paper should discuss other works which have examined the SOA mass from isoprene as function of RH: Dommen et al., (2006). This study is barely mentioned and no comment is made on how the results compare. Yet, this previous work might be the only way to compensate for the limited dataset: Two plots comparing the results from this paper and Dommen et al. (2006) are attached to this review and show how the discussion could be made and would benefit this paper. The first plot,

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“SOA mass”, shows that the SOA masses obtained in this work are generally consistent with the “high NO” (> 280 ppb) data from Dommen et al., which reinforces the present discussion of a “high NO<sub>x</sub>”-type mechanism involving MPAN and MG. In addition, this plot shows that the SOA mass varies almost as the square of the initial concentration of isoprene (in fact, slightly below order 2), suggesting that most of the SOA mass is under the form of “dimers”, such as 2-MG. The SOA mass produced at lower NO concentration seems, however, to vary with a higher degree in [isoprene]<sub>0</sub> suggesting the implication of larger “oligomers”.

The second plot, “RH”, confirms that, once the SOA mass is divided by the square of [isoprene]<sub>0</sub>, it does vary inversely with RH, the results of the present work being consistent with those of Dommen et al. (2006) (note, however, that RH was not varied in the high NO experiments of Dommen et al. (2006), and these points are thus not shown). This strongly reinforces the main conclusion of this paper and shows the interest of discussing this previous study.

## 2) Experimental determination of SOA mass

No detail is given in the Experimental section on how the SOA mass was determined. This is essential because this is likely to include some uncertainties impacting the results. In addition, as pointed out by Reviewer 1, it would be important to know if a potential uptake of water has been taken into account.

## 3) Discussion of other relevant studies

While the introduction discusses other studies of SOA mass vs RH (for aromatics, for instance) and even the potential role of glyoxal in isoprene SOA, the study of SOA formation from glyoxal by Volkamer et al., 2009 is completely overlooked. This previous work evidenced an effect of the liquid water content of the aerosol on the SOA yield, directly relevant to the present work. This would also reinforce this paper, even though the trend reported is opposite, as an effect of RH on SOA yield is demonstrated. A discussion of this work (albeit short) is indispensable in this paper.

#### 4) pH and reaction mechanisms

Some of these points were already addressed in my preliminary review.

The identification of the products in the SOA at high and low RH is probably the most interesting results of this work. However, some aspects of the discussion of the possible mechanisms are plagued by some misconceptions.

- the main explanation proposed for the differences in SOA mass between low and high RH is that the seeds are more acidic at low RH, which should enhance esterification reactions (by acid catalysis). Unfortunately, by definition, the pH of ammonium sulfate seeds can not be lower than 5, the value at saturation. This can hardly be considered as "acidic". Moreover, this value can not change significantly between RH = 15 % and RH = 90 % because, in order to change, the particles have to take up large amounts of water, causing an increase of volume and a "dilution" toward pH = 7. But such water uptake occurs only above critical supersaturation, i.e. well above RH = 100% for ammonium sulfate. The pH of the seeds in these experiments was therefore close to 5 over the entire range of RH. This should be easy to confirm with measurements.

- Another aspect to take into consideration is that at RH = 15- 42 % a large fraction of the ammonium sulfate particles are likely to be solid, according to the phase diagram of Xu et al., J. Phys. Chem. B, 102, 7462, 1998.

- The discussion of the reaction mechanisms in this paper starts from the assumption that esterifications are involved, because the previous work of Surratt et al., (2010) proposed (but did not prove) that esterifications were involved in these processes. Esterification reactions are well known to be extremely slow, as supported by a plethora of literature. For instance, under typical aerosol conditions, the kinetics experiments of Minerath et al. 2008 showed that they would have a typical half-life of 4600 days. Thus, unlike what is discussed in the text, they are extremely kinetically limited. And at pH = 5- 7 these reactions would be nowhere near observable in these experiments.

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Other reactions, however, would be favored in “less aqueous” media: dehydrations, for instance, but not only. Moreover, other products of the same brut formula than 2-MG and the higher “oligomers” proposed in Surratt et al. (2010) could account for the exact masses found in the SOA – and results from reactions very different from esterification. The discussion is still open. But the title of this manuscript could turn out to be unfortunate once these mechanisms are elucidated. I would suggest the authors to use more caution in the title and refer to the high-molecular weight products or “oligomers” rather than to the reactions.

Minor comments:

- at several places in the text, references to Paulot et al. (2009) are inappropriate. For instance, in the introduction (li 11), referring to Paulot et al. for global estimates of SOA from isoprene is not justified. Only global models can do that. Also, on li. 27-28, it is incorrect that Paulot et al. has elucidated SOA formation mechanisms. This work focused exclusively on gas-phase mechanisms and only suggested that the results could bring some explanation on the SOA formation, nothing more.

- the reference to Froyd et al., 2010 to support a SOA enhancement due to organosulfates (li. 14 of p. 5410) is not correct either. Froyd et al. reported atmospheric observations, not chamber studies, and could thus not observe an “enhancement”. The next sentence is fully correct, but the term “ambient” should be replaced by “high-altitude”, since these measurements were made in the free troposphere-lower stratosphere.

- References to the gas-phase oxidation mechanism of isoprene and the formation of MACR and MPAN are off. These mechanisms have been elucidated well before the 2000’s. For MACR: Paulson, Flagan, Seinfeld, “Atmospheric photooxidation of isoprene”, Int. J. Chem. Kinet., 24, p. 79 and 103 (2 articles), 1992 and Paulson and Seinfeld, “Development and evaluation of a photooxidation mechanism for isoprene”, JGR, 97, 20703, 1992. For MPAN: Bertman and Roberts, “A PAN analog from isoprene photooxidation”, GRL, 18, 1461, 1991.

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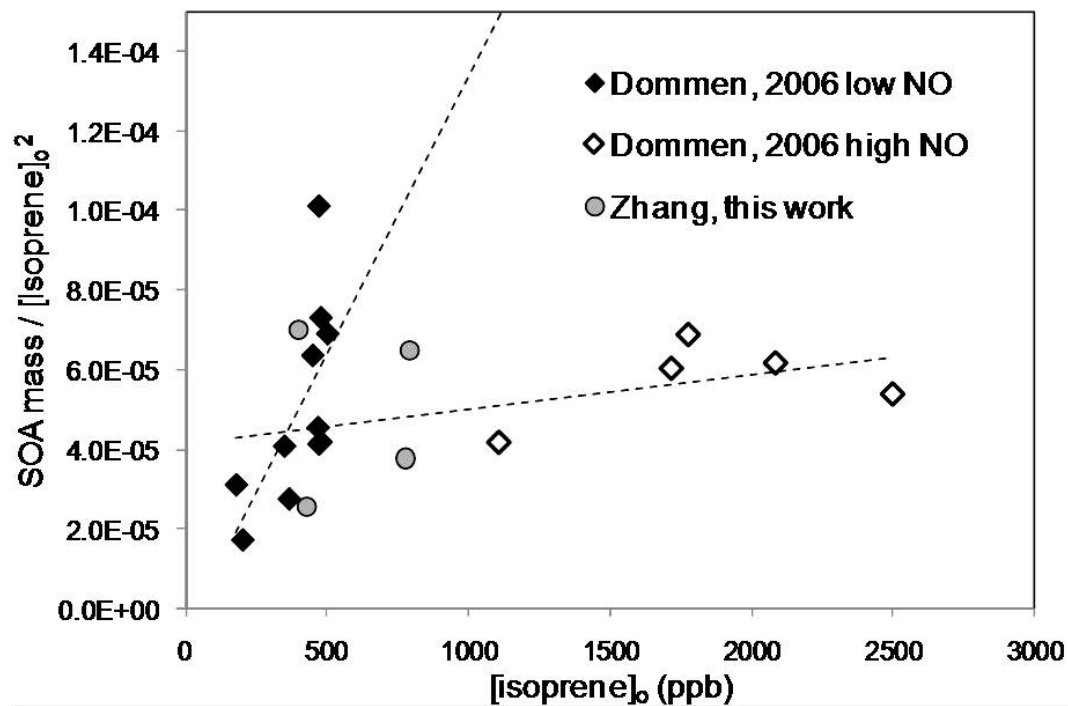


Fig. 1.

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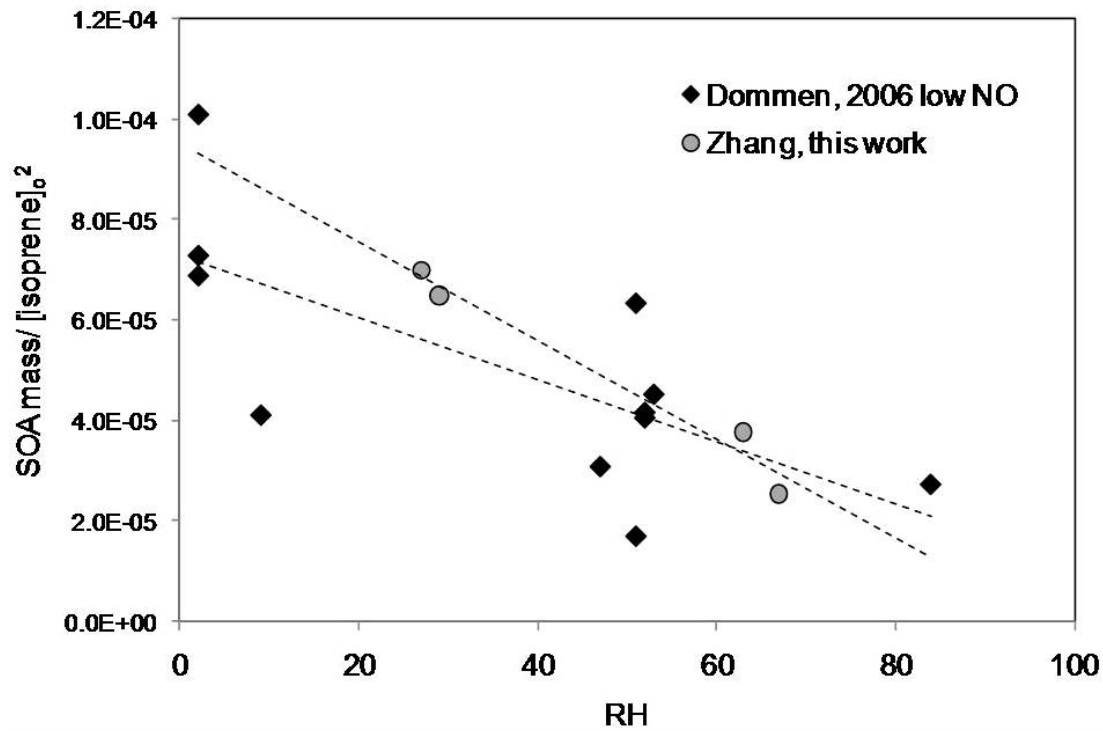


Fig. 2.

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