Different roles of water in secondary organic aerosol formation from toluene and isoprene

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Abstract. Roles of water in the formation of secondary organic aerosol (SOA) from the irradiations of toluene-NO_2 and isoprene-NO_2 were investigated in a smog chamber. Experimental results show that the yield of SOA from toluene almost doubled as relative humidity increased from 5% to 85%, whereas the yield of SOA from isoprene under humid conditions decreased by 2.6 times as compared to that under dry conditions. The distinct difference of RH effects on SOA formation from toluene and isoprene is well explained with our experiments and model simulations. The increased SOA from humid toluene-NO_2 irradiations is mainly contributed by O−H-containing products such as polyalcohols formed from aqueous reactions. The major chemical components of SOA in isoprene-NO_2 irradiations are oligomers formed from the gas phase. SOA formation from isoprene-NO_2 irradiations is controlled by stable Criegee intermediate (SCI) that is greatly influenced by water. As a result, high RH can obstruct the oligomerization reaction of SCI to form SOA.

1 Introduction

Water is an important environmental factor that can influence the formation of secondary organic aerosol (SOA) through the physical or chemical processes, and is often represented with relative humidity (RH) or liquid water content (LWC). Toluene and isoprene are two important precursors of SOA, which are representatives of volatile organic compounds (VOC) from anthropogenic and biogenic sources. Both toluene and isoprene can produce glyoxal during their oxidation processes in the atmosphere. As widely reported, glyoxal is a typical precursor of SOA formed in the aqueous phase (Volkamer et al., 2009;

Lim et al., 2010,2013; Ervens et al., 2011; Shen et al., 2016). The difference is that toluene contains an aromatic ring, which is mainly oxidized by OH radicals, while isoprene contains two C=C bonds, which can also be oxidized by O_3 in addition to OH. Thus, toluene and isoprene can provide insight into the roles of water in SOA formation from different kinds of VOCs.

Sadezky et al. (2006, 2008) reported that SCIs (CH_2OO, C_2H_4OO, C_3H_6OO and C_4H_8OO) play a central role in SOA formation from the ozonolysis of ethyl butenyl ether, trans-3-hexene, 2, 3-dimethyl-2-butene, and trans-4-octene. They further suggested that SCI-derived oligomers are formed by the reactions of RO_2 with SCI. Sakamoto et al. (2013) showed that the reactions of SCI (CH_2OO) with hydroperoxides (ROOH) from ethylene can form SOA. Inomata et al. (2014) showed that the reaction of an SCI with carboxylic acids or hydroperoxides can contribute to SOA formation from the ozonolysis of isoprene. Zhao et al. (2015, 2016) also showed that the SOA generated from the ozonolysis of trans-3-hexene and α-cedrene is primarily composed of oligomers formed from the addition of SCI to RO_2 radicals. Although these studies have demonstrated the importance of SCI-derived oligomers in SOA formation from the ozonolysis of alkenes, the role of SCIs in SOA formation from isoprene-NO_2 irradiations has not been reported.

RH has a positive correlation with the mass yield of SOA from aromatics, such as p-xylene (Healy et al., 2009), toluene (Kamens et al., 2011; White et al., 2014) , o-, p-xylene (Zhou et al., 2011), benzene and ethylebenzene (Jia and Xu, 2014). This has been mainly attributed to aqueous-phase reactions, such as active uptake of glyoxal in particle water. An exception is from the study of Cocker et al. (2001) who found that the yield of SOA from m-xylene and 1,3,5-trimethylbenzene in the presence of propene was unaffected by RH (5% and 50%). This is probably due to the presence of propene in their reaction systems, which can reduce the OH radicals, leading to the decrease in the yield of SOA (Song et al., 2007).

SOA from isoprene has been widely studied, as summarized by Carlton et al. (2009). An earlier study from Dommen et al. (2006) showed that RH had little effect on the SOA yield from isoprene-NO_x (NO, NO_2) irradiations in the absence of seed particles at 2% and 84% RH. A study from Zhang et al. (2011a) showed that RH had a negative effect on SOA formation from isoprene-NO_x irradiations with seed particles of $(NH_4)_2SO_4$ under two RH conditions (15-40% and 40-90%) and ascribed the rise of SOA yield under lower RH to the enhancement of 2-methylglyceric acid (2-MG) and its corresponding oligomers. Nguyen et al. (2011) found that RH did not affect the yields of SOA from isoprene in their isoprene-NO_x-H_2O_2 irradiations

without seed particles under dry (2%) and humid (90%) conditions, but they observed enhancement of 2-MG -derived oligomers under low RH, which is consistent with Zhang et al. (2011a). Zhang et al. (2012) studied SOA formation from methacrolein (MACR, one of major products from isoprene) under different ratios of MACR/NO. Their results showed that the effect of RH on formation of SOA depended on the yields of SOA precursors (e.g. methacryloyl peroxynitrate, MPAN).

In addition, isoprene-derived organosulfates (Zhang et al., 2011a; Zhang et al., 2012) and isoprene epoxydiols (IEPOX) - derived products (Nguyen et al. 2014) are enhanced under higher RH. A recent study from Lewandowski et al. (2015) showed that the aerosol yield from isoprene-NO irradiations decreased with increasing RH (9% to 49%). The role of water in SOA formation is so complex that more research is still required to understand mechanisms of SOA formation.

MPAN is one of key precursors of SOA from isoprene under high NO_x conditions (Surratt et al., 2010), which can react with OH to produce epoxides (methacrylic acid epoxide (MAE), hydroxymethyl-methyl-a-lactone (HMML)). Lin et al. (2013) reported that MAE was an important precursor to 2-MG, a tracer of isoprene-derived SOA. Nguyen et al. (2015) showed that HMML could form SOA. Since SCIs, IEPOX, MPAN, HMML and MAE co-exist in isoprene-NO_2 irradiations, there are cross reactions in the system. Thus, the study is still needed to demonstrate the role of these precursors in oligomer formation from isoprene-NO_2 irradiations.

Both toluene and isoprene can produce glyoxal during their oxidation processes. Why was the positive effect of RH on the SOA yield of isoprene not observed? We consider that different chemical processes are likely responsible for the different effects of RH on the SOA yields from toluene and isoprene. One of the most important differences between isoprene and toluene reaction systems is oxidation pathways. To clarify the different mechanisms of SOA formed under different humid conditions, this paper presents the experimental results of mass yields and chemical components of SOA from toluene and isoprene under controlled RH conditions, as well as the explanation of the mechanism of SOA formation.

2 Experimental section

All the experiments were carried out in a 1.3-m^3 FEP reactor (DuPont 500A, USA). The equipment and experimental

procedures were similar to our previous works (Jia and Xu, 2014, 2016; Ge et al., 2017). Thus, only a brief introduction is given here. Two ionizing air blowers were around the reactor to remove the electric charge on the surface of the reactor. A light source was provided by black lamps (F40BL, GE, USA), with a center wavelength of 365 nm. The photolysis rate of NO_2 was determined to be 0.35 min^{-1} inside the reactor. The humidity was controlled by bubbling the high pure water (18.2 MΩ.cm at 25 ℃, Millipore /Direct-Q3) with background air. NaCl seed particles were prepared by a constant output atomizer (Model 3076, TSI, USA).

Background air was prepared by a Zero Air Supply (Thermo model 111 and model 1150, USA) with 3 additional VOC traps (BHT-4, Agilent). NO_x, O_3 and SO_2 were measured by corresponding analyzers of Thermo model 42C, model 49C and model 45i (trace level). The concentrations of NO_x, O_3 and SO_2 in background air were determined to be less than 1 ppb. The particles in background air could not be detected with SMPS in the absence of irradiations, but the particle number concentration of 10^4/cm^3 was obtained at an irradiation time of about 5 hrs. It was considered from some experiments and model simulations that the particles were H_2SO_4 (less than 1 μg/m^3), which was formed from oxidation of SO_2 by OH radicals.

Gas-phase organics were measured with a gas chromatograph-mass spectrometer (GC-MS: Agilent model 7890A GC and Agilent model 5975C mass selective detector, USA), which was equipped with a thermal desorber (Master TD, Dani, Italy). Particle number and mass concentrations were determined by SMPS (TSI model 3936, composed by DMS TSI 3080 and CPC TSI 3776).

LWC was determined following the method of the reduced Dry-Ambient Aerosol Size Spectrometer (DAASS) (Engelhart et al., 2011). During the dry mode, the SMPS was modified by adding a large diameter Nafion dryer (Permapure MD-700-48F-3, the RH of the sample air can be reduced from 85% to 3.5%) to the sampling inlet and a multi-tube Nafion dryer (Permapure PD-200T-24E-M, the RH of sheath can be reduced from 85% to 7%) to sheath flow. During the humid mode, the humid air in SMPS was quickly replaced by humid air in the chamber by venting the sheath air at 10 L/min, and then the humid aerosol was measured by SMPS. As a result, the LWC was determined by the difference of the particle mass concentrations between dry and humid modes.

To analyse the chemical components of SOA, the particles ranged from 100 to 650 nm were collected on a 25 mm disk using

a Dekati low-pressure impactor (DLPI, Dekati Ltd., Finland) at 10 L/min. Organic functional groups of SOA were measured by a Fourier transform infrared spectroscopy apparatus (FTIR, Nicolet iS10, Thermo Fisher, USA). The mass spectra of SOA were measured by electrospray ionization high-resolution mass spectrometer (ESI-HRMS, Exactive-Orbitrap mass spectrometer, Thermo Fisher Scientific). The average molecular size information of the humic-like substances (HULIS) present in SOA was determined by UV-Vis spectroscopy (Perkin–Elmer Lambda 25, USA) based on the ratio of E2/E3, in which E2 and E3 denote the absorbance at 250 nm and at 365 nm, respectively (Peuravuori et al., 1997; Duarte et al., 2005).

The liquid reactants of toluene (Xilong Chemical Co., Ltd., 99.8% purity), isoprene (Alfa Aesar, 99.9% purity) or H_2O_2 (30 weight % in H_2O) were injected into the airline and were evaporated with background air. NO_2 (520 ppm in N_2, Beijing Huayuan Gas Company) was injected into the reactor directly. For the experiments of the oxidation of isoprene by OH, OH radicals were generated from the photolysis of H_2O_2 by UV lights (UVA-340, Q-Lab Corporation, USA). For the experiments of isoprene-O_3 dark reaction, O_3 was produced by an ozone generator with pure O_2 (99.995%). N-hexane (>97% purity, Beijing Tongguang Fine Chemicals Company) was used as an OH scavenger in the ozonolysis of isoprene. To evaluate the possible contributions of SOA from n-hexane in the ozonolysis of isoprene with n-hexane, two experiments of the irradiations of hexane-H_2O_2 were performed for 6 hours, in which no SOA was observed by SMPS under both dry and humid conditions.

The initial conditions and purposes for the experiments are listed in Table 1, most of which are the irradiations of toluene-NO_2 and isoprene-NO_2. The initial concentrations of isoprene and toluene were about 0.90 and 0.85 ppm respectively, and initial NO_2 concentrations were about 320 ppb. At the end of each experiment, isoprene was almost completely consumed after 6-h reactions, and about 400 ppb of toluene was reacted at the end of 7-h reactions. The RH was controlled to be dry (6~10% RH) or humid (78~88% RH) conditions for different experiments. Two sets of experiments with artificially added NaCl seeds (about 10 μg/m³) were performed to quantify the role of particle water on SOA formation in humid toluene and isoprene reactions. To find out how RH affects the oxidation pathways of isoprene by OH and O_3 in isoprene-NO_2 irradiations, additional experiments of isoprene-H_2O_2 irradiations and isoprene-O_3 reactions were carried out. The initial H_2O_2 and O_3 concentrations were around 5 and 1.5 ppm, respectively.

To evaluate the potential contribution of SOA precursors (e.g. glyoxal, IEPOX, MPAN, HMML, MAE and SCI) from toluene

and isoprene reaction systems, a model of the Master Chemical Mechanism (MCM v3.3.1, website: http://mcm.leeds.ac.uk/MCM, Jenkin et al., 2015) was used, which includes the chamber dependent reactions. To examine the influence of RH on oligomer formation from SCI, the reactions of SCI with carbonyls were added to MCM, which were expressed with $X+SCI=X(SCI)_1$, $X(SCI)_1+SCI=X(SCI)_2$... $X(SCI)_{n-1}+SCI=X(SCI)_n$, where $n=1$-10 and X represents carbonyls. The rate constant for these reactions was set to be 5×10^{-12} cm^3 molecule^{-1} s^{-1} (Vereecken et al., 2012). Since most of RO_2 was consumed by NO_x, $SCI+RO_2$ reactions were not included in our model. The carbonyls were chosen based on the results of mass spectra data from isoprene-NO_2 irradiations shown in section 3.4.1. A set of ordinary differential equations was built and solved using Matlab.

3 Results and discussion

3.1 RH effects on SOA yields

3.1.1 Determination of LWC

The LWC in particles makes up a great percentage under humid conditions (as shown in Figure 1). To calculate the yield of SOA, the LWC has to be excluded. On the other hand, since LWC was only measured at the end of reaction, to obtain the time evolution of SOA concentrations we needed to deduct LWC during the whole reaction period. The value of LWC depends on chemical components of particles and environmental conditions (temperature and humidity). The volume growth factor (VGF) was used to estimate the contributions of LWC in particles, which was defined by Engelhart et al. (2011) as the ratio of the particle volume at humid air to the particle volume at dry air. Assuming that all the particles are spheres and have the same growth factor, the VGF is equal to the growth factor (GF) cubed as:

$$VGF = \frac{V_{hydrated}}{V_{dried}} = (\frac{D_{hydrated}}{D_{dried}})^3 = GF^3 \tag{1}$$

$V_{hydrated}$ and V_{dried} indicate the total measured volumes of hydrated or dried particles, respectively. $D_{hydrated}$ and D_{dried} are the diameter of hydrated or dried particles, respectively, calculated from their volumes.

VGF is determined to be 1.28 (GF=1.09, RH=78%) for the particles from toluene-NO_2 irradiations, 1.18 (GF=1.06, RH=79%)

from isoprene-NO_2 irradiations, 1.40 (GF=1.12, RH=77%) from isoprene-H_2O_2 irradiations, and 1.30 (GF=1.09, RH=88%) from isoprene-O_3 reaction systems. There have been many studies about the growth factor of SOA. Aklilu and Mozurkewich (2004) gave a GF range of 1.05-1.12 for atmospheric organic particles (79% RH). Stroud et al. (2004) predicted a GF of 1.1 for the organic aerosols from toluene-NO-isopropyl nitrite irradiations at 79% RH. Prenni et al. (2007) reported the GF of 1.065±0.02 at 85% RH for SOA formed from toluene. Jimenez et al. (2009) obtained GF= 1.057±0.02 at 95% RH for SOA from isoprene. In general, our results of GF are in good agreement with previous estimates, indicating that the LWC measured by our modified SMPS is reliable.

3.1.2 SOA yields

We assumed that the VGF did not change during the reaction course. Thus, the LWC from toluene and isoprene under humid conditions can be determined by VGF. Figure 2 shows that in touene-NO_2 irradiations, the mass concentrations of SOA at 81% RH are much larger than those at 10% RH, with a ratio of maximum mass concentration of SOA at 81% RH to that at 10% being 2.2. However, in isoprene-NO_2 irradiations, the mass concentrations of SOA at 80% RH are much lower than those at 7% RH, with the ratio of maximum mass concentration of SOA being 0.57, which is almost the same as that from isoprene-O_3 reactions (the ratio is 0.45). For isoprene-H_2O_2 irradiations, the mass concentrations of SOA from humid conditions are generally larger than those under dry conditions. Nevertheless, the maximum mass concentration of SOA from humid conditions is 177.9 μg/m^3 (the ratio is 1.01), which is close to that from dry conditions.

The mass yield of SOA generally increases with time. The maximum yields during the experimental course were used for the following discussion. The mean maximum yields of SOA from toluene were obtained to be 5.58±0.76% (dry) and 8.97±0.84% (humid) respectively (Figure 3). Our results are within the range obtained by other investigators (Kamens et al., 2011; Odum et al., 1997; Ng et al., 2007). Previous studies (Kamens et al., 2011; Zhou et al., 2011; Jia & Xu 2014; Wang et al., 2016) mainly ascribed the positive effect of RH on SOA yields from aromatics to LWC, which can enhance the formation of SOA by aqueous reactions, such as reactive uptake of glyoxal in aerosol water. Our yields of SOA from toluene are smaller than those from Ng et al. (2007) (around 11% at 4% RH) and Hildebrandt et al. (2009) (11-17% at 21% RH), which is probably

due to the additional and excessive OH radical sources (HONO or H_2O_2) used in their experiments. In addition, the temperature in this study is higher than the previous studies, which may be another reason accounting for the lower SOA yields in this work.

A negative effect of RH on SOA yields was observed in the systems of isoprene-NO_2-hv and isoprene-O_3. The mean maximum yields from isoprene-NO_2 irradiations are reduced from 3.14±0.35% (dry) to 1.19±0.38% (humid) (Figure 3). This negative RH effect is in good agreement with the corresponding results from Zhang et al. (2011) and Lewandowski et al. (2015). The yields of SOA from our isoprene-O_3 reactions are 3.00% (dry) and 1.40% (humid), which are quite close to the results from the isoprene-NO_2 system. While RH has very weak effect on the SOA yields from isoprene-H_2O_2 irradiations in our study. The maximum yields of SOA were determined to be 7.7% (dry) and 7.8% (humid) from photooxidation of isoprene-H_2O_2, which are in good agreement with the results (around 8%) of isoprene-H_2O_2 irradiations under dry conditions from Clark et al. (2016). A similar yields (7%) of SOA from photooxidation of isoprene-NO_x-H_2O_2 was also obtained in the results from Nguyen et al. (2011). Based on the experimental conditions in Nguyen et al. (2011), we estimated that for their reaction system over 99% of isoprene was oxidized by OH and the remaining 1% by O_3 by using simulations based on the MCM. Thus, the reaction system by Nguyen et al (2011) can be considered to be closer to isoprene-H_2O_2 system. In addition, some other previous studies (Gaston et al., 2014; Riedel et al. 2015; Zhang et al. 2018) showed that RH has a negative effect on the formation of SOA from isoprene-OH systems due to acid dilution effect. In these studies, acidic sulfate seed particles were used and the acid-catalyzed effect was very obvious. Thus, higher RH can reduce the acidity of the seed particles by particle water. In our study acidic seed particles were from a little amount of H_2SO_4 formed from the gas-phase reaction of SO_2 and OH. It was estimated that the mass concentration of H_2SO_4 particles was less than 1 μg/m^3. When liquid water content increased from 1 μg/m^3 to the maximum 54 μg/m^3 under humid conditions, the pH value was estimated to be in the range of 2 to 3.7, indicating that the pH variation was small in our experimental conditions. Therefore, compared with previous studies, the acid dilution effect was not remarkable in our work. These results show that high RH can reduce the maximum yields of SOA from the reaction channel of isoprene with O_3 (O_3 channel) and that RH has little effect on the maximum yields from the reaction channel of isoprene with OH (OH channel) without sufficiently high mass concentrations of acid particles. This shows that the

ozonolysis of isoprene is probably a key pathway influencing the SOA formation in isoprene-NO_2 irradiations. Thus, it shows that the ozonolysis of isoprene is probably a key pathway influencing SOA formation in isoprene-NO_2 irradiations in our experimental conditions, which will be further discussed in later section.

In our isoprene-NO_2 irradiations, based on the MCM simulation (Exp. 25), the amount of isoprene oxidized by OH, O_3 and NO_3 is 59%, 25% and 16% at the end of reactions, respectively. There are cross reactions when NO_2 and O_3 are both present. Thus, we cannot deduce SOA contribution simply by initial ratios of isoprene oxidized by OH and O_3. Since SOA is mainly formed by the secondary or later generation products, we can evaluate the contribution of reaction pathways to formation of SOA in terms of SOA precursors from different channels. As described previously, SCIs can be taken as the SOA precursors from the O_3 channel, while IEPOX, MPAN, HMML and MAE can be used as SOA precursors from the OH channel. The MCM simulations show that the total yield of SCIs was dominant as compared to OH channel precursors such as IEPOX, MPAN, HMML and MAE. The former accounts for 70% of total concentrations (ppb) of SOA precursors while the latter (IEPOX+MPAN+HMML+MAE) 30% at the end of reaction in isoprene-NO_2 irradiations. Therefore, even though 59% of isoprene was consumed by OH and only 25% by O_3, the formation of SOA in isoprene-NO_2 was mainly from the O_3 channel. For these three oxidation channels, RH has little effect on SOA yields from OH channel oxidization Previous studies have shown that humid has little effect on SOA formation from NO_3 oxidation of alkenes (Bonn and Moorgat, 2002; Fly et al., 2009; Boyd et al., 2015). Thus, only O_3 channel is greatly influenced by RH. The maximum possibility is that O_3 channel can produce SCIs that can be consumed by water. Thus, although most of isoprene was oxidized by OH and the SOA yield from the OH channel was over 2 (5) times greater than that from the O_3 channel under dry (humid) conditions, the O_3 channel was still a major pathway influenced by water vapor in the isoprene-NO_2 system, which will be discussed in the following section.

3.2 UV-Vis spectra of SOA

Toluene and isoprene have a similar yield of glyoxal based on MCM simulation and a close value of *VGF* in this study. Thus, it would be reasonable to expect that RH should have a positive influence on the SOA yield from isoprene. However, the yield is greatly reduced in the humid systems of isoprene-O_3 and isoprene-NO_2, and almost unchanged in isoprene-H_2O_2 irradiations.

Zhang et al. (2011a) and Nguyen et al. (2011) both reported that oligomers were greatly reduced under humid conditions, and considered that high RH suppressed the oligomerization reactions with water as a product. The molecular sizes of SOA can reveal the degree of oligomerization reactions. Thus, we used the UV-Vis spectra to determine the molecular size information of SOA indirectly. Larger molecules displayed higher absorbance in longer wavelength regions as surmised by Mostafa et al. (2014) All the spectra are characterised with a continuous absorption that increases with decreasing wavelength from 200 nm up to about 1100 nm (Figure 4), which indicates the presence of conjugated double bond molecules (such as oligomers).

We used the UV-Vis spectra to determine the molecular size information of SOA, which can provide information about oligomerization degree of molecular through the ratio of E2/E3 (absorbance at 250 nm divided by absorbance at 365 nm) indirectly. Lower E2/E3 ratios are associated with higher molecular weight (Peuravuori et al., 1997; Duarte et al., 2005). The ratios of E2/E3 are 1.27 (1.53), 1.29 (2.25), 1.69 (1.97) and 1.55 (1.73) under dry (humid) conditions from our systems of toluene-NO_2, isoprene-NO_2, isoprene-O_3 and isoprene-H_2O_2, respectively. The E2/E3 ratios show that high RH can indeed reduce molecular sizes of SOA and suppress the oligomerization reactions. Nevertheless, if the suppression of the oligomerization reactions under humid conditions is the main reason for the decrease in SOA yield from isoprene, why is the maximum yield from isoprene-H_2O_2 irradiations unchanged under humid conditions? Besides the weak acid dilution effect in our experimental conditions, there must be an intrinsic mechanism regarding the influences of RH on the SOA yield from isoprene. In addition, oligomers have been also identified as important products of SOA from aromatics, and water is a byproduct during oligomerization process (Kalberer et al., 2004; Lim et al., 2010; Gaston et al., 2014). However, a negative effect of RH on SOA yield from aromatics has never been observed. This is because there are likely competing processes that are responsible for SOA formation from aromatics under humid conditions. Oligomers are generally inhibited by higher RH, while the organics formed by aqueous reactions are enhanced.

3.3 IR spectra of SOA

3.3.1 Toluene

Figure 5 (a and b) shows the typical infrared spectra of SOA from the irradiations of toluene under both dry and humid conditions. The prominent features on SOA spectra are the board hydrogen bonded O−H stretching, the carbonyl C=O stretching, the organic nitrate (ONO_2) bands, the C−OH bands of alcohols or polyalcohol. The bands all greatly increase by over 2 times as RH increases from 10% to 81%. These changes of band strength with RH are quite similar to the changes of the SOA mass yield with RH.

To further reveal the chemical properties of the increased products formed from humid conditions, the SOA sample from humid conditions was evaporated. First, we found that the IR spectrum of SOA almost did not change after being heated at 100 ℃ for 15 minutes. Then the sample was further evaporated at 110 ℃ for 15 minutes. After the evaporation at 110 ℃, the major absorption bands were considerably changed. As a result, the spectrum is almost the same as the spectrum of SOA collected under dry conditions (Figure 5c). The major reduced absorptions are from the O−H and C−OH bands (Figure 5d). These bands are assigned to hydrates of glyoxal and other water soluble compounds in SOA (Volkamer et al, 2009; Lim et al, 2010; Kamens et al., 2011; Jia and Xu, 2014; Wang et al., 2016). Therefore, it is considered that alcohols (such as hydrates) are major contributors to toluene SOA under humid conditions.

LWC is an important factor that can greatly influence the contribution of SOA from aqueous reactions. The maximum LWC was measured to be about 44 $\mu g/m^3$ from humid toleuene-NO_2 irradiations. To determine the role of LWC in SOA formation, extra LWC was introduced into the reaction system by adding 10 $\mu g/m^3$ of NaCl particles. The initial LWC was determined to be 30 $\mu g/m^3$, and maximum LWC was 74 $\mu g/m^3$ during 6 hours of reaction. The SOA mass concentration was obtained by subtracting the mass concentrations of NaCl, $NaNO_3$ and LWC from total mass concentration of particles. Compared with the experiment without NaCl, the SOA mass concentrations increased by 16% in experiment with NaCl, and all the bands assigned to O−H, C=O and C−OH were enhanced by 50%, 29% and 35% respectively (Figure 5e). This demonstrates that the increase of LWC can greatly enhance the formation of SOA from hydration of glyoxal. Therefore, it is concluded from our study that the formation of SOA from toluene is controlled by LWC under humid conditions, and that most of SOA is formed by aqueous reactions in touene-NO_2 irradiations.

3.3.2 Isoprene

3.3.2.1 Isoprene-NO_2 system

The spectra of SOA from the irradiations of isoprene-NO_2 are characterized by the high abundance of $C=O$ and ONO_2 groups (Figure 6). There are 3 bands assigned to different kinds of $C-O$ or $C-O-O$ groups in the region of 927 -1243 cm^{-1} under dry conditions (Pretsch et al., 2009). These bands are indicators of alcohols and polymeric structures (Czoschke et al., 2003). Thus, oligomers and organic nitrates are dominant species in SOA. Under humid conditions, the absorption intensities of the bands ($O-H$, $C=O$, ONO_2, $C-O$ or $C-O-O$) are all reduced by 2 times. The tert-nitrate can hydrolyze in particle water by the replacement of $tert-ONO_2$ to $-O-H$ group (Liu et al., 2012). Because such replacement hardly changes the vapor pressure of corresponding species (Pankow et al., 2008), newly formed alcohols should remain in the aerosol phase. We also did extra experiments to test the hydrolysis of organic nitrates. After the SOA sample from dry isoprene-NO_2 irradiation was exposed to humid air (90% RH) for 1 hour, we did not find any apparent change in ONO_2 group. Meanwhile, the peak height ratios of $ONO_2/O-H$ from SOA are almost the same under dry and humid conditions. Thus, the hydrolysis of nitrates is not the major reason for the decrease of particle phase organic nitrates. It also indicates that aerosol phase oligomers can hardly be influenced by RH. Then, high RH likely inhibited the formation of particle-phase organics by reducing the oligomerizations in the gas phase (e.g. SCI-derived oligomers).

RH generally enhances SOA formation by the aqueous reactions. Similarly, the aqueous reactions also exist in isoprene-NO_2 irradiations. However, the maximum LWC from humid isoprene-NO_2 irradiations was measured to be 8 $\mu g/m^3$ at the end of reaction, which is much smaller as compared to 44 $\mu g/m^3$ in toluene irradiations. Taking glyoxal as an example, although the maximum concentrations of glyoxal were simulated to be 39 ppb in isoprene-NO_2 irradiations, which is only 60% of its maximum concentrations of 65 ppb from toluene irradiations, due to the limitation of LWC, the SOA from the aqueous reactions was significantly reduced in isoprene-NO_2 irradiations. To further confirm the role of LWC, we did an additional experiment with NaCl seeds (initial LWC of 30 $\mu g/m^3$) in isoprene-NO_2 irradiations. The results show that the absorptions of the bands from $O-H$ and $C-OH$ increase by 20% to 30% as compared to that without additional LWC (Figure 6). It is true

that increasing LWC can indeed enhance SOA formation in isoprene-NO_2 irradiations; however, the absorptions of $C\!=\!O$, ONO_2 and $C\!-\!O$ from dry conditions are still 2 times larger than those from the experiment with extra LWC. This demonstrates that the increase in SOA through aqueous reactions is far less than the decrease due to H_2O-related reactions under humid conditions. Thus, high water vapor can probably inhibit some key processes responsible for SOA formation from isoprene-NO_2 irradiations, which will be discussed in the following contents.

3.3.2.2 Isoprene-H_2O_2 and Isoprene-O_3 systems

To determine which process responses to the decrease of SOA under humid conditions from isoprene-NO_2 irradiations, IR spectra of SOA from the OH and O_3 channels were studied respectively. Since isoprene is the chain unit of terpenes, the abundance of functional groups in oxidation products from isoprene and terpenes is expected to be close. O-H-containing products from terpene are 10 more enriched from the OH channel oxidation than from the O_3 one (Calogirou et al., 1999). Our extra experiments show the similar characteristics of IR spectra of SOA from both isoprene and α-pinene (figure not shown). The peak height ratio of $O\!-\!H/C\!=\!O$ is 0.24 in the SOA from α-pinene-O_3 system, while it is as high as 2.19 in the SOA from α-pinene-OH system. Here the absorption ratio of O-H to C=O was used to examine the difference between the O_3 and OH oxidation channels.

The IR spectra of SOA from the isoprene-H_2O_2 system are characterized by strong absorptions of hydrogen bonded $O\!-\!H$ and $C\!-\!OH$ and weak absorption of $C\!=\!O$ under both dry and humid conditions (Figure 7 top), with the peak height ratios of $O\!-\!H/C\!=\!O$ being 1.63 (dry) and 1.45 (humid), which strongly supports that alcohols or polyalcohols are major components of SOA from isoprene-H_2O_2 irradiations. Under humid conditions, the peak at 1090 cm^{-1} assigned to $C\!-\!O\!-\!C$ group from esters is slightly decreased, while the band at around 3200 cm^{-1} from $O\!-\!H$ absorption is broadened as compared to the dry condition. It indicates that esters (e.g. oligomers) decrease while the compounds containing $O\!-\!H$ increase under humid conditions. Nevertheless, the relative abundances of $O\!-\!H$, $C\!=\!O$ and $C\!-\!OH$ groups are almost the same between dry and humid conditions, which shows a weak effect of RH on SOA from isoprene-H_2O_2 irradiations as compared to isoprene-NO_2 irradiations. In OH channel, isoprene can be oxidized to form RO_2 (ISOPO$_2$). If there is no NO, ISOPO$_2$ will be further oxidized to isoprene

epoxydiols (IEPOX) by OH and HO$_2$ radicals. IEPOX are key intermediates of SOA in isoprene-OH reactions (Surratt et al., 2010). Under dry conditions, IEPOX can be adsorbed on H$_2$SO$_4$ seeds to form polyalcohols (e.g. 2-methyltetrols) through acid-catalyzed heterogeneous reactions, which can further form oligomers by esterification (Lin et al., 2012). Under humid conditions, IEPOX can be absorbed into particle water to produce polyalcohols (Nguyen et al., 2014). In addition, the decrease of C−O−C group indicates that the formation of oligomers is inhibited by the abundance of particle water as discussed in section 3.2.2, which is in agreement with the result of Lin et al. (2014). Because polyalcohols (dominant) and IEPOX-derived oligomers are all in the aerosol phase, the total mass concentration of SOA does not change much under humid conditions in isoprene-H$_2$O$_2$ irradiations. In other words, RH does not change the partition of IEPOX in our experimental conditions. This is consistent with the result of Riva et al. (2016) that water has a weaker impact on IEPOX-derived SOA yield.

In the isoprene-O$_3$ systems, if the bands from ONO$_2$ are excluded, both the shape and band intensities of IR spectra of SOA are quite similar to those of SOA from isoprene-NO$_2$ irradiations. All the bands assigned to O−H, C═O and C−O are reduced by over 2 times under humid conditions (bottom panel of Figure 7). The ratios of O−H/C═O are 0.36 (0.44) under dry (humid) conditions. The results are consistent with our expectation that lower ratios of O−H/C═O should be in SOA from the ozonolysis of isoprene. Since OH radicals were well removed in our experiments, SCI became the key intermediates of SOA. The C−O−O group is an indicator for the participation of SCI in SOA from the ozonolysis of isoprene. The C−O−O group is very apparent under dry conditions, which decreases by 60% under humid condition. Oligomer products in SOA have been found to be formed by the reactions of n (n=1-10) SCI with RO$_2$ in the ozonolysis of small enol ethers and trans-3-hexene (Sadezky et al., 2008; Zhao et al., 2015). Thus, SCI derived oligomers are also deduced to be the key components in SOA from the O$_3$ channel of isoprene. The model simulated results show that when RH increases from 10% to 88%, the consumption of SCI by water increases from 13% to 58%, while the SCI-derived oligomers decrease from 87% to 42%. The reaction products of SCI with H$_2$O have relative high vapor pressures as compared to oligomers, so they are mainly in the gas phase. Therefore, humid condition can reduce the SOA formed by SCI-related reactions in the isoprene-O$_3$ systems.

In isoprene-NO$_2$ irradiations, the ratios of O−H/C═O are 0.35 (0.36) under dry (humid) conditions, which are almost the same as the corresponding values in isoprene-O$_3$ but totally different from the values in isoprene-H$_2$O$_2$. The yields, IR spectra (ratios

of O−H/C=O) and the influence of RH on SOA production from the isoprene-O_3 system are almost the same as those from isoprene-NO_2 irradiations. In isoprene-NO_2 irradiations, even though 60% of isoprene was oxidized by OH, because of the presence of NO, most of $ISOPO_2$ from oxidation of OH could be quickly consumed by NO to form MPAN (around 15 ppb under both dry and humid conditions) and other products, leading to the decrease of IEPOX from 224.0 ppb (in isoprene-H_2O_2) to 41.2 ppb (in isoprene-NO_2). The yield of MACR is generally greater in isoprene-NO_2 irradiations and isoprene-O_3 systems than that in isoprene-H_2O_2 irradiations. MACR can react to form MPAN in the presence of NO_2, which can be oxidized by OH to form SOA precursors of epoxides (e.g., HMML, MAE), such as in the Nguyen et al. (2011) work. Epoxides can further be oxidized to produce 2-MG and related oligomers (Surratt et al., 2010; Lin et al., 2013; Nguyen et al., 2015). 2-MG-derived oligomers can be enhanced under lower RH (Zhang et al., 2011). Both the results from Nguyen et al. (2014) and MCM simulations further show that if there are enough OH radicals, most of MPAN can be further oxidized by OH to produce epoxides. However, since there were no extra OH sources in our systems, MCM simulations show that only 12% (24%) of MPAN under dry (humid) conditions was oxidized by OH to produce HMML and MAE. The maximum concentrations of HMML and MAE were only 6.8 and 2.7 ppb under dry conditions (Figure 4), which is too small to explain the yields of SOA in isoprene-NO_2 irradiations. If we simply assume that the concentrations of SOA were proportional to the IEPOX concentration as in isoprene-H_2O_2 irradiations, over 70% of SOA should come from IEPOX in dry or humid isoprene-NO_2 irradiations. However, the IR spectra of SOA from dry or humid isoprene-NO_2 are totally different from those in isoprene-H_2O_2 irradiations. On the contrary, they are similar to those from isoprene-O_3 system. Thus, IEPOX is not the major contributor to SOA in isoprene-NO_2 systems. On the other hand, similar to the isoprene-O_3 system, SCI-related reactions in the isoprene-NO_2 system were probably key pathways.

3.4 Mass spectra of isoprene SOA

To further determine whether SCI-derived oligomers are the major components of SOA from isoprene-NO_2 irradiations, the high resolution mass spectra of SOA under dry and humid conditions were obtained with ESI-HRMS (Figure 8). The mean molecular size of SOA was reduced from 352 under dry conditions to 295 under humid conditions, which is in good agreement

with the results by UV/Vis spectra. The peaks on the spectrum show highly regular mass differences, especially in the range of 300 ~800 m/z, which is a typical structure for polymers or oligomers (Kalberer et al., 2004). The total intensity of peaks in the range of 300 to 800 m/z under humid conditions is reduced by 75% as compared to that under dry conditions. This demonstrates that oligomers are probably a major component of SOA from isoprene-NO_2 irradiations, which are greatly reduced under humid conditions. The mass spectrum of SOA from the ozonolysis of isoprene is similar to the one from the isoprene-NO_2 system. The spectrum of SOA from isoprene-H_2O_2 (Figure 9) shows a very different feature from that SOA from isoprene-NO_2. It does not reveal obviously regular structures of the peaks for oligomers.

3.4.1 Analysis of oligomers with KMD method

To further characterize whether SCIs are the major building blocks of the oligomers in SOA from isoprene-NO_2 irradiations, a Kendrick mass defect (KMD) analysis was used. The KMD analysis is a standard method to visualize the complex organic mass spectra (Kendrick, 1963). The Kendrick mass (KM) is converted from the IUPAC mass M by multiplying a factor of NM_{base}/M_{base} (i.e., the factor is 14.00000/14.01565 for the base unit of CH_2) using equation (2). NM_{base} is the exact mass M_{base} rounded to the nearest integer. KMD is calculated as the difference between the nominal KM (NKM) and KM using equation (3). The basic principle of KMD method is that a homologous series of compounds differing only by a number of base units have identical KMD values. Thus, the KMD analysis allows for the rapid identification oligomers by a plot of KMD *versus* KM, in which homologous compounds can line up in the horizontal direction. Since the KMD analysis has a great advantage to clearly determine the molecular composition of hundreds of individual compounds in SOA samples, it has been applied extensively for complex SOA sample analyses using HR-MS (Reinhardt et al., 2007; Walser et al., 2008; Nguyen et al. 2010, 2011; Nizkorodov et al., 2011). In addition, since different series of homologous oligomers may have similar KMD values, the KMD data need to be pre-sorted by z* valuewhich is calculated by equation (4) (Hsu et al., 1992).

$$KM = M \times \frac{NM_{base}}{M_{base}} \qquad (2)$$

$$KMD = NKM - KM \qquad (3)$$

$$z^* = \text{modulo}(\frac{NM}{NM_{base}}) - NM_{base} \tag{4}$$

3.4.1.1 Base units of oligomers: SCIs

There are 16 kinds of SCIs produced in isoprene-NO_2 irradiations based on MCM v3.3.1 simulation, in which CH_2OO (CH_2O_2, with the yield of 50.1%), MACROO ($C_4H_6O_2$, 18.3%), MVKOO ($C_4H_6O_2$, 12.2%), MGLOO ($C_3H_4O_3$, 11.3%) and GLYOO ($C_2H_2O_3$, 2.6%) account for 95% of total SCIs. To explain that these SCIs exist in SOA as base units of CH_2O_2, $C_4H_6O_2$, $C_3H_4O_3$ and $C_2H_2O_3$, a wide set of other base units (OH, CO, NO_2, ONO_2, CH_2, CH_2O and COO) are also included for KMD analysis. The ratio of oligomers with a given base unit to total mass is defined to characterize the contribution of different base units to SOA. It should be pointed out that large uncertainties exist in the estimate of relative contributions of different units because of the poor quantification performance using ESI-MS techniques. Due to the cross containing of units in oligomer molecules, the sum of ratios is larger than 100%. The compounds with a same base unit (M-[base unit]$_n$, n=0,1,2,3…) that contains at least 3 compounds (the maximum n bigger than 2) are considered as one class of oligomers. The results show that only the ratios of oligomers with the base units of CH_2O_2, $C_4H_6O_2$, $C_3H_4O_3$ and $C_2H_2O_3$ are proportional to the yields of corresponding SCIs from the isoprene-NO_2 system. Figure 10 displays the correlation diagram between the ratios of oligomers (with CH_2O_2, $C_4H_6O_2$, $C_3H_4O_3$ and $C_2H_2O_3$ as repeating units) to total mass and top 5 SCI yields (CH_2OO, MACROO,MVKOO, MGLOO and GLYOO). It shows that the ratios linearly increase with increasing yields under both dry and humid conditions. Thus, this demonstrates that the oligomers with CH_2O_2, $C_4H_6O_2$, $C_3H_4O_3$ and $C_2H_2O_3$ repeat units are from contribution of these SCIs of CH_2OO, MACROO (& MVKOO), MGLOO and GLYOO in the isoprene-NO_2 system. Therefore, these 5 SCIs are chosen as the base units for KMD analysis, which shows that the ratios of compounds containing SCI units are reduced by 45% on average as RH increases from 7% to 85%. This is also in good agreement with MCM simulation of decrease in SCI-derived oligomers by 44% and with the decrease of intensity of peroxide C−O−O absorption in FTIR (Figure 6). In addition, the KMD analysis is also used to determine the chemicals of oligomers in SOA from isoprene-H_2O_2. All the above base units are tested, and the results show that CH_2O-containing oligomers are the major products in SOA, and the lengths of oligomers are much shorter than those from isoprene-NO_2. The maximum repeat unit number of n is less than 3 in most families of

oligomers in SOA from isoprene-H_2O_2. By contrast, the maximum value of n is larger than 5 in oligomer families of SOA from isoprene-NO_2. This indicates that SCIs incline to produce long chain oligomers.

3.4.1.2 Base unit of CH_2OO

It has been considered that the CH_2OO radical can serve as an oligomer unit in SOA from the ozonolysis of ethylene (Sakamoto et al. 2013). CH_2OO has the highest yields (50.1%) of all the SCIs from isoprene. The KMD analysis shows that the mass of CH_2OO-containing oligomers account for 46.2% (29.4%) of total mass on the MS under dry (humid) conditions. Figure 11 displays the selected mass spectra of oligomers with CH_2OO as chain units and their corresponding KMD plots under dry and humid conditions, which shows that both the length of oligomer chains and the number of oligomers are greatly reduced under humid conditions. The number of oligomers under humid condition is reduced by 64% as compared to dry conditions. Another feature of CH_2OO-based oligomers is that the molecular sizes of their monomers are larger than 300 (C14-C17), which probably come from other oligomers formed during reactions. This indicates that most CH_2OO-based oligomers are formed in the particle phase.

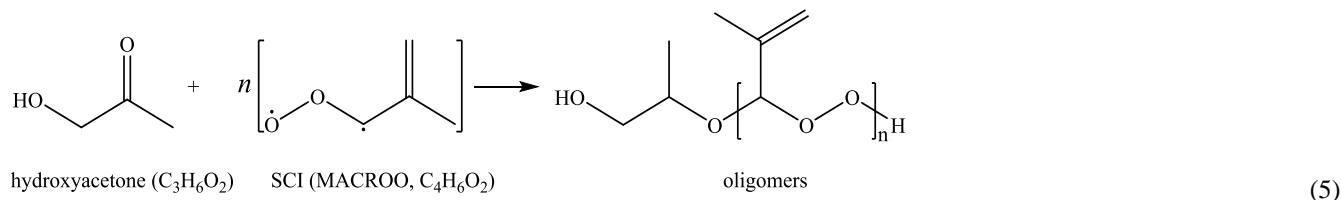
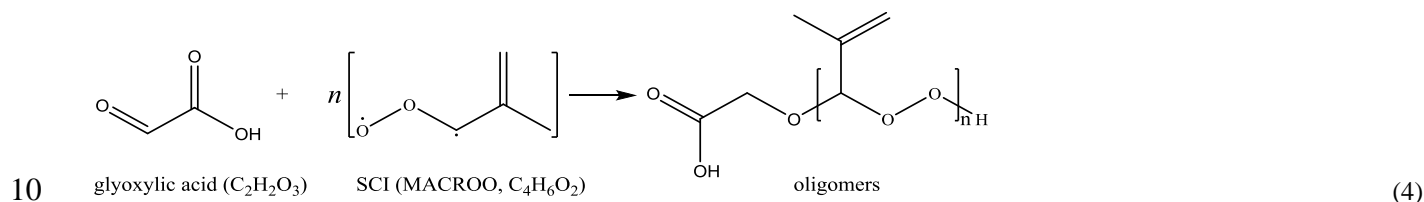
3.4.1.3 Base units of MACROO & MVKOO

Figure 12 shows the mass spectra and KMD plot of oligomers with $C_4H_6O_2$ (MACROO and MVKOO) as base units. The KMD analysis results show that the ratio of $C_4H_6O_2$- based oligomers to total compounds is 39.7% (17.2%) under dry (humid) conditions. In addition to CH_2OO, MACROO and MVKOO based oligomers have the second highest contribution to SOA among all the SCIs. Similar to CH_2OO, the maximum number of chain units is 6 in oligomers from $C_4H_6O_2$. However, the molecular size of monomers is much smaller than that from CH_2OO. The most frequent monomer is $C_3H_6O_2$ as shown in Figure 12. Based on Chemspider database and MCM simulation, we deduced that $C_3H_6O_2$ is from hydroxyacetone (ACETOL), which is the most abundant carbonyl-containing products in isoprene-NO_2 reaction system. The maximum concentration of ACETOL is over 90 ppb based on our experimental conditions. $C_2H_2O_3$ is deduced to be glyoxylic acid that is one of products from isoprene irradiation. SCIs can react with carbonyl and alcohol products (e.g., ACETOL), RO_2 and H_2O. However,

different from the isoprene-O_3 system, MCM simulations show that most of RO_2 is consumed by NO in isoprene-NO_2 irradiations. Thus carbonyl and alcohol products become the major monomers for SCI oligomerizations.

An addition of a C−O−O group can change the vapor pressure of oligomers (containing n SCI units) by a factor of 2.5×10^{-3} (Pankow et al., 2008). The vapor pressures of SCI-derived oligomers (e.g. $C_3H_3O_2$-[C_4H_6OO]$_n$) are estimated to be less than 10^{-7} atm ($n \geq 2$) and 10^{-12} atm ($n \geq 4$). The compounds can self-nucleate as their vapor pressures are less than 10^{-9} atm (Kamens et al., 1999). It indicates that the initial particles in the O_3 oxidation channel of isoprene are formed by the self-nucleation of oligomers ($n \geq 4$). The oligomers with $n \geq 2$ probably further condensed on these particles. Thus, MACROO or MVKOO based oligomers can be formed in the gas-phase (e.g. reaction 4 and 5). With the increase of chain units, these oligomers can either self-nucleate or further oligomerise in the aerosol phase.

glyoxylic acid ($C_2H_2O_3$)   SCI (MACROO, $C_4H_6O_2$)   oligomers   (4)

hydroxyacetone ($C_3H_6O_2$)   SCI (MACROO, $C_4H_6O_2$)   oligomers   (5)

3.4.1.4 Other base units of oligomers

It is worth noticing that the yield of $CH_3OC_3H_3OO$ ($C_4H_6O_3$) is only 1.4% based on the MCM simulation. However, the contribution of $C_4H_6O_3$ to oligomers is as high as 25.3% (9.0%) under dry (humid) conditions (Table 2). Thus, $C_4H_6O_3$ is not totally from $CH_3OC_3H_3OO$. 2-MG usually serves as molecular tracers for isoprene SOA (Kleindienst et al., 2007). As reported by Zhang et al. (2011) and Nguyen et al. (2011), $C_4H_6O_3$ was the repeated unit of 2-MG's corresponding oligomers in SOA from isoprene-NO_x irradiations. Lin et al. (2013) has reported that $C_4H_6O_3$ was from MAE in MACR-NO_x irradiations. Thus, $C_4H_6O_3$ is probably formed from dehydration of 2-MG and MAE in oligomers. Considering the low yield of MAE in our

system, we considered that most of $C_4H_6O_3$- based oligomers are probably contributed by 2-MG in our work. The ratios of CH_2OO, MACROO and MVKOO based oligomers are almost 2 times larger than that from 2-MG under both dry and humid conditions. Thus, even though the ratio of $C_4H_6O_3$ base oligomers was decreased by 65% as RH increased from 7% to 85%, 2-MG derived oligomers would not be the major reason for the decrease of SOA yield from isoprene-NO_2 irradiations. In addition to $C_4H_6O_3$, CH_2 and CH_2O based oligomeric compounds also have high ratios in isoprene-NO_2 systems, which have been also reported as the most prominent units in SOA products from the ozonolysis of isoprene in the Nguyen et al. (2010) study under dry conditions. However, different from SCI based oligomers, the ratios of CH_2 and CH_2O based oligomers decreased by 18% and 14% as RH increased from 7% to 85%, respectively. Thus, the reduction of SCI based oligomers is the major reason for the decrease of SOA yields from isoprene-NO_2 photooxidations.

3.5 Mechanisms for the different roles of water in isoprene-NO_2 systems

3.5.1 Vapor wall loss vs SCI-H_2O reaction

It is noted that the wall loss of semi-volatile organic compounds (SVOC) can lead to the underestimation of the yield of SOA (Matsunaga & Ziemann 2010; Loza et al., 2010; Zhang et al., 2014; Yeh & Ziemann 2015; Ye et al., 2016; Palm et al., 2016; Krechmer et al., 2016; La et al., 2016; Nah et al., 2017). Since SCI-derived oligomers are the major products of SOA from isoprene-NO_2 irradiations, a question arises about which process is dominant for the reduction of SOA production under humid condition, wall loss of SCI related oligomers (in gas-phase) or the reaction between SCI and H_2O. The MCM simulation shows that SCIs are so reactive that most of them are consumed by reactions before they are lost to the wall (Figure 14). The percentage of the SCI consumed by H_2O was increased from 6% to 46% as RH increased from 5% to 85% due to the extremely high concentration of gas H_2O. The removal of SCI by H_2O (85%RH) can lead to a decrease of SCI–derived oligomers by 43% as compared to 5% RH. The result is comparable with the decrease of SOA yields of 62% from isoprene-NO_2 irradiations. Meanwhile, as discussed in the previous section, the vapor pressure of SCI-derived oligomers were very low that they were ready to condense on particles. The upper limit of wall loss rate constant of 4.8×10^{-4} s^{-1} for SVOC was calculated from the equation given by McMurry and Grosjean (1985), while the condensation rate constant of SVOC to the particles was calculated

to be over 0.65 s^{-1} in our study based on the equation from La et al (2016). This indicates that the condensation rate of gas-phase oligomers to particles is much fast than that to the wall. Therefore, the reactions between SCIs and H_2O rather than the wall loss of SVOC is the major cause for the decrease of SOA formation from isoprene-NO_2 irradiations in this work.

3.5.2 Effects of water on SOA formation: O_3 vs OH

5   To quantify the RH effect of SOA and relatively possible contribution of SCI-derived oligomers from 2 species in isoprene-NO_2 irradiations, the reactions of SCIs with formic acid, glyoxylic acid and ACETOL were added into MCM. Simulations show that the total mass concentration of oligomers from these reactions was 558.4 (271.2) $\mu g/m^3$ at 7% (80%) RH, and the mass concentrations form other SOA precursors IEPOX, MPAN, HMML and MAE were 182.8 (167.0), 27.4 (28.9), 28.1 (27.4), and 11.2 (10.9) $\mu g/m^3$ at 7% (80%) RH (Figure 13). It is obvious that the mass concentrations of SCI-derived oligomers

10   reduced by 51% as RH increased from 7% to 80%, while the concentrations of other precursors had little change under different RH conditions. Thus, SCI-derived oligomers from glyoxylic acid and ACETOL should have a great potential for formation of SOA, compared to other precursors.

Our results clearly show that the different effects of RH on SOA yields originate from the oxidation channels (Figure 5). Both the OH and O_3 channels can well explain the differences of results in isoprene-NO_2 irradiations from the Zhang et al. (2011)

15   and Nguyen et al. (2011) studies. In the Zhang et al. study, there were no additional OH radical sources in their systems. Thus, the SOA was mainly from the O_3 channel. Similar to our isoprene-O_3 systems, a negative effect of humidity on SOA yield was observed in their work. In the Nguyen et al. work, due to sufficient OH radical source, over 99% of isoprene was oxidized by OH, and SCI concentrations were very low. Even though high NO_x was used, most of MPAN could be further oxidized by OH to produce epoxides. Therefore, SOA was mainly from the OH channel in Nguyen et al.'s work. This is why the yield of SOA

20   in their work was not influenced by RH. Our results obviously show that SOA is formed by reactive uptake of SOA precursors (e.g. IEPOX) in the OH channel, and by the condensation of SCI-derived oligomers in the O_3 channel. In the presence of NO_2, the formation of SOA is also controlled by the SCI-related reactions without extra OH sources. However, the SCI-related reactions (SCI-derived oligomers) can be inhibited by high water vapor. In previous studies, SOA was usually modeled based

on the vapor pressures of SVOC, which only considers the effect of temperature. Our study strongly suggests that RH is also a key factor in SOA formation.

4 Conclusion

Opposite effects of RH on SOA formation from the irradiations of toluene and isoprene have been elucidated in our work. Different influences of RH on both SOA yields and mean molecule size demonstrate the different mechanisms related to SOA formation from the irradiations of toluene and isoprene. High RH can greatly enhance the SOA formation in toluene-NO_2 system, so that the maximum yields of SOA from toluene increased from 5.58% (dry) to 8.97% (humid). FTIR spectra show that the increased part of SOA under humid conditions was mainly contributed by aqueous reactions of water soluble products (e.g. glyoxal). Different from toluene-NO_2 irradiations, water has a complex role in isoprene systems. In isoprene-H_2O_2 irradiations systems, RH has no remarkable effects on SOA yields. FTIR spectra show that water can inhibit the oligomerization reactions; however, polyalcohols were still the major products in both dry and humid conditions from isoprene-H_2O_2 irradiation, which was mainly from the reactive uptake of IEPOX in the presence of H_2SO_4 particles from background gas. In isoprene-O_3 and isoprene-NO_2 irradiation systems, high RH has a negative effect on SOA yields, which decreased from 3.14% (dry) to 1.19% (humid). According to the FTIR, ESI-HRMS, KMD analysis and MCM simulations, it is considered that the oligomers with SCIs as base units were the major products of SOA in isoprene-O_3 systems and isoprene-NO_2 irradiation systems. Under humid conditions, the SCIs can be consumed by water in the gas-phase, leading to the decrease of the formation of oligomers from SCIs.

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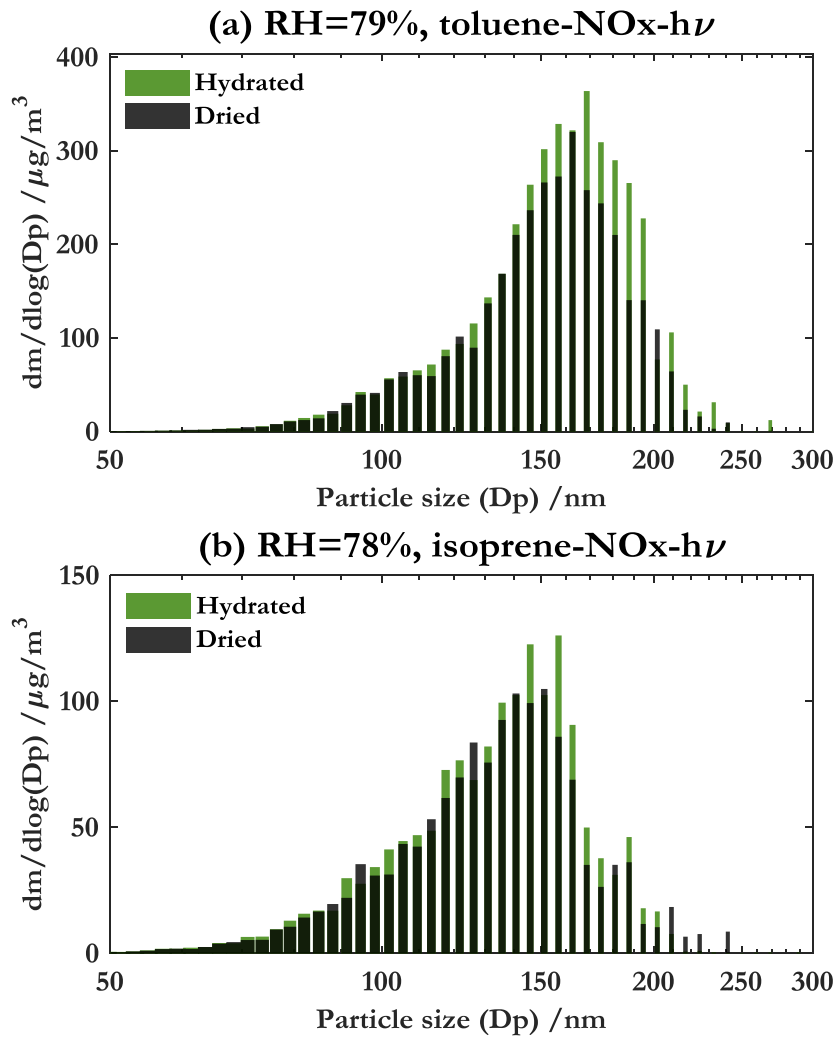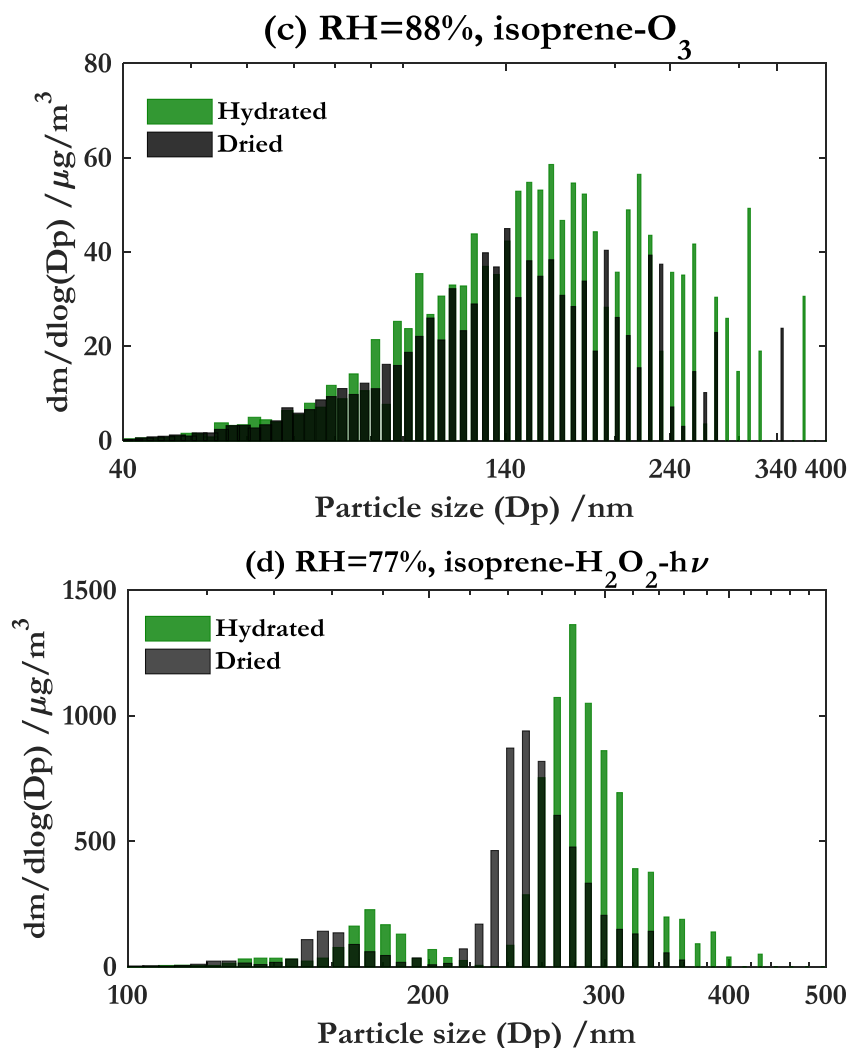
Figure 1: Mass cocnentration ditributions of both dryed and hydrated particles from both toluene and isoprene systems at 3 hr after the initiation of reaction.
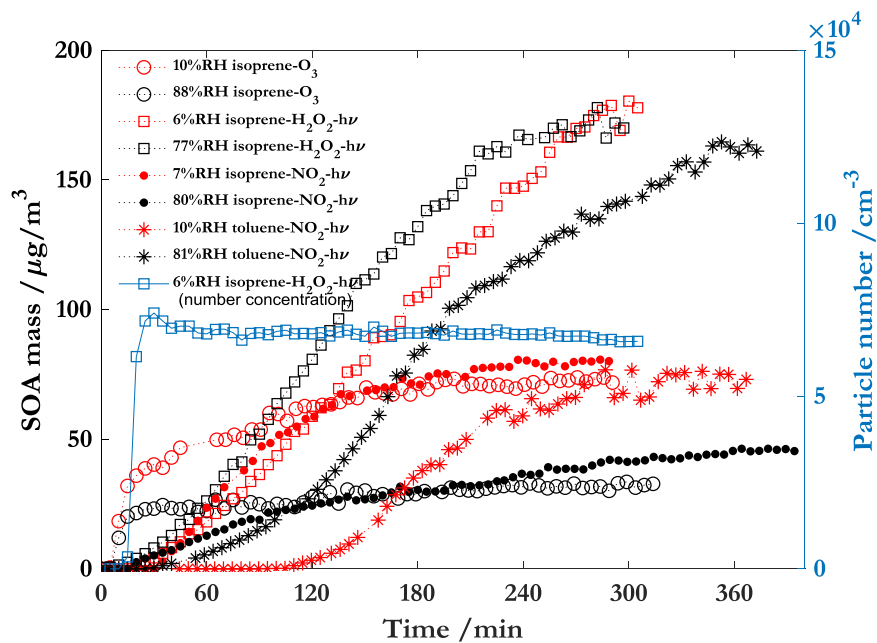
Figure 2: Mass concentration time profiles of SOA from different toluene and isoprene reaction systems under dry and humid conditions. An SOA density of 1.4 g/cm³ was used and applied to the SMPS mass correction (Dommen et al., 2006; Sato et al., 2007). The blue square markers are the number concentration of SOA from isoprene-H₂O₂ irradiations at 6% RH. The wall loss rate constant of particles was less dependent on RH conditions, so an average value of 4.8×10⁻³ /min was used to correct the SOA formation.
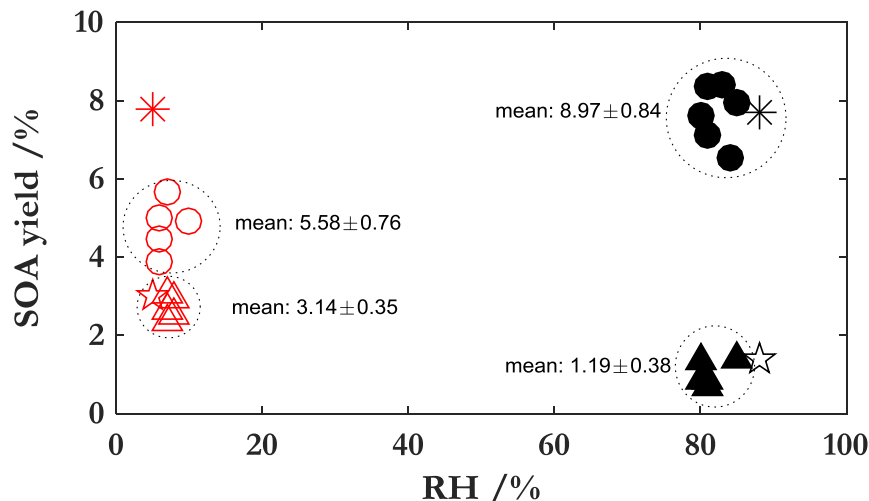
Figure 3: Maximum yields of SOA from toluene and isoprene under dry (red color) and humid (black color) conditions (O: toluene-NO₂-hv; △: isoprene-NO₂-hv; ☆: isoprene-O₃; ✳: isoprene-H₂O₂-hv).
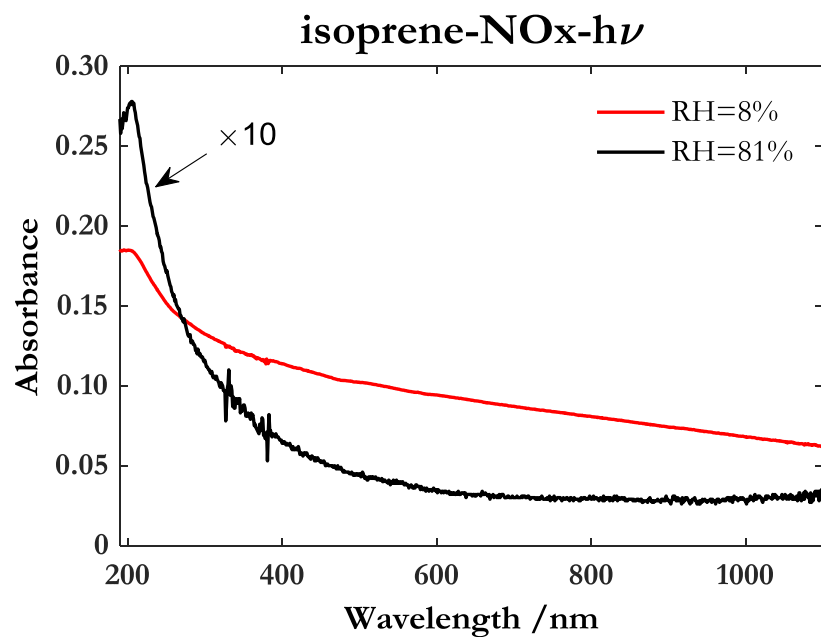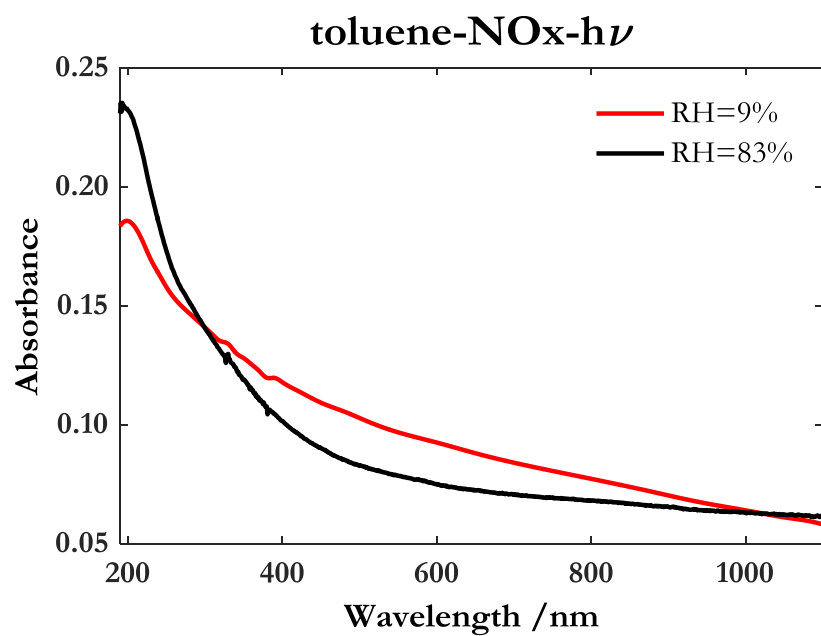
Figure 4: UV-Vis spectra of SOA from toluene and isoprene photooxidations under dry and humid conditions.
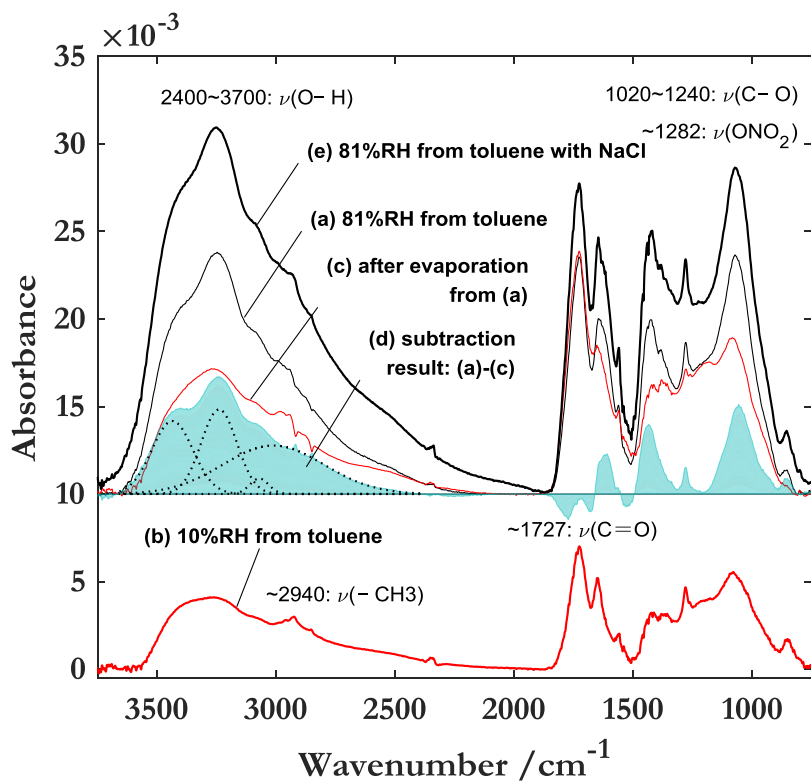
Figure 5: Infrared spectra of SOA from toluene irradiations under humid (top: a) and dry (bottom: b) conditions. The infrared spectrum of (c) was obtained after evaporation of SOA from (a) for 15 min at 110 ℃; the difference spectrum between (a) and (c) is in blue area (d); the infrared spectrum of (e) is with extra LWC by NaCl seeds. Main bands are hydrogen bonded O−H stretch in alcohols or acids (2400-3700 cm^{-1}), the carbonyl (C═O) band at 1727 cm^{-1}, the organic nitrous (ONO$_2$) bands at 1636, 1278, and 855 cm^{-1}, the C−OH bend band at 1423 cm^{-1}, and the C−OH stretch at 1080 cm^{-1}.
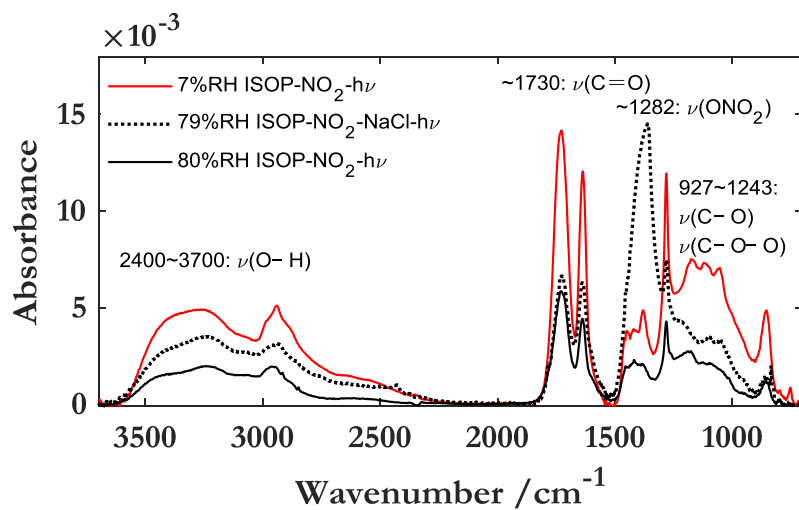
Figure 6: Infrared spectra of SOA from isoprene irradiations under dry and humid conditions. The bands at 1636, 1282, and 855 cm⁻¹ are from ONO₂. The bands at 1170 and 1121 cm⁻¹ are assigned to C−O−C in oligomers or C−O in carboxylic acids, and the band at 1055 cm⁻¹ is from alcohols. The absorption shoulder from 927 to 1080 cm⁻¹ is assigned to C−O and O−O in peroxide group (C−O−O) (Pretsch et al., 2009).
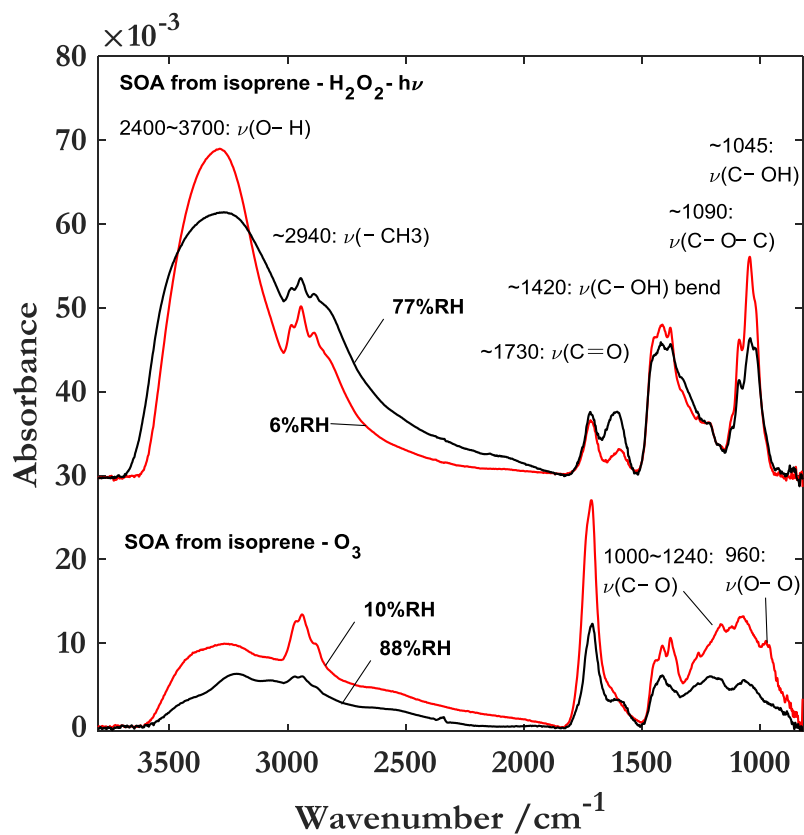
Figure 7: Infrared spectra of SOA from isoprene with different oxidants under dry and humid conditions. The bands at 1051 and 960 cm^{-1} are assigned to C−O and O−O groups in peroxide C−O−O (Pretsch et al., 2009).
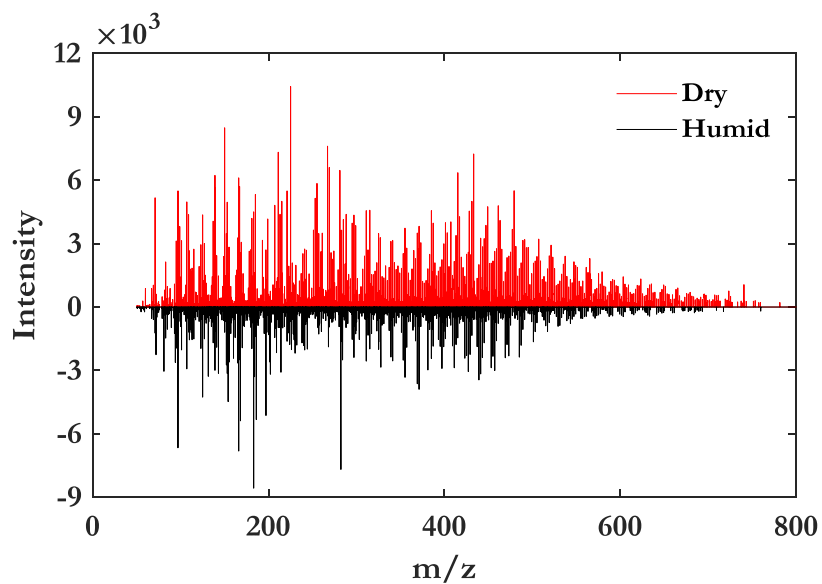
Figure 8: Positive ion mode ESI-Orbitrap mass spectra of SOA from isoprene-NO₂ irradiations under dry (top panel) and humid (bottom panel) conditions.
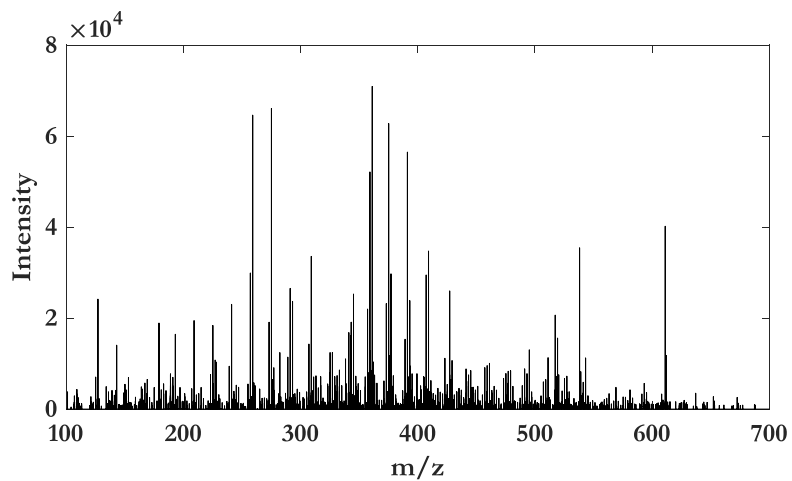
Figure 9: Positive ion mode ESI-Orbitrap mass spectra of SOA from isoprene-H₂O₂ irradiations under dry conditions.
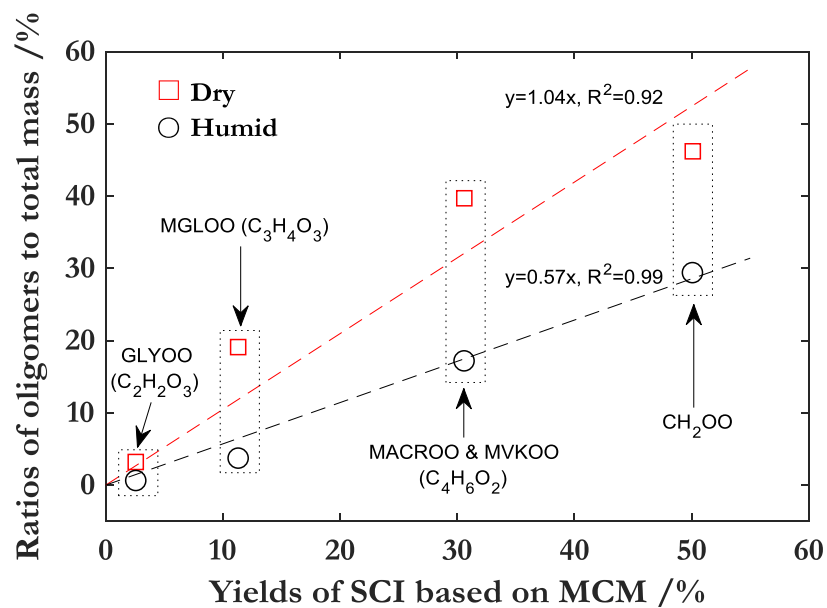
Figure 10: The correlation of yields of top 5 SCIs (CH₂OO, MACROO & MVKOO, MGLOO and GLYOO) and the ratios of CH_2O_2, $C_4H_6O_2$, $C_3H_4O_3$ and $C_2H_2O_3$ based oligomers to total mass under dry and humid conditions from isoprene-NO_2 irradiations. Only the oligomers that belong to families (M-[SCI]$_n$, n=0,1,2,3…) with maximum number of n larger than 2 were taken into consideration.
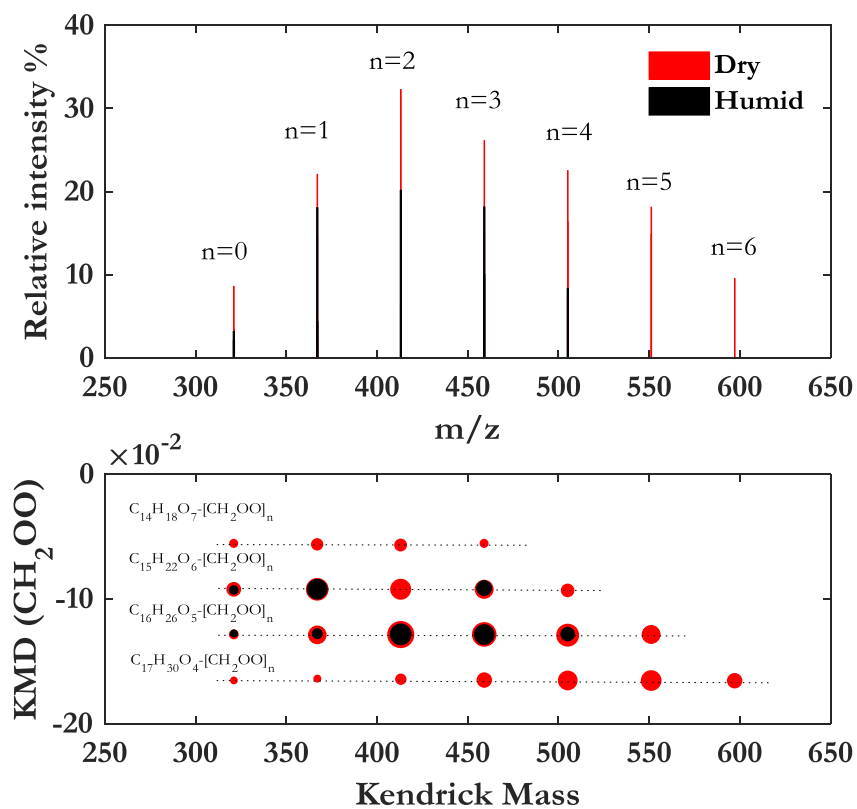
Figure 11: Positive mode mass spectra of oligomers with CH₂OO as chain units in SOA from isoprene-NO₂ irritations under dry and humid conditions (*top*) and corresponding plots of KMD (CH₂OO) versus nominal KM (CH₂OO) (*bottom*). The horizontal lines connect the family of compounds with an equal elemental composition differing only by [CH₂OO]ₙ (n=0,1,2,3…) groups.
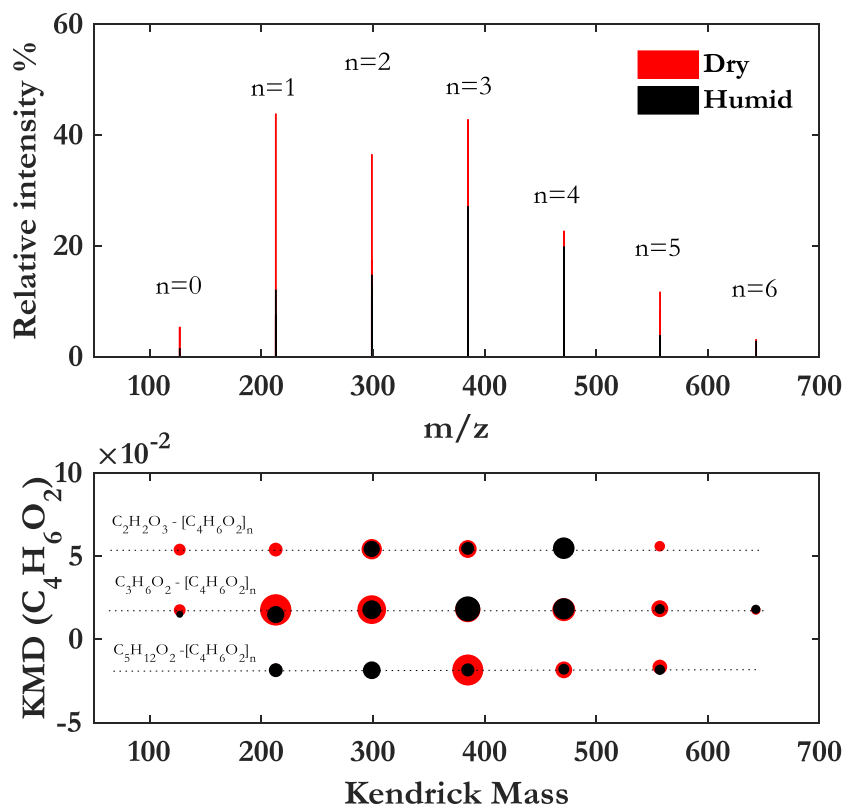
Figure 12: Mass spectra of oligomers with C₄H₆O₂ (MACROO and MVKOO) as repeating unit and their Kendrick plots using C₄H₆O₂ as Kendrick base. Species separated by C₄H₆O₂ groups fall on the horizontal lines.
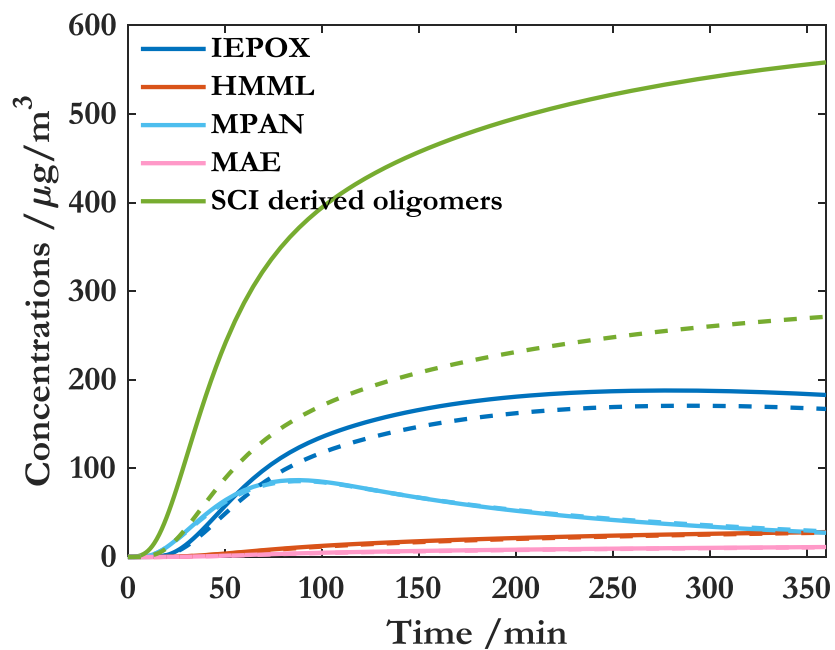
Figure 13: MCM-simulated time profiles of SOA precursors in isoprene-NO₂ irradiations. SCI-derived oligomers were from the reactions of SCI with glyoxylic acid and ACETOL.
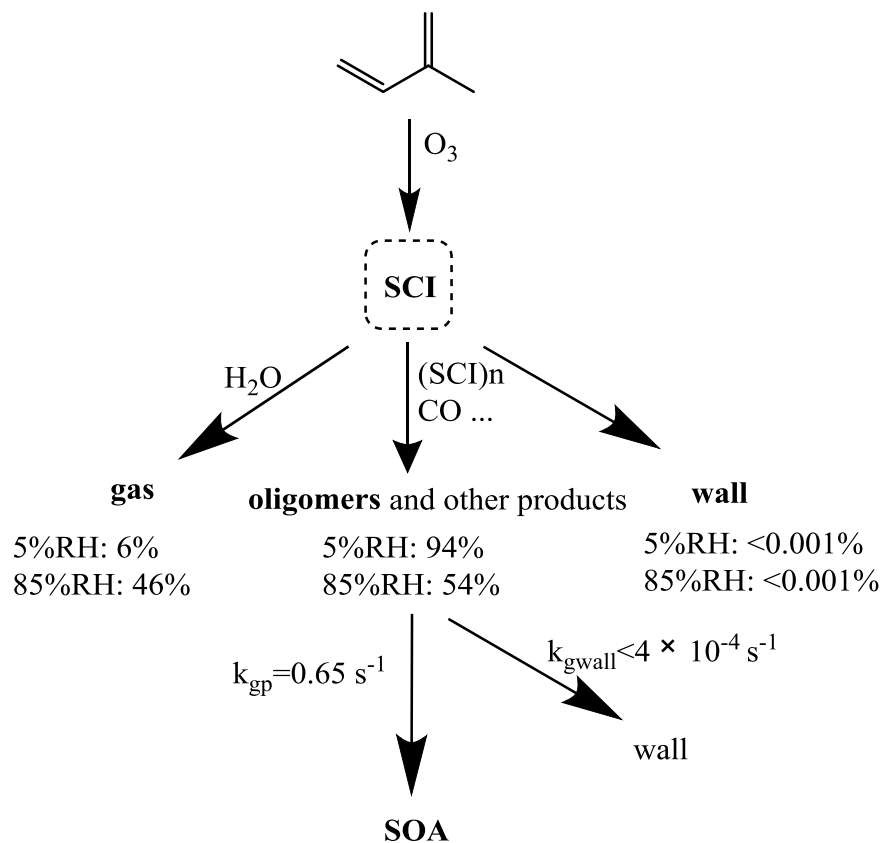
Figure 14: Wall losses vs gas-phase reactions between H₂O and SCI
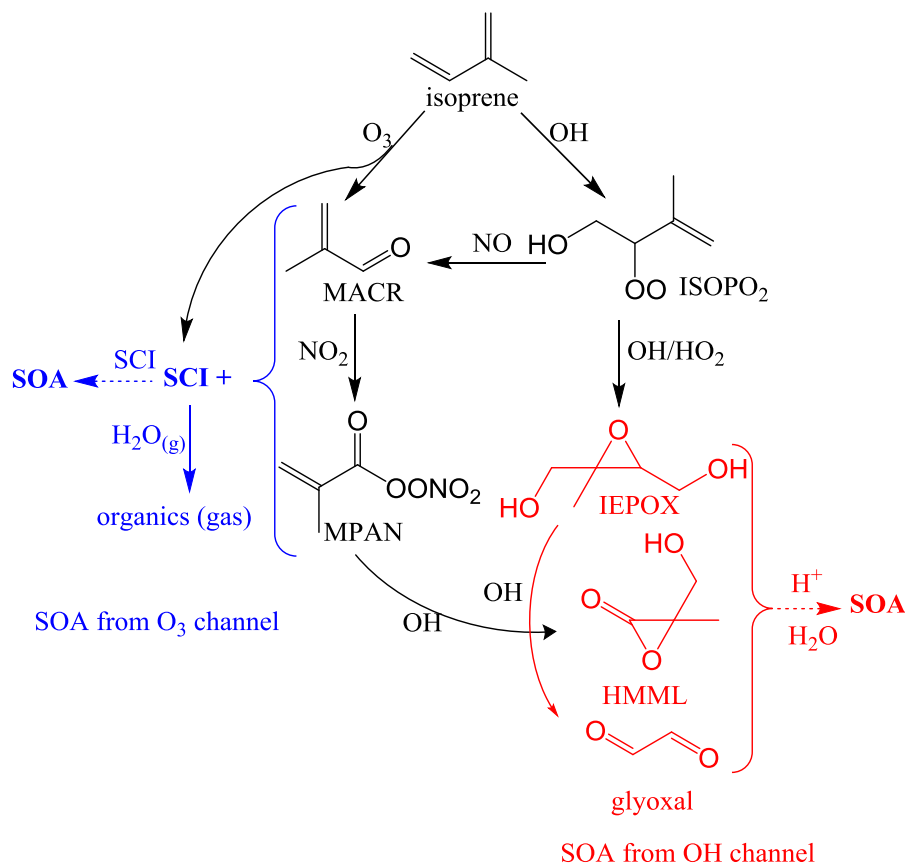
Figure 15: Mechanisms for SOA formation from the O₃ and OH oxidation channels of isoprene.

Table 1 Expermental conditions of toluene and isoprene irradiations

VOCs	#	T /K	RH /%	VOC /ppm	NO /ppb	NO₂ /ppb	Aim
Toluene	1	304	6	0.915	4.3	307.7	SOA size & yield
	2	304	85	0.804	5.3	303.6	
	3	304	84	0.933	1.5	293.9	
	4	304	6	1.037	0.2	323.3	
	5	302	6	0.879	12.0	328.0	
	6	303	10	0.917	1.9	326.7	FTIR
	7	303	81	0.846	7.8	301.0	
	8	304	7	0.930	9.0	325.0	FTIR with NaCl seeds
	9	303	81	0.906	10.0	334.0	
	10	304	9	0.914	10.6	386.5	UV/Vis

	11	304	80	0.910	7.7	364.1	
	12	305	79	0.927	12.1	288.1	LWC by FTIR
	13	305	79	0.918	10.6	294.7	LWC by SMPS
	14	302	7	0.896	7.0	353.0	
	15	302	85	0.804	6.0	364.0	size and
	16	301	7	0.850	0.0	311.7	yield
	17	302	80	0.844	0.3	308.5	
	18	303	7	0.901	0.0	299.5	
	19	303	81	0.799	0.3	270.2	FTIR
	20	302	80	0.828	0.2	273.0	
Isoprene	21	301	8	0.790	0.0	283.1	
	22	303	9	0.873	3.0	301.0	FTIR with
	23	303	79	0.827	4.0	325.0	NaCl seeds
	24	303	8	0.823	0.1	332.5	UV/Vis
	25	303	81	0.877	0.3	363.0	
	26	305	81	0.831	1.5	288.8	LWC by FTIR
	27	304	78	0.823	0.5	313.5	LWC by SMPS
	28	303	7	0.810	0.2	295.1	ESI-HRMS
	29	303	85	0.804	0.5	290.2	ESI-HRMS

Table 2 List of major base units and their corresponding ratios of oligomers to total mass from SOA in isoprene-NO_2 irradiations.

Base unit	Unit name	SCI yields by MCM	Ratio of oligomers to total mass		
			Dry /%	Humid /%	Delta /%
CH_2O_2	CH_2OO	50.1	46.2	29.4	36.3
$C_4H_6O_2$	MACROO & MVKOO	30.6	39.7	17.2	56.7
$C_3H_4O_3$	MGLOO	11.3	19.1	3.7	80.4
$C_2H_2O_3$	GLYOO	2.6	3.2	0.6	80.1
$C_4H_6O_3$	dehydrated 2-MG (or $CH_3OC_3H_3OO$)	(1.4)	25.3	9.0	64.6
CH_2	-	-	76.4	62.7	17.9
CH_2O	-	-	78.5	67.6	13.8