Response to referee comments for acp-2013-969

"Reactivity of stabilized Criegee intermediates (sCI) from isoprene and monoterpene ozonolysis toward SO_2 and organic acids" by M. Sipilä et al.

We thank both referees for a detailed review of our manuscript. Comments were very valuable and we believe that addressing the issues raised by the referees will improve the manuscript. Answers and resulting forthcoming changes to our manuscript are below.

REFEREE 1:

This manuscript describes experiments aimed at examining the yields and reaction kinetics of stabilized Criegee Intermediates (sCI), important atmospheric species formed in the ozonolysis of alkenes. Varying amounts of SO2 are added to a gas-phase mixture of ozone, alkenes (limonene, pinene, or isoprene), propane (to scavenge OH), and H2O, and measurements of H2SO4 are used to constrain the sCI chemistry. This is an important topic in atmospheric chemistry, since many of the available competing pathways lead to the formation of important atmospheric constituents (OH, sulfate, etc.), and such measurements are necessary for understanding the role of ozonolysis reactions in the atmosphere. However, the analysis and interpretation of the data rely on a highly simplified view of the chemistry in the reactor (described by reactions R2-R6), and neglect several potentially important pathways. These need to be explicitly considered before this work can be published in ACP.

Major comments (competing chemical reactions):
The key to the measurements is the determination of [H2SO4]sCI (equations 3 and 4), the concentration of sulfuric acid formed by titration of the sCI by SO2. In this work it is determined by running at extremely high SO2 concentration (top right corner of Figures 1-3), and assuming all H2SO4 formed is from sCI+SO2. However the validity of this assumption is questionable, since other sources of sulfuric acid may also exist. Most importantly, this work neglects oxidation of SO2 by OH. It is stated that the propane reacts with ">98%" of the OH radicals, but at the highest SO2 concentrations this number is quite a bit lower, on the order of 90%. Thus _10% any OH formed from prompt decomposition of the CI (which will occur independent of SO2 concentration) will react with SO2 to form H2SO4. Also, it seems likely that the main fate of RO2 radicals (formed from OH+propane and O3+alkene) will be reaction with SO2 (forming SO3) under these conditions as well. The effects of these reactions on [H2SO4] and hence on calculated sCI yields need to be assessed.

Thanks to the reviewer for thorough reading and valuable comments.

<u>OH scavenging:</u>
It´s only better than 96.9% with $[SO_2] = 2.4\times10^{14}$ molecule cm^{-3}. Calculation was done with $[SO_2] = 1.6\times10^{14}$ molecule cm^{-3} and later in the a-pinene system also with 1.9 and 2.4×10^{14} molecule cm^{-3}. (With $[SO_2] = 1.6\times10^{14}$ molecule cm^{-3} it was better than 97.7%.)

But nevertheless, 3.1% of prompt OH could be transformed to additional SA, but only for the highest SO2, otherwise it is much lower. It is speculative at the moment what´s the prompt OH yield for a-pinene and limonene. The effect of additional SA via $OH+SO_2$ should be clearly smaller than 10% for highest SO2 regarding SA formation via $sCI+SO_2$. And for lower SO_2 is can be totally neglected.

$k(OH+C_3H_8)$ = 1.09×10^{-12} cm^3 $molecule^{-1}$ s^{-1} (R.Atkinson, ACP, 3, 2233 – 2307 (2003))
$k(OH+SO_2)$ = 1.3×10^{-12} cm^3 $molecule^{-1}$ s^{-1} (R.Atkinson, ACP, 3, 4, 1461 - 1738 (2004))
highest $[SO_2]$ = 2.4×10^{14} molecule cm^{-3} and $[C_3H_8]$ = 8.2×10^{15} molecule cm^{-3} as given in ”Laboratory Experiments” and table 1

RO_2+SO_2:
There are no clear experimental indications in literature indicating a fast enough reaction RO_2 + SO_2, e.g. CH_3O_2 + SO_2, $k < 5 \times 10^{-17}$ cm^3 $molecule^{-1}$ s^{-1}, DeMore et al., JPL Publication 97-4 (1997).
Same result comes from quantum chemistry, Kurten, T. et al. *J. Phys. Chem. A*, **2011**, *115* , 8669-8681.
Moreover, the RO2 concentrations in our experiment are in the same order or lower than atmospheric RO2 levels. If there would be a significant RO_2 + SO_2 reaction, all atmospheric OH measurements via SO_2 titration and SA CIMS detection would be wrong.

Both reactions will be discussed in revised manuscript.

Similarly, a number of carbonyls and acids are formed from the OH+alkane and O3+alkene reactions. These products can also affect sCI reactivity but are ignored in this paper. An estimate of the importance of these species is necessary.

Total reacted alkene concentrations are 7.6×10^8, 3.5×10^8 and 1.7×10^8 molecule cm^{-3} for a-pinene, limonene and isoprene, respectively (see table 1). Due to the low RO_2 concentrations (not higher than alkene conversion!) – RO_2 + RO_2 is not so fast - and low residence time it´s not clear what fraction of RO2 is converted to carbonyls. In a conservative estimate we can assume that carbonyl concentration is equal (should be clearly lower!) the reacted alkene, see numbers above. Acid formation yields are about 5% of reacted alkene, i.e. 1/20 of reacted alkene, i.e. in the order of 10^7 molecule cm^{-3}.

k(sCI+carbonyl) / k (sCI+SO2) < or << 1, see C. A. Taatjes, et al., *Phys. Chem. Chem. Phys.*, 2012, **14**, 10391 in line with unpublished results from our lab. Even for lowest $[SO_2]$ = 3.2×10^{11} molecule cm^{-3}, sCI+carbonyl cannot be competitive with $sCI+SO_2$ due to $[carbonyl]_{max}$ of a few 10^8 molecule cm^{-3} and k(sCI+carbonyl) / k (sCI+SO2) < or << 1.

k(sCI+acid) / k (sCI+SO2) about 3, see this work qualitatively in line with Welz et al., Angew.Chem. (2014). And also here, even for lowest $[SO_2]$ = 3.2×10^{11} molecule cm^{-3}, sCI+acid cannot be competitive with $sCI+SO_2$ due to [acid] of a few 10^7 molecule cm^{-3} and relative reactivity given

Some comment on the possible role of wall loss of sCIs would be helpful. This is mentioned in Berndt 2012 but it is appropriate to discuss it here as well.

The first-order rate coefficient for the diffusion-limited wall loss of sCI can be estimated according to $k_{wall\ loss}$ = $3.65 \cdot D/r^2$, D = diffusion coefficient of sCI and r stands for the tube radius. As the diffusion coefficient a value of 0.1 cm^2 s^{-1} was assumed ($D(H_2SO_4)$ = 0.08 cm^2 s^{-1}) resulting in $k_{wall\ loss}$ = 0.023 s^{-1}. Thermal decomposition of sCI is expected to be much more rapid (Welz et al., 2012; Berndt et al. 2012) making sCI wall loss negligible in the kinetic analysis. We will mention this in revised manuscript.

P. 3079, line 19: The OH scavenging efficiency by propane is given as “>98%”. However this 98% value appears to be an upper limit, not a lower one. As discussed above, the scavenging efficiency is quite a bit lower when [SO2] is high. Even in the absence of SO2, 98% of the OH is scavenged by propane only at the highest concentration of propane given (8.2e15 molec/cm3, from Table 1). At the lowest concentration (1.64e15 C1564 molec/cm3), this value is _92%, with 8% of the OH reacting with alkene.

Now, the value of 96.9% OH scavenging efficiency is in each case a lower limit considering $OH+C_3H_8$ vs. $OH+SO_2$. We used $[C_3H_8]$ = 8.2×10^{15} molecule cm^{-3} in the SO_2 range of 1.6×10^{13} - 2.4×10^{14} molecule cm^{-3}, i.e. an OH scavenging efficiency by C_3H_8 of 99.8 - 96.9%.

$[C_3H_8] = 1.64\text{x}10^{15}$ molecule cm^{-3} was applied in the SO_2 range of $3.2\text{x}10^{11} – 1.6\text{x}10^{13}$ molecule cm^{-3}, i.e. an OH scavenging efficiency by C_3H_8 of 99.98 - 98.8%. See also the discussion above.

Other comments:
The paper relies very heavily on "Berndt et al. [2013]" however this is not in the reference section (nor in Web of Science). Do the authors mean Berndt [2012]? Or Berndt [2014]?

We mean 2014, This will be corrected.

P. 3074, lines 1-2; P. 3085, lines 19-22; p. 3086, lines 17-19: Multiple times in the paper it is asserted that the observation that sCI+organic acids are faster than sCI+SO2 implies that sCIs can play a major role in oxidation of these (and maybe other) atmospheric constituents. But this is not necessarily true, since the importance of a given oxidation pathway of a compound is determined by its rate relative to other available pathways. Thus the importance of sCI-initiated oxidation of acids can be determined only by comparing values of k[sCI] to values of k[OH], etc. Such a comparison would seem to be necessary to assess the atmospheric importance of these reactions.

Since we only determine reaction rate ratio between sCI+acid and sCI+SO2, we cannot make a direct comparison. Order of magnitude estimation can be made if we assume that the absolute reaction rate coefficient of sCI+SO2 is in the range of 6e-13 as suggested e.g. by Mauldin et al., 2012. Then reaction rate coefficient for sCI+HCOOH and sCI+ CH3COOH would be in the range of 1e-12. Reaction rate coefficient for OH + CH3COOH is 8e-13 and for OH+HCOOH 4e-13. Therefore at similar sCI and OH concentrations the two oxidation reactions are both important for the fate of acid. As shown by Mauldin et al., the summertime sCI concentrations are similar to OH peak concentrations in boreal forest. Therefore, it is possible, that sCI oxidation plays a crucial role in HCOOH and CH3COOH budget. However, accurate estimations are difficult and requires more research efforts. The discussion will be added to the revised manuscript.

Also Welz et al. (Angew.Chem., 2014) measured for sCI + HCOOH/CH_3COOH rate coefficients $>10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} favouring the sCI reaction over OH much stronger.

P. 3082, lines 10 and 15: I believe the number of sCIs from a-pinene and isoprene are actually four and five, respectively. (For a di-substituted CI of formula R-C(OO)-R', two isomers are possible, even though both are syn.)

From a-pinene 3 different structures (isomers incl. syn/anti conformers) and 4 from isoprene as given in the manuscript.

P 3083, line 11: If CH2OO reacts quickly with water vapor (relative to SO2), this would have major implications for our understanding of CI chemistry, and the inclusion of the Welz results in models. This should probably be mentioned.

There are conflicting statements in literature. All old relative measurements for $CH_2OO + H_2O$ versus $CH_2OO + SO_2$/others say that the water reaction dominates in atmosphere. Results from CH_2I_2 flash photolysis technique (similar to Welz et al.) describe a quite slow water reaction, see D. Stone et al., *Phys. Chem. Chem. Phys.*, 2014, **16**, 1139. This very slow water reaction pushes the importance of CH_2OO + SO_2/acids extremely. Though our present data does not directly evidence that CH2OO reacts fast with water, the potential indication and how that would be reflected to e.g. CTM simulations is worth mentioning. Sentence or two will be added.

P. 3084, line 16: How valid is the assumption that reaction of water dominates decomposition for CH2OO? Is there previous work showing this? (On the following page, it is stated that the opposite is true for CH3C(OO)CH3.)

Especially sCI + water seems to be strongly dependent on the sCI structure, Berndt et al., 2014. Here it is an assumption that bases on the different behavior of type I and type II sCI (page 3083). It is also possible that the difference is caused by anti-confomer sCI. The assumption needs to be made in order to be able to make a comparison to Welz.

P. 3086, line 22: This incredibly strong statement is highly questionable - I think it better represents the specific interests of the authors rather than the assessment of the atmospheric chemistry community as a whole.

Ok, we admit that ELVOC production in gas phase auto-oxidation is close to our hearts and thus the statement may reflect our specific interests. Statement will be updated also because the “most significant open question” is not open anymore (Ehn et al., 2014, Nature). Also changes in introduction that take into account Ehn et al. results will be made.

Other central, open questions in atmospheric oxidation chemistry include the global importance of NO3- and Cl- initiated oxidation, and the role of RO2 isomerization in atmospheric photochemistry, to name a few. The references to the Ehn results (here as well as on page 3074, lines 12-14) as the “most significant open question in atmospheric oxidation” therefore should be removed.

Statement will be removed.

Referee 2:

GENERAL COMMENTS

The work in this manuscript builds on the moderately-sizable body of data relating to sCI reactions with SO2 and contributes novel data regarding the sCI yield from isoprene and monoterpenes, similar to the work of Berndt et al (2012) where they studied other alkenes. The reaction of sCI + SO2 was monitored by the relatively-new NO3- API-CIMS technique, via detection of H2SO4 from its cluster with NO3
- ions. The relative rates of sCI + organic acid vs.
sCI + SO2 that results from this work is a useful contribution to the literature, as other available estimates (e.g., of the rate of CH2OO+formic acid vs. CH2OO +H2O (Neeb et al Atmos. Environ 1997)) are somewhat more uncertain. If the work by Berndt et al (2012) is an indication, I believe the authors to be knowledgeable on the nuances of the sCI reactions. However, the representation of the current state of knowledge in this manuscript could afford to be more inclusive of previous works, and below I call to the authors’ attention some relevant citations. I am surprised that the discussion of the acetone oxide reaction with formic acid is so brief; I believe it would benefit greatly from acknowledgement of previous work that first describe the sCI + formic acid reaction and a discussion on how the current results here compare.

We will improve the discussion regarding the the sCI + organic acid and also acknowledge the existing literature, including Neeb 1997, better.

A discussion of the atmospheric relevance of the work should also be added (do the results here support that SO2 is important for the loss of Criegees in the atmosphere?).

Our measured ratios between k_loss and k_scI+SO2 are in the range of few 1e12. This means that reaction with SO2 can become a significant sink for sCI only when [SO2] is close to 1e12 or higher. Such concentrations are unlikely present in any close natural environment including forested areas, where sCI concentrations could be expected to be high. Therefore, reaction with SO2 has minor importance from point of view of sCI loss. However, sCI + SO2 reaction can be a significant source of sulphuric acid, contributing up to tens of percents of total low tropospheric H2SO4 formation as shown in earlier studies (Mauldin et al., 2012; Boy et al. 2013; Pierce et al., 2013). Our present values are in line with reaction rate estimates published in Mauldin et al. and applied by Boy et al. and thereby the previous conclusions on the sCI's contribution to global H2SO4 burden can be considered valid. We will improve the discussion in revised manuscript.

The work presents novel insights into sCI reactions, and I recommend publication in ACP only after the detailed comments have been thoroughly addressed.

DETAILED COMMENTS

1. Page 3073, lines 2-5: ("Until the recent discovery of the atmospheric relevance of stabilized Criegee intermediates…") The atmospheric relevance of stabilized Criegees, specifically the sCI + H2O reaction, has been shown 2 decades ago. The first report of the atmospheric relevance of the Criegee bimolecular reactions is that of Becker et al (1990) in the journal Nature, where they observed products of the sCI + H2O reaction in a forest. The authors provide support for the suggestion that sCI can react with SO2 in the atmosphere at faster rates than expected, through the Mauldin et al (2012) work. The important distinction here is that Mauldin et al (2012) observe higher H2SO4 can be explained by SO2 + OH, and they attribute the difference to a "Compound X" which they hypothesize is the stabilized Criegee. This sentence should be reworded to be specific to the sCI+SO2 reaction, and not to imply that none of the sCI reactions were thought to be important in the atmosphere until recently.

The sentence will be rephrased to: "*Until the recent discovery of the atmospheric relevance of* ***reaction of*** *stabilized Criegee intermediates* ***with SO2****…*"

2. Page 3074, lines 14 – 19: Related to #1, the authors might want to be careful here ("…the observation that the stabilized Criegee intermediates…add to the oxidation capacity of the atmosphere…"). Maudlin et al (2012) is the relevant citation, but this paper only bring up the possibility that there is a "Compound X" that may oxidize SO2, and they hypothesize that it might be the stabilized Criegee. Also, Berndt et al (2012) was cited even though the work does not support this statement directly (it was a kinetic laboratory study as the authors know, and did not measure rate coefficients of sCI + H2O). Perhaps change "observation" to "suggestion"?

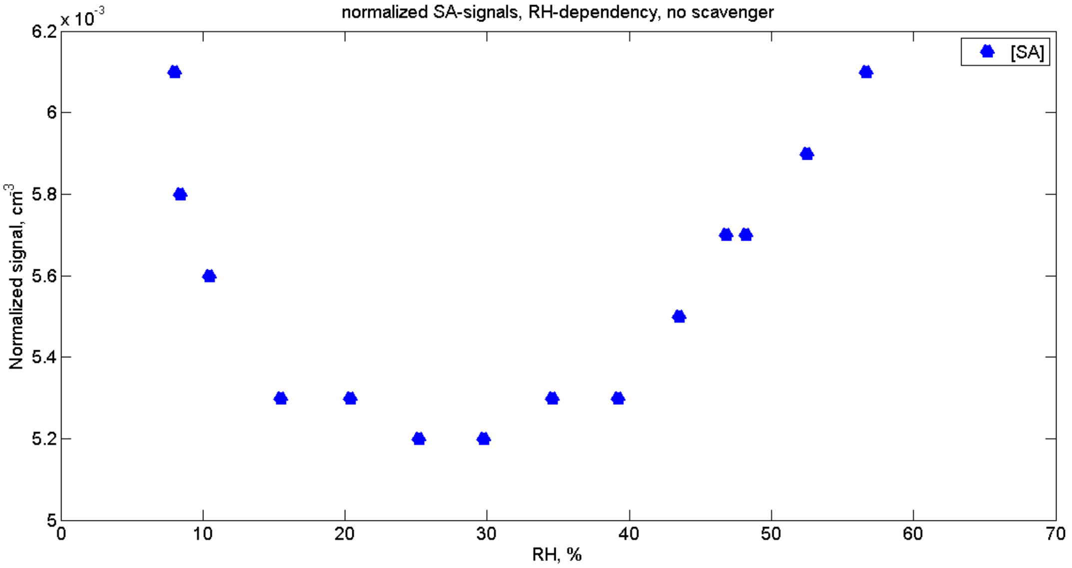
Sentence will be changed according to referee's suggestion.

3. Page 3077, lines 10 – 11: The way this statement is worded makes it not strictly true. The reactions of atmospherically-relevant sCIs have indeed been investigated with many other compounds besides SO2. This study explores CH2OO and acetone oxide – and rate coefficients and product distributions of these sCI with respect to H2O, Formaldehyde, CO, NOx, Acetaldehyde, and Formic acid have all been studied theoretically or measured before. Please see Fenske et al (2000), Table 1 for a good summary of rate coefficients. Also please see #5 for citations for previous work that studied the sCI + formic acid reaction.

This is a very good comment. The sentence "*Still, the reactions of atmospherically relevant sCIs with compounds other than SO2 have not been investigated so far*." will be removed and substituted with more comprehensive discussion of previous work. Previous literature suggested by referee will be taken into account.

4. Methods section: How do the NO3- ions interact with water vapor in the ion chemistry of the CIMS? This is important for understanding the results because the authors varied the humidity of the experiments. I am not aware of a previous paper on this technique that describes the effect of water vapor on NO3
- chemistry. For other CIMS techniques, water
has an important effect on ion clustering. For example, in PTRMS (H3O+.(H2O)n clusters form), Iodide CIMS (I-.(H2O)n clusters form), Acetate CIMS (CH3COO-.(H2O)n clusters form), CF3O- CIMS (CF3O-.(H2O)n clusters form) and the water clusters have either a small or large affect the detection of analytes, depending on the structure of the analyte, so that a calibration is needed in many cases. Please state explicitly how the sulfuric acid ion sensitivity changes with water vapor and if water clusters are used for normalization. If your previous characterizations show that water vapor does not affect NO3- ion chemistry pertaining to H2SO4 detection, please explicitly state this show the characterization.

CI-APi-TOF technique is relatively new and we do acknowledge that detailed knowledge on RH dependency does not exist. Reason is two-fold. First, water vapor can affect the level of hydration of sulphuric acid thereby affecting the charging, diffusion coefficient and collision diameter. Second nitrate.water clusters also have different collision diameter than pure nitrate ion and clustering could, potentially change the proton affinity of the primary ion. Also steric effects may play a role. We have experimentally investigated the total RH effect for RH range between 10 and 60 percent, and within measurement accuracy did not see significant change in detected sulphuric acid concentration. See figure below. However, we have indications from field studies that RH exceeding ~80% starts to cause more remarkable changes in the ionization. Exact reasons and magnitude of the effect at high RH is a topic of our ongoing studies. However, any inaccuracies in measured [SA] is subtracted since we report relative rate coefficients. We will add a sentence saying that within measurement accuracy no significant RH effects were observed. If necessary, we can also visualize the effect e.g. by a figure similar to one shown below, but as this is more technical detail we would rather like to keep the paper compact.



5. Introduction section: Please add a paragraph to introduce the sCI + organic acid reaction and cite the previous studies. For example: Neeb et al (1995) first showed spectroscopic evidence of this reaction, and speculated an ester is formed from the CH2OO + formic

acid reaction due to analogy with the aqueous phase. Neeb et al named the resulting ester hydroperoxymethyl formate (HPMF). Thamm et al (1996) synthesized the HPMF compound through ozonolysis followed by addition of formic acid, and characterized it with various spectroscopy methods. Hasson et al (2001) confirmed HPMF production at lower RH in a chamber. Neeb et al (1997) estimated the rate coefficient of the CH2OO reaction with formic acid relative to the reaction with water (14000 x kSCI+H2O). Also, how do the relative rates reported in this work compare with the Neeb et al (1997) study?

We will make the introduction to previous work more comprehensive and add the suggested references. We will also make an order of magnitude (we cannot get accurate value out from our data) comparison to Neeb et al. study. Assuming that our k_loss would equal to k_sCI+H2O (and unimolecular decomposition would be negligible):

k(loss) / k(sCI+SO2) = k(sCI+H2O) [H2O] / k(sCI+SO2) = A
k(sCI+acid) / k(sCI+SO2) = B

k(sCI+H2O) [H2O] / A = k(sCI+acid) / B

k(sCI+acid) / k(sCI+H2O) = [H2O] * B / A.

@ RH = 20/50 % [H2O] = 0.58e17 / 2.89e17

B / A from tables 2&3 ~ 1e-12, with [H2O] ~1e17

yields estimation k(sCI+acid) / k(sCI+H2O) ~ 1e5 = 100 000. This is estimation for the upper end of the ratio and thus value by Neeb et al. (14 000) would be not in conflict with our result. However, as noted, k_loss includes also unimolecular decomposition and thus the ratio is certainly smaller than 100000.

6. Section 3.1. The authors found that kloss/kSCI+SO2 reactions did not change with humidity for the a-pinene and limonene; however, Tillman et al (ACP 2010) found that the OH and carbonyl yields from ozonolysis of a-pinene was dramatically higher with higher RH. This should factor in the kloss value as kdecay, so what does that mean for the reaction of SO2?

There are conflicting statements in literature regarding the OH yield as a function of RH. Most of the studies found no clear RH dependence. Tillmann et al. reporting an increase of the OH yield from 53% (RH: 0%) to 67% (RH: 44%) without error limits. They used a very indirect way of OH yield determination. It´s not clear if it is a significant difference. So, any conclusion for sCI + SO_2 are not justified.

Same situation for pinonaldehyde formation. The pinonaldehyde yield as a function of RH seems to be dependent on the experimental approach. There are also different mechanistic explanations for pinonaldehyde generation.

7. Section 3.1. Can the authors discuss what the results mean in terms of atmospheric significance? For example, for a kloss/kSCI+SO2 for isoprene of 2.5 x 1012 molec cm-3 at RH ~ 10%, if SO2 is to have a 1:1 reactivity ratio with respect to H2O for sCI from isoprene, if I understand correctly then one would need 2.5 x 1012 molec cm-3 of SO2 or ~100 ppb of SO2. And at RH 50%, one would need 850 ppb to be as competitive as water and decomposition. Even for a competition level of 10% with respect to water and unimolecular decomposition, then this would mean 10-85 ppb of SO2 is needed. Certainly 10 – 85 ppb of SO2 is possible in some polluted regions, according to US EPA records, but is high [SO2] found in heavily-forested areas where isoprene and monoterpenes emissions are elevated? This type of discussion should be included to see whether the

suggestions that the sCI + SO2 reaction is atmospherically important, regionally or globally, can be supported.

Contribution of sCI + SO2 to surface levele H2SO4 in forest with [SO2] rarely exceeding 1 ppb was assessed in Mauldin et al., 2012 (Nature). There the k_loss was “guessed” to be 5 (basing on theoretical considerations). Resulting k(sCI+SO2) (for apinene SO2) was 6 e-13. Therefore the relative rate coefficient k(loss) / k(sCI+SO2) used in Mauldin et al., was 0.833e13. This value is higher than ours and thereby, based on present data might rather underestimate than overestimate the role of sCI in surface level SO2 oxidation. As said above already, SO2 in forested environment is a minor sink for sCI, but sCI + SO2 reaction can still be a major source of sulphuric acid.

The accurate assessment of the role of sCI + SO2 in [H2SO4] budget is a topic of our future study, but, in the revised manuscript, we will discuss the atmospheric relevance of the SO2 reaction both from point of view of sCI fate and H2SO4 birth.

8. Section 3.2. The authors suggest that the reaction of acetone oxide with organic acids is not water-dependent so they didn’t study the reaction at different RH. This might be true for that specific sCI. However, the reaction of formic acid with CH2OO is very waterdependent (it is only important under dry conditions, see Neeb et al 1995 and Hasson et al 2001). This is worth mentioning because it’s important to note the reaction of organic acids with sCI is strongly dependent on specific structure and conformation.

In the revised version we will mention that sCI structure and conformation affects the reactivity toward organic acids and that our results cannot be directly extended to cover all sCI’s.

9. Page 3081, lines 3 – 4, and Page 3073, 26, and page 3074, lines 1-2, and Page 3085, lines 20 - 22: I do not understand how “a more general role” of sCI is elucidated here. This is vague and should be rephrased. I believe the authors mean to say that for acetone oxide, the reaction with formic acid in the atmosphere is important relative to its reaction with SO2. In an absolute term, if we can assume kSCI+SO2 for acetone oxide is 7.7 x 10-13 (Berndt et al 2012), then using the results derived here, kSCI+formic for acetone oxide is ~ 2 x 10-12 cm3 molec-1 s-1 (a factor of 3 higher). If kSCI+H2O is on the lower end of the literature range (1 x 10-18) and the RH is moderate ~50%, then one would still need to have almost 7 ppb of formic acid for equal reactivity as with water.
1 – 10 ppb of formic acid is a common range in forested region, so at 50% RH and this assumed kSCI+H2O,
acetone oxide might indeed be lost to formic acid in non-negligible amounts. However, if kSCI+H2O is any larger than that (which is entirely possible because the upper limit can be 10-15) or if RH is very high, then it’s easy to see how the sCI + formic reaction becomes less competitive (or not competitive). Further, the most abundant and long-lived sCI in the atmosphere is CH2OO and its reaction with water is much faster than acetone oxide because this sCI is “all anti” whereas acetone oxide is “all syn.”
The authors should add a discussion along those lines to the manuscript, to support whether the organic acid reactions they study are relevant to the atmosphere (just take a typical mixing ratio of formic acid and acetic acid in a forested region). It is important not to generalize to all sCI from the reaction of one, because, as the authors know, sCI structure is a controlling factor for reactivity.

Discussion regarding the relevance of the reaction will be added. Again, from point of view of sCI reaction with water and/or self decomposition any other reactions can be minor or negligible. However, from point of view of acid, or from point of view of reaction products from sCI+acid, the situation can be completely different. See the discussion regarding sCI + SO2 -> H2SO4 above. Nevertheless, sentences regarding the atmospheric relevance from both sCI and acid point of view will be added.

Technical changes:
Page 3084, line 2: Change “facts” to “observations”

OK

Page 3084, line 3: Add “sulfur-containing” or “sulfur-bearing” to the description of secondary ozonide, which is usually meant to refer to the product of the aldehyde +sCI reaction.

OK

Page 3085, line 6: Do the authors mean Berndt et al (2012) or Berndt et al (2014, submitted) that are included in the reference list, instead of Berndt et al (2013), which is not found in the references?

Should be 2012. Will be corrected. Aalso Berndt et al., 2014 reference will be changed, since it is published in Atm. Environ.

References:

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