Review for: acp-2013-969

Reactivity of stabilized Criegee intermediates (sCI) from isoprene and monoterpene ozonolysis toward SO_2 and organic acids

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GENERAL COMMENTS

The work in this manuscript builds on the moderately-sizable body of data relating to sCI reactions with SO_2 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 + SO_2 was monitored by the relatively-new NO_3- API-CIMS technique, via detection of H_2SO_4 from its cluster with NO_3^- ions. The relative rates of sCI + organic acid vs. sCI + SO_2 that results from this work is a useful contribution to the literature, as other available estimates (e.g., of the rate of CH_2OO+formic acid vs. CH_2OO +H_2O (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. A discussion of the atmospheric relevance of the work should also be added (do the results here support that SO_2 is important for the loss of Criegees in the atmosphere?).

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 + H_2O 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 + H_2O reaction in a forest. The authors provide support for the suggestion that sCI can react with SO_2 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 H_2SO_4 can be explained by SO_2 + 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+SO_2 reaction, and not to imply that none of the sCI reactions were thought to be important in the atmosphere until recently.

2. <u>Page 3074, lines 14 – 19:</u> 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 SO_2, 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 + H_2O). Perhaps change "observation" to "suggestion"?

3. <u>Page 3077, lines 10 – 11:</u> 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 SO_2. This study explores CH_2OO and acetone oxide – and rate coefficients and product distributions of these sCI with respect to H_2O, 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.

4. <u>Methods section</u>: How do the NO_3- 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 NO_3^- chemistry. For other CIMS techniques, water has an important effect on ion clustering. For example, in PTRMS ($H_3O^+.(H_2O)_n$ clusters form), Iodide CIMS ($I^-.(H_2O)_n$ clusters form), Acetate CIMS ($CH_3COO^-.(H_2O)_n$ clusters form), CF_3O- CIMS ($CF_3O^-.(H_2O)_n$ 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 NO_3- ion chemistry pertaining to H_2SO_4 detection, please explicitly state this show the characterization.

5. <u>Introduction section</u>: 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 CH_2OO + 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 CH_2OO reaction with formic acid relative to the reaction with water (14000 x $k_{SCI+H2O}$). Also, how do the relative rates reported in this work compare with the Neeb et al (1997) study?

6. Section 3.1. The authors found that $k_{loss}/k_{SCI+SO2}$ 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 k_{loss} value as k_{decay}, so what does that mean for the reaction of SO_2?

7. Section 3.1. Can the authors discuss what the results mean in terms of atmospheric significance? For example, for a $k_{loss}/k_{SCI+SO2}$ for isoprene of 2.5 x 10^{12} molec cm^{-3} at RH ~ 10%, if SO_2 is to have a 1:1 reactivity ratio with respect to H_2O for sCI from isoprene, if I understand correctly then one would need 2.5 x 10^{12} molec cm^{-3} of SO_2 or ~100 ppb of SO_2. 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 SO_2 is needed. Certainly 10 – 85 ppb of SO_2 is possible in some polluted regions, according to US EPA records, but is high [SO_2] 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 + SO_2 reaction is atmospherically important, regionally or globally, can be supported.

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 CH_2OO is very water-dependent (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.

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 SO_2. In an absolute term, if we can assume $k_{SCI+SO2}$ for acetone oxide is 7.7 x 10^{-13}

(Berndt et al 2012), then using the results derived here, $k_{\mathrm{SCI+formic}}$ for acetone oxide is ~ 2 x 10^{-12} cm^3 $molec^{-1}$ s^{-1} (a factor of 3 higher). If $k_{\mathrm{SCI+H2O}}$ 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 $k_{\mathrm{SCI+H2O}}$, acetone oxide might indeed be lost to formic acid in non-negligible amounts. However, if $k_{\mathrm{SCI+H2O}}$ 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 CH_2OO 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.

Technical changes:

Page 3084, line 2: Change "facts" to "observations"

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.

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?

References:

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