

## ***Interactive comment on “Reactivity of stabilized Criegee intermediates (sCI) from isoprene and monoterpene ozonolysis toward SO<sub>2</sub> and organic acids” by M. Sipilä et al.***

**Anonymous Referee #1**

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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 SO<sub>2</sub> are added to a gas-phase mixture of ozone, alkenes (limonene, pinene, or isoprene), propane (to scavenge OH), and H<sub>2</sub>O, and measurements of H<sub>2</sub>SO<sub>4</sub> 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

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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 [H<sub>2</sub>SO<sub>4</sub>]sCI (equations 3 and 4), the concentration of sulfuric acid formed by titration of the sCI by SO<sub>2</sub>. In this work it is determined by running at extremely high SO<sub>2</sub> concentration (top right corner of Figures 1–3), and assuming all H<sub>2</sub>SO<sub>4</sub> formed is from sCI+SO<sub>2</sub>. However the validity of this assumption is questionable, since other sources of sulfuric acid may also exist. Most importantly, this work neglects oxidation of SO<sub>2</sub> by OH. It is stated that the propane reacts with “>98%” of the OH radicals, but at the highest SO<sub>2</sub> 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 SO<sub>2</sub> concentration) will react with SO<sub>2</sub> to form H<sub>2</sub>SO<sub>4</sub>. Also, it seems likely that the main fate of RO<sub>2</sub> radicals (formed from OH+propane and O<sub>3</sub>+alkene) will be reaction with SO<sub>2</sub> (forming SO<sub>3</sub>) under these conditions as well. The effects of these reactions on [H<sub>2</sub>SO<sub>4</sub>] and hence on calculated sCI yields need to be assessed.

Similarly, a number of carbonyls and acids are formed from the OH+alkane and O<sub>3</sub>+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.

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.

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 [SO<sub>2</sub>] is high. Even in the absence of SO<sub>2</sub>, 98% of the OH is scavenged by propane only at the highest concentration of propane given (8.2e15 molec/cm<sup>3</sup>, from Table 1). At the lowest concentration (1.64e15

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molec/cm<sup>3</sup>), this value is ~92%, with 8% of the OH reacting with alkene.

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]?

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 sCl+organic acids are faster than sCl+SO<sub>2</sub> implies that sCl's 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 sCl-initiated oxidation of acids can be determined only by comparing values of k[sCl] to values of k[OH], etc. Such a comparison would seem to be necessary to assess the atmospheric importance of these reactions.

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

P. 3083, line 11: If CH<sub>2</sub>OO reacts quickly with water vapor (relative to SO<sub>2</sub>), this would have major implications for our understanding of Cl chemistry, and the inclusion of the Welz results in models. This should probably be mentioned.

P. 3084, line 16: How valid is the assumption that reaction of water dominates decomposition for CH<sub>2</sub>OO? Is there previous work showing this? (On the following page, it is stated that the opposite is true for CH<sub>3</sub>C(OO)CH<sub>3</sub>.)

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. Other central, open questions in atmospheric oxidation chemistry include the global importance of NO<sub>3</sub>- and Cl- initiated

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oxidation, and the role of RO<sub>2</sub> 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.

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