Atmos. Chem. Phys. Discuss.,
doi:10.5194/acp-2016-919-RC2, 2016

Atmospheric Chemistry and Physics
Discussions
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Interactive comment on “Identifying Criegee intermediates as potential oxidants in the troposphere” *by* Anna Novelli et al.

Anonymous Referee #2

Received and published: 14 December 2016

This paper summaries steady-state calculations of the expected concentration of stabilized Criegee intermediates (SCIs) during two field campaigns (HUMPPA-COPEC 2010 and HOPE 2012). Several methods are used to estimate the concentration of SCIs in these environments, including estimates based on the missing H_2SO_4 oxidant, the ozonolysis of measured unsaturated compounds, unexplained total OH reactivity, and unexplained OH production rates. These different methods result in estimated SCI concentrations between 5 x 10^3 and 2 x 10^6 cm^{-3} in these environments, although given the uncertainty associated with some of the assumptions used in these calculations the authors conclude that a value of 5 x 10^4 cm^{-3} with an uncertainty of approximately and order of magnitude is the most appropriate estimate of the SCI concentration in these environments.

The authors then provide empirical evidence that the artifact in their LIF-FAGE measurements during these field campaigns is the result of decomposition of SCIs in their low pressure detection cell. The evidence includes strong correlations of the observe OH background signal with temperature, ozone, and BVOC concentrations. In addition, scavenging experiments where SO^2 is added externally also removes the interference. However, the observed background OH signal corresponds to an equivalent concentration that is several orders of magnitude greater than the calculated SCI concentration suggesting that SCIs are not the only contributor to the background signal. Although the authors attempt to provide some possible explanations to account for this discrepancy, including a greater decomposition rate inside their detection cell and a different transmission efficiency of SCIs through their inlet compared to OH, they cannot fully explain the observed discrepancy.

The paper is well written and suitable for publication in ACP after the authors have addressed the following comments:

1) The title of the paper is somewhat misleading, as the paper does not explicitly identify Criegee intermediates given that the background OH signal cannot be solely attributed to SCIs. A more appropriate title might be “Estimating the concentration of Criegee intermediates as potential oxidants in the atmosphere.”

2) The description of the different methods used to calculate the steady-state concentration is long and may detract from the overall conclusions of the paper. Moving some of this discussion to the Supplement would help maintain the focus of the paper on the resulting concentration estimates and interference discussion. Did the authors compare their estimations of the concentration of SCIs to that predicted by the Master Chemical Mechanism?

3) The strongest piece of evidence that the source of the OH background signal is due to SCIs is the SO_2 scavenging experiment described on page 30 and Figure 10. However, the paper would benefit from an expanded discussion of these measurements. What are the equivalent OH concentrations corresponding to the signals shown in Fig-

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ure 10? Do they correspond to the high equivalent OH concentrations discussed on page 33? Did the authors attempt more than one scavenging experiment at different times during the day and/or night? Was the background signal consistently scavenged during multiple experiments? Were there periods when addition of SO_2 did not scavenge all of the background signal? Providing more details on these experiments would give additional confidence that SCIs were responsible for the high background OH signal.

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