

## **Review of “Identifying Criegee Intermediates as Potential Oxidants in the Atmosphere” by A. Novelli, K. Hens, C. T. Ernest, M. Martinez, A. C. Nölscher, V. Sinha, P. Paasonen, T. Petäjä, M. Sipila, T. Elste, C. Plass-Dülmer, G. J. Phillips, D. Kubistin, J. Williams, L. Vereecken, J. Lelieveld, and H. Harder**

This paper focuses on the analysis of data from two field measurement campaigns, and combines results from laboratory experiments to assess relationships between inferred amounts of stabilized Criegee intermediates (SCI) in the atmosphere, and their possible contribution to the background signals in the measurement of hydroxyl radicals (OH) by a particular laser induced fluorescence (LIF)-based instrument. The physical chemistry of SCI is currently a subject of great interest, as is improved understanding of the components of the background in LIF-based OH instrumentation. Analysis of data collected during comprehensive ambient field campaigns is a sensible way to attack this problem. The authors have done a good job of precisely describing their assumptions and the potential pitfalls of various approaches. They have used various statistical parameters (e.g. correlation coefficients) to allow the reader to understand the robustness of the relationship under discussion. The literature is well-cited, and indeed the reference list serves as a useful list of recent Criegee intermediate-related papers.

### **General comments.**

- 1) This reviewer finds the discussion of the average concentration of SCI over an entire field campaign not very useful. It would be much better to work with an entire time series of SCI, followed by development of average diurnal cycles, and dependence of the derived concentrations on various parameters such as ozone, NO<sub>x</sub>, OH reactivity, reactivity from all BVOC, reactivity from all alkenes, and so on. This would give the reader a better feel as to what to expect from SCI behavior in various atmospheric environments.
- 2) Regarding the rate coefficient for SCI with SO<sub>2</sub>, this reviewer suggests going with the larger value obtained by several groups, and simply mentioning in the discussion that if the Mauldin et al., 2012 value is correct, then the concentrations of SCI increase by a factor of 66 (3.3E-11 / 5E-13). As the current discussion implies, the values derived with the Mauldin et al. value seem high when various constraints are imposed.
- 3) The data for both studies is lacking measurements of important species. For example, HUMPPA-COPEC 2010 is missing some terpenes, mono-alkenes, small alkanes, and aromatic compounds. HOPE 2012 is more complete, but is missing hydrogen peroxide, HONO, and a pentane isomer. Both studies are light on oxygenated species (5 compounds). Other measurements such as NO<sub>y</sub>, alkyl and peroxy nitrates, nitric acid, and HO<sub>x</sub> radicals would help to put the measurements in an overall context of pollutant level and oxidizing capacity. It should be possible to use other studies in the region to estimate concentrations of these other species, using perhaps, ratios to CO or some other approach.
- 4) The presentation of data in a table with average values give the reader only one dimension of their behavior with time, radiation, temperature, and other species. Time series plots of all the species in the Supplemental Information would be preferred, but in their place, additional information in the table would be helpful. Suggest including with the average (mean) values, include median, and standard deviation of the mean. For species with significant diurnal variations, average diurnal plots would be useful. Also, values in mixing ratio units (e.g. ppbv and pptv) should be used rather than molecular units. Plots of average ozone, OH, and HO<sub>2</sub> versus NO or NO<sub>x</sub> would help the reader understand the chemical regime of the air masses measured. Such plots may help the authors decide how to divide the data into various measurement regimes (e.g. background, polluted, mixed, anthropogenic, biogenic).

- 5) In several places, the sum of the VOC concentration is given. This reviewer is not convinced that this is a very useful parameter, since the various VOCs measured have very different reactivities with OH, ozone, and NO<sub>3</sub>. It might be better to use the sum of the OH reactivity due to the VOCs to describe the varying composition of air masses (e.g. when discussing the tree cutting event).
- 6) With a more complete set of species measured and estimated, it makes sense to perform model runs with the Master Chemical Mechanism (or other mechanism) modified as needed based on the latest information on SCI reactions and photolysis. These runs will aid in the budget analysis of individual SCI and their sum, as well as budgets of other species (e.g. OH, sulfuric acid).
- 7) Some species and parameters are so important to the analyses described in this paper as to deserve further discussion on their validity (e.g. OH reactivity). Have the methods been compared in the laboratory and/or the field with other techniques? Do the values behave as expected and as seen in other studies as functions of time of day, NO<sub>x</sub>, OH reactivity, etc? While everyone in such campaigns submits their data in the best possible state that has been carefully quality assured and quality controlled, mistakes can be made. Detailed data examinations can sometimes reveal such problems.
- 8) This reviewer is not convinced that the current title describes the content of the paper. Suggest changing the title to more accurately reflect the paper contents and conclusions.

**Specific comments.**

Page 2, line 11. Suggest "...through the addition to sulphur dioxide."

Page 2, line.11. The term "central value" is used here and elsewhere in the paper. Does this refer to the mean or median value or something else? Suggest using standard statistical terms.

Page 4, line 6. Suggest "...while lower limits have been determined..."

Page 5, line 23. In giving an OH value, is this meant to be globally, daily maximum, or campaign average. This value seems a bit high for the daily maximum remote locations, and perhaps a bit low for polluted situations. Suggest adding a bit more text to describe what is mean by this value.

Page 6, line 1. Suggest another word in place of "relevant", perhaps "significant".

Page 7, line 15. An OH scavenger is mentioned, but its identify is not revealed. Suggest saying specifically what compound is used.

Page 9, line 1. Suggest "...titration of OH<sub>atm</sub> is performed..." and "...to determine their backgrounds in different environments."

Page 9, line 5. The description of "better operation" is vague. Suggest a bit more information or rewording.

Page 9, line 20. Suggest "...Scots Pines..."

Page 9, line 22. Suggest "...aerosol particle concentrations, size distributions..."

Page 10, line 6. Check to make sure BVOC is defined earlier in the paper.

Page 10, line 6-8. Given the importance of the OH reactivity measurements, suggest adding more information including the estimated uncertainties.

Page 11, line 22-25. The discussion of this method of OH reactivity has a bit more information. Suggest making the discussion similar for both methods. Discussion of a comparison of these two techniques would be beneficial, if it has been done.

Page 12, line 14. This equation arises out of the steady state assumption for sulfuric acid. Suggest adding a bit of discussion of the assumptions that why steady state should be expected.

Page 13, line 1. Suggest "...the rate coefficients of SCI..."

Page 13, line 2. It is stated that the steady state concentration of SCI can be calculated, but equation (2) is that assuming steady state for sulfuric acid. One can calculate the SCI value, but it is not the steady

state value. As discussed earlier, suggest doing this calculation for every data point for which all the data needed are available. Then perform statistics and comparison with the full time series.

Page 15, line 9-11. It is not clear what the steady state concentration (although it is not the steady state concentration, as discussed earlier) remains in agreement with. Suggest a bit more text to clarify this. Also, suggest "...based on the measured concentrations of VOC..."

Page 15, line 14. It appears to this reader that the calculation yields total sulfuric acid loss (rather than production). Of course, in steady state, production and loss are equal.

Page 16, equation 3. This equation yields values of individual SCI using the assumption of steady state. In addition to loss of SCI from unimolecular decomposition, it appears that reaction with water, and other reactions should be included. Also the equation should be clearer as to which terms are being summed. This reviewer believes that the summation should be over  $k$ ,  $[\text{VOC}]$ ,  $Y_{\text{SCI}}$ , and the loss terms. Ozone is the only parameter that should be outside the summation. Suggest constructing a full time series for this estimate of SCI.

Page 16, line 8. Suggest "We assume..."

Page 16, line 13. Doesn't  $Y_{\text{SCI}}$  depend on the VOC that reacts? If so, then the value should be different for each one.

Page 17, line 12. Suggest "...in a pristine forest environment..."

Page 18, line 24. Should the statement "...half of the measured OH..." actually be "...one-third of the measured OH..."?

Page 19, line 22. The phenomenon of unexplained OH production when OH reactivity is high is interesting. It makes sense to this reviewer that this observation could be due, at least in part, to errors in the measurement of OH reactivity. It also could show up when NO<sub>x</sub> is high, if NO<sub>x</sub> correlates with OH reactivity. If so, could it be to errors in measuring HONO or errors in the estimate of  $J(\text{HONO})$ ? The point is that it is not necessarily related to VOC levels or chemistry. Does the need for unexplained OH production disappear when the OH reactivity calculated from individual measured species is used rather than the directly measured OH reactivity?

Page 20, line 1. Suggest "...during low sun..." since a positive value for  $J(\text{O1D})$ , even though small, is not night time.

Page 20, line 15. The statement that only certain VOC are considered is confusing, because those VOC causing the unknown OH reactivity are themselves unknown. Suggest rewording this discussion.

Page 21, line 11. It is not clear exactly what is meant that the ratio of syn- to anti-SCI is within a factor of 5. Does that mean the ratio can go from 0.2 to 5? Or is anti-SCI always greater than or equal to syn-SCI? A bit more discussion would be helpful.

Page 22, line 18. Suggest "...which can represent an important primary source..." since whether HONO photolysis is important depends on conditions.

Page 23, line 1-2. You could assume a range of HONO levels and do the calculations with those to see what the impact is.

Page 23, section 3.5. While Figure 3 is a clever and useful way to show all the estimates of SCI concentrations, it might also be helpful to put the values into a table. Estimates of uncertainties for each value should also be given.

Page 24. Perhaps calculations with a range of unimolecular decomposition and other reactions would be instructive. Estimates on individual SCI species would be preferred. A discussion of the atmospheric impacts (e.g. oxidation of SO<sub>2</sub>, oxidation of VOCs) of SCI over the range of values calculated would be welcome.

Page 25. While the sensitivity of the LIF instrument to OH cannot be used to calculate SCI concentrations from the OH background, this reviewer believes that the OH backgrounds should be normalized by the instrument sensitivity to account for internal instrument changes (e.g. laser power, white cell alignment) when discussing the OH background dependence on temperature and other parameters.

Page 25, line 10. Suggest saying that there is a strong correlation except for the 26-28 July (which are discussed later).

Page 25, line 21. This reviewer does not see how southern Germany has a larger fraction of non-biogenic VOC than Finland, based on the values in table SI-2. Suggest checking this statement for accuracy.

Page 29, line 11. Suggest "The reason for the lack of correlation..."

Page 31. In order to understand the possible impact of SCI on the instrument background, some information on residence times in various parts of the instrument would be helpful.

Page 32, line 6-8. Since OH produced by ozonolysis reactions quickly reacts, a mechanism for conversion of peroxy radicals to OH is critical. One possibility is  $\text{HO}_2 + \text{O}_3$ , and while not very fast, could be important.

Page 36, line 4. Suggest "Hence, higher SCI values appear to be less likely."

Page 38-48. Some of the references are not in alphabetical order.

Table 1. See earlier comments about Table SI-1 and 2. The "a" footnote is missing. Suggest adding more species (e.g. NO<sub>x</sub>, CO, etc.) to this table.

Figure 3. It appears the box for  $k_{\text{SCI}+\text{SO}_2} \sim 10^{-11}$  for HOPE 2012 should be moved to the left.

Figure 11. The flow lines for the skimmer do not seem reasonable. They should move toward the wall at least somewhat.