

Interactive comment on “Atmospheric isoprene ozonolysis: impacts of stabilized Criegee intermediate reactions with SO₂, H₂O and dimethyl sulfide” by M. J. Newland et al.

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We would like to thank both Reviewers for their positive and insightful comments. Specific points are addressed below:

Anonymous Referee #1

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"The authors have used the EUPHORE chamber to measure the loss of SO₂ during isoprene ozonolysis as a function of relative humidity and dimethyl sulfide (DMS) concentration. This enabled the determination of quantities such as the yield of stabilized
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Criegee intermediate (SCI), the relative rate coefficients for the reaction of SCI with H₂O vs. with SO₂, and the relative rate coefficients for the reaction of SCI with DMS vs. with SO₂. The authors found a SCI yield of 0.56 ± 0.03 , in good agreement with a recent experimental estimate by Sipilä (Atmos. Chem. Phys. 2014, 14, 12143) based on H₂SO₄ formation and an older theoretical estimate by Zhang (Chem. Phys. Lett. 2002, 358, 171). The derived relative rate coefficients allow the authors to conclude that reaction with water is the main sink for isoprene-derived, and that SCI may be a significant DMS oxidant at dawn and dusk, when both [OH] and [NO₃] are low. Overall, I judge the paper to be of high quality. The experimental work and data analysis have been done carefully, and the authors have been transparent about their methodology. The relevant literature has been thoroughly cited and discussed fairly. Moreover, the subject matter treated by the manuscript is clearly important in that it provides evidence that the stabilized Criegee intermediate derived from isoprene ozonolysis will likely not be a significant oxidant of SO₂. One suggestion: Since the authors cite the Hasson (2001) isoprene-SCI yield of 0.27 (in Table 1), they should try to account for the discrepancy between the present result and this earlier result."

Hasson et al. (2001) derived their isoprene total SCI yields by measuring the sum of the difference between (i) the H₂O₂ production under dry and high RH conditions and (ii) the difference between hydroxyl-methyl hydroperoxide (HMHP) production under dry and high RH conditions. The H₂O₂ is assumed to be formed from decomposition of a hydroxy-alkyl hydroperoxide formed from the reaction of the non-CH₂OO SCI (i.e. CRB-SCI) with H₂O, the HMHP is assumed to be formed in the reaction of CH₂OO with H₂O. The determined difference in yields for H₂O₂ is 0.11 and for HMHP is 0.15, hence the total yield of 0.26 (wrongly given as 0.27 in Table 1 – this has been corrected to 0.26). However, Hasson et al. do not measure the formic acid yield (to which HMHP decomposes). This could lead to an underestimation of the CH₂OO yield due to HMHP decomposition, which would lead to an underestimation in the HMHP and hence overall SCI yield. Indeed Hasson et al. note that their HMHP yield from isoprene ozonolysis is roughly half of that determined by Neeb et al. (1997) suggesting that they are missing

a significant part of the CH₂OO yield. The approach followed also cannot account for SCI that decompose via the hydroperoxide mechanism, since these would not be expected to form H₂O₂. While recent work has shown that such decomposition is likely very small for CH₂OO (Newland et al., 2015; Chhantyal-Pun et al., 2015), it is likely to be important for some of the CRB-SCI (though our work determines a fairly small overall contribution). Additionally, it is also possible that some of the hydroxyl-alkyl hydroperoxides formed by CRB-SCI + H₂O are stabilised and hence would not be measured by Hasson et al..

The following sentences have been added to Section 3.1:

Hasson et al. (2001) calculated a total SCI yield of 0.26 by measuring the sum of the difference between the H₂O₂ production under dry and high RH conditions (to give the non-CH₂OO SCI yield) and the difference between hydroxyl-methyl hydroperoxide (HMHP) production under dry and high RH conditions (to give $\varphi_{\text{CH}_2\text{OO}}$). One reason for the significantly lower value for the total SCI calculated by Hasson et al. compared to this work is the low value of $\varphi_{\text{CH}_2\text{OO}}$ determined, compared to e.g. Neeb et al. (1997) who determined $\varphi_{\text{CH}_2\text{OO}}$ of twice that determined by Hasson et al., using a similar methodology.

"I have no technical corrections to note."

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 8839, 2015.