We thank Rickard et al. for helpful comments. Our reply is given below.

AUTHORS’ REPLY to SC1:

We fully agree the following comments by Rickard et al. (DOI:10.5194/acp-2020-484-SC1):

"… the isoprene-ozone system is significantly more complex than these previously studied ozonolysis systems, with a range of different SCI species formed, with different yields and exhibiting different bimolecular and unimolecular kinetics."

Rickard et al. are right about that there are various stabilized CIs (CH₂OO, MVKO, and MACRO) generated in the isoprene-ozone system. In addition, there are multiple conformers (syn/anti and cis/trans) for MVKO or MACRO. "Therefore 9 different types and configurations of SCI can be formed in the isoprene ozonolysis system" as Rickard et al. have mentioned (DOI:10.5194/acp-2020-484-SC1). For this issue, we would add the following sentences to clarify (after Line 80).

"For MVKO, there are 4 possible conformers. Following the nomenclature of Barber et al., syn/anti-MVKO has a methyl/vinyl group at the same side of the terminal oxygen, while cis and trans refer to the orientation between the vinyl C=C and the carbonyl C=O bonds (Barber et al., 2018). It has been reported that syn- and anti-MVKO do not interconvert due to a high barrier between them but the barrier between cis and trans forms is low enough to permit fast interconversion at 298 K (Barber et al., 2018; Vereecken et al., 2017). Caravan et al., have shown that anti-MVKO is unobservable under thermal (298 K) conditions due to short lifetime and/or low yield, and thus, the UV-Vis absorption signal is from an equilibrium mixture of cis and trans forms of syn-MVKO (Caravan et al., 2020). For simplicity we will use MVKO to represent syn-MVKO in this work."

The conformer populations in the ozonolysis system may differ from those in the photolytic generation of MVKO using the diiodo precursor. However, the thermal lifetime of anti-MVKO (< 0.5 ms) (Vereecken et al., 2017; Barber et al., 2018) would be too short to support any significant concentration of anti-MVKO for participating in bimolecular reactions. For the remaining longer-lived cis and trans conformers of syn-MVKO, fast interconversion between the cis and trans forms would lead to an equilibrium mixture in both cases of ozonolysis and photolytic generation of CIs. In this regard, the conformer
populations of stabilized syn-MVKO would be similar in both cases. Thus, our direct kinetic results can be used to constrain the relevant reaction pathways for the ozonolysis systems.

More importantly, as already stated in the paper of Newland et al. (Newland et al., 2015), "However, it is important to note that no constraints regarding the products of the proposed DMS + SCI reaction were obtained; OH reaction with DMS is complex, proceeding through both abstraction and addition/complex formation channels, the latter rendered partially irreversible under atmospheric conditions through subsequent reaction with O₂ (Sander et al., 2011). The observed behaviour (Fig. 5) is not consistent with reversible complex formation dominating the SCI-DMS system under the conditions used; however it is possible that decomposition of such a complex to reform DMS, or its further reaction (e.g. with SO₂, analogous to the secondary ozonide mechanism proposed by Hatakeyama et al., 1986), would be consistent with the observed data, and also imply that the reaction may not lead to net DMS removal. Time-resolved laboratory measurements and product studies are needed to provide a test of this mechanistic possibility."

Indeed, there are multiple possibilities in the complicated isoprene-ozone system. Again our current results for individual CIs may provide useful constraints for such systems.

We agree that due to the large volume to surface ratio in the experiments of Newland et al., surface reaction may not be very important. We would revise the relevant text (after Line 212) to:

"For the determination of the relative rate of the CI + DMS reaction, Newland et al. monitored the consumption of SO₂ over a measurement period of up to 60 min until approximately 25% of isoprene was consumed (Newland et al., 2015). Additional uncharacterized reaction pathways (e.g., reactions with the products and/or catalytic reactions) would lead to a bias in the inferred rate coefficients. A part of this high complexity of the isoprene-ozone-DMS-SO₂ system has been discussed by Newland et al. in the section of Experimental Uncertainties (Newland et al., 2015). Our direct measurements and kinetics are very straightforward; the obtained results for individual CIs may provide useful constraints for related ozonolysis systems."
Finally, an interesting aspect raised by a referee (Referee 1) is:

"As this other study generated the Criegees via ozonolysis (O$_3$/isoprene), it does ask the question how we best understand ozonolysis in the atmosphere. Is stabilized Criegee chemistry the most important component of ozonolysis?"

This is possible. But we only generated individual CIs using a well-established photolytic method and cannot comment or answer this question.

References:


