Authors' response to discussion comment by Barbara Nozière on: Jenkin et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2019-44.

We are very grateful to Barbara Nozière for contributing a comment to the discussion of our paper, and for reminding us of the paper by Nozière and Hanson (2017) reporting speciated monitoring of organic peroxy radicals using CIMS, and consideration of a series of cross-reactions of different peroxy radicals.

As indicated in Barbara Nozière's comment, there were already kinetics studies of a number of peroxy radical cross-reactions (summarized in Table 11 of our paper), based on UV absorption detection. Although those studies were complicated by overlap of the peroxy radical absorption spectra, they were nonetheless direct measurements based on observation of the time-dependence of the peroxy radical absorptions at different wavelengths. In practice, the majority of the kinetics studies of peroxy radical self-reactions, cross-reactions and reactions with HO_2 are based on this type of measurement, which collectively form a substantial and invaluable data base.

When we became aware of the Nozière and Hanson (2017) study during the course of our work, we were encouraged that the kinetics data using their alternative technique were reported to endorse the existing data, although we noted that the rate coefficients were also reported to have very large uncertainties of a factor of ×5/5. The data were therefore not factored into our preferred values at the time, and we were hoping that there would be subsequent studies reported with a more optimistic assessment of uncertainties (e.g. with the improvements outlined by Nozière and Hanson in their Conclusions section). As a result, we failed to discuss or cite this study in our paper, which was an oversight. This would be corrected in a revised manuscript.

Prompted by Barbara Nozière's comment, we have reviewed the Nozière and Hanson paper again. We are reminded that kinetic data are actually reported for one previously unstudied cross reaction (*c*-$C_6H_{11}O_2$ + *t*-$C_4H_9O_2$) which should have been considered in our work. However, we have also noted that one measurement ($CH_3C(O)O_2$ + *t*-$C_4H_9O_2$) is in substantial disagreement with existing data, and we would very much value Barbara Nozière's opinion on this. Summarising the results:

(i) The Nozière and Hanson rate coefficients for the $CH_3C(O)O_2$ + CH_3O_2 and CH_3O_2 + *t*-$C_4H_9O_2$ reactions are in very good agreement with our tabulated data for these reactions, which are based on the IUPAC task group recommendations. That for the CH_3O_2 + *c*-$C_6H_{11}O_2$ reaction is also in agreement with our tabulated value, based on Villenave and Lesclaux (1996). We would make these points in a revised manuscript. We note that Nozière and Hanson (2017) were apparently unaware of the Villenave and Lesclaux (1996) determination.

(ii) As indicated above, we overlooked the new data for the *c*-$C_6H_{11}O_2$ + *t*-$C_4H_9O_2$ reaction, and this would be considered in a revised manuscript.

(iii) The Nozière and Hanson rate coefficient for the $CH_3C(O)O_2$ + *t*-$C_4H_9O_2$ reaction (3.7×10^{-14} cm^3 $molecule^{-1}$ s^{-1}) is a factor of 300 lower than that reported by Villenave et al. (1998) (1.1×10^{-11} cm^3 $molecule^{-1}$ s^{-1}). It also challenges the main conclusion of the Villenave et al. work, that the rate coefficients for all $CH_3C(O)O_2$ + RO_2 reactions are approximately 10^{-11} cm^3 $molecule^{-1}$ s^{-1}, which has been widely adopted in mechanism development and modelling studies. Villenave et al. (1998) reached this conclusion by studying the reactions of $CH_3C(O)O_2$ with a series of primary, secondary and tertiary RO_2 with widely different self-reaction reactivities. Nozière and Hanson (2017) were apparently unaware of the Villenave et al. (1998) determination, and therefore did not discuss this large disagreement and its wider implications. As indicated above, we would like to take advantage of this discussion to seek Barbara Nozière's opinion regarding possible reasons for this large discrepancy.

References

Nozière, B. and Hanson, D. R.: Speciated monitoring of gas-phase organic peroxy radicals by chemical ionization mass spectrometry: cross-reactions between CH_3O_2, $CH_3(CO)O_2$, $(CH_3)_3CO_2$, and *c*-$C_6H_{11}O_2$. J. Phys. Chem. A, 121, 8453-8464, 2017.

Villenave , E., and Lesclaux, R.: Kinetics of the cross reactions of CH_3O_2 and $C_2H_5O_2$ radicals with selected peroxy radicals, J. Phys. Chem., 100, 14372-14382, 1996.

Villenave , E., Lesclaux, R., Seefeld, S., and Stockwell, W. R.: Kinetics and atmospheric implications of peroxy radical cross reactions involving the $CH_3C(O)O_2$ radical, J. Geophys. Res., 103 (D19), 25273-25285, 1998.