

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

Thank you for providing additional information on your paper (Nozière and Hanson, 2017) and for the associated discussion of uncertainties. In relation to your opening comment, I would like to reiterate and re-emphasize that the failure to cite your work was simply an oversight that will be corrected should our paper be accepted for publication. The work we describe has been in development for several years, and we needed to update methods and references in many of the different areas described as new work was reported. Unfortunately (and inevitably), a few references fall through the net, even when they have been noted and considered.

I fully agree that it is important that new and complementary methods are applied to confirm or challenge rate coefficients reported in previous studies. As you discussed in Nozière and Hanson (2017), and noted in my previous comment, several of your reported rate coefficients confirm previously reported determinations that employed time-resolved UV absorption detection in conjunction with flash photolysis (FP). This is very encouraging and helpful, given the large data base of kinetics based on that type of experiment.

However, I also agree that such determinations that rely on prevailing mechanistic understanding should ideally be re-analysed periodically as that understanding evolves. The previous studies of peroxy radical reactions were mainly carried out in the late 1990s and early 2000s. As you indicated, there have been advances in understanding since that time, most notably for these cross-reactions the recognition of a significant propagating channel for the reaction of HO₂ with CH₃C(O)O₂ and with other oxygenated peroxy radicals. More recent kinetics studies of the CH₃C(O)O₂ + HO₂ reaction thus report 298 K rate coefficients that differ from those derived from earlier FP-UV absorption studies by about a factor of about 1.5 (e.g. Groß et al., 2014) with this difference being consistent with that obtained by re-analysis of the older experiments with the updated understanding (e.g. Le Crâne et al., 2006).

The CH₃C(O)O₂ + HO₂ reaction plays a minor secondary role in kinetics studies of the cross-reactions of peroxy radicals with CH₃C(O)O₂. The influence of the updated understanding would therefore be expected to have only a very subtle impact on the analysis of the older FP-UV studies, and your determination of the CH₃C(O)O₂ + CH₃O₂ rate coefficient would seem to confirm this.

The CH₃C(O)O₂ + *t*-C₄H₉O₂ reaction

As discussed before, your rate coefficient for the CH₃C(O)O₂ + *t*-C₄H₉O₂ reaction ($3.7 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) using CIMS is a factor of 300 lower than that reported by Villenave et al. (1998) ($1.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), using FP-UV. I am grateful for your thoughts and comments, and for offering to look further into this discrepancy.

I have some experience of the FP-UV experimental method. In my opinion, the Villenave et al. (1998) data provides very strong evidence for a rapid reaction between CH₃C(O)O₂ + *t*-C₄H₉O₂. My reasoning for this is as follows:

- At the start of their experiment, CH₃C(O)O₂ and *t*-C₄H₉O₂ are the only peroxy radicals present in the mixture. If the rate coefficient for CH₃C(O)O₂ + *t*-C₄H₉O₂ was a factor of 300 lower, the reaction would have been completely unobservable on their experimental timescale. The *t*-C₄H₉O₂ + *t*-C₄H₉O₂ reaction is also (much) too slow to occur on their experimental timescale. Thus, the system would simply become the CH₃C(O)O₂ self-reaction (with a constant absorption offset resulting from the un-reacting *t*-C₄H₉O₂).
- CH₃C(O)O₂ dominates the absorption at 207 nm (e.g., Fig. 1(b) of Villenave et al., 1998), such that the initial decay in absorption at that wavelength provides a good measure of the initial removal rate of CH₃C(O)O₂. It would be extremely easy to confirm that the presence of *t*-C₄H₉O₂ perturbs the behaviour of CH₃C(O)O₂, compared with its decay (by self-reaction) in

the absence of $t\text{-C}_4\text{H}_9\text{O}_2$. Because the self-reaction of $\text{CH}_3\text{C}(\text{O})\text{O}_2$ is rapid, any clear enhancement in the initial decay rate in the presence of a comparable quantity of $t\text{-C}_4\text{H}_9\text{O}_2$ (as observed by Villenave et al., 1998) means the $\text{CH}_3\text{C}(\text{O})\text{O}_2$ and $t\text{-C}_4\text{H}_9\text{O}_2$ reaction is similarly rapid. **In my opinion, this is almost unequivocal evidence for a rapid reaction from a direct time-resolved observation.** The initial decay rate and concentrations of $\text{CH}_3\text{C}(\text{O})\text{O}_2$ and $t\text{-C}_4\text{H}_9\text{O}_2$ would allow a first estimate of the rate coefficient, without the need to perform any simulations; although full optimization was achieved through simulation of the system.

- You are correct that CH_3O_2 builds up as the reaction progresses, and that this makes an important contribution to the absorption. The full simulation of the system over the entire experiment and at other wavelengths is then able to confirm that the broader mechanistic interpretation of the secondary chemistry is consistent.

In your comment, you indicate that your data for the $\text{CH}_3\text{C}(\text{O})\text{O}_2$ and $t\text{-C}_4\text{H}_9\text{O}_2$ reaction cannot support a rapid cross-reaction, and that (qualitatively) the rate constant must be much smaller than that of the $\text{CH}_3\text{C}(\text{O})\text{O}_2$ and CH_3O_2 reaction. Clearly additional studies would be useful to understand this disagreement, and I am grateful that you have offered to look further into this. I have now taken a more detailed look at the information provided in Nozière and Hanson (2017) regarding the $t\text{-C}_4\text{H}_9\text{O}_2$ experiments. I feel that there may be some issues and complications with the experiments and analysis, and I hope the following comments and questions might be helpful in your further investigations.

- The reaction of Cl atoms with i -butane is used as the source of $t\text{-C}_4\text{H}_9\text{O}_2$. In practice, this reaction proceeds significantly by H atom abstraction from both the $>\text{C}(\text{-})\text{H}$ group and the $-\text{CH}_3$ groups and is estimated to generate about 60 % $i\text{-C}_4\text{H}_9\text{O}_2$ and 40 % $t\text{-C}_4\text{H}_9\text{O}_2$ in the presence of O_2 (e.g. Aschmann and Atkinson, 1995; Choi et al., 2006). As a result, the $\text{C}_4\text{H}_9\text{O}_2$ signals have contributions from two isomers, although you interpret them as being purely $t\text{-C}_4\text{H}_9\text{O}_2$.
- Your analysis is simplified because the self-reaction of $t\text{-C}_4\text{H}_9\text{O}_2$ ($k = 3.0 \times 10^{-17}$) is uncompetitive. This is not true for $i\text{-C}_4\text{H}_9\text{O}_2$ ($k \approx 10^{-12}$), which therefore needs to be taken into account.
- The further chemistry of $i\text{-C}_4\text{H}_9\text{O}_2$ generates $i\text{-C}_4\text{H}_9\text{O}$, which either decomposes (55 %) or reacts with O_2 (45 %) in air at 298 K (Calvert et al., 2015, page 365). The former reaction produces HCHO and $i\text{-C}_3\text{H}_7$ (and subsequently $i\text{-C}_3\text{H}_7\text{O}_2$), whereas the latter produces HO_2 and 2-methylpropanal. As a result, the Cl + i -butane system contains $i\text{-C}_4\text{H}_9\text{O}_2$, $t\text{-C}_4\text{H}_9\text{O}_2$, $i\text{-C}_3\text{H}_7\text{O}_2$, CH_3O_2 and HO_2 , rather than just $t\text{-C}_4\text{H}_9\text{O}_2$, CH_3O_2 and HO_2 . This would seem to complicate the interpretation substantially, and require a lot of other reactions to be taken into account.
- $i\text{-C}_3\text{H}_7\text{O}_2$ is isobaric with $\text{CH}_3\text{C}(\text{O})\text{O}_2$ and may therefore interfere with the $\text{CH}_3\text{C}(\text{O})\text{O}_2$ kinetics in the “ $\text{CH}_3\text{C}(\text{O})\text{O}_2 + t\text{-C}_4\text{H}_9\text{O}_2$ ” experiments. Is formation of $i\text{-C}_3\text{H}_7\text{O}_2$ in the $\text{C}_4\text{H}_9\text{O}_2$ system possibly confirmed by the signal at $m/z = 112$ in Fig. 3C?
- In Nozière and Hanson (2017), you state that the reported rate coefficients for $\text{CH}_3\text{C}(\text{O})\text{O}_2 + t\text{-C}_4\text{H}_9\text{O}_2$ (3.7×10^{-14}) and $c\text{-C}_6\text{H}_{11}\text{O}_2 + t\text{-C}_4\text{H}_9\text{O}_2$ (1.5×10^{-15}) are close to their “expected values” of the geometric means of the self-reaction rate coefficients. They are, however, a factor of ~ 100 lower than the geometric means of the $\text{CH}_3\text{C}(\text{O})\text{O}_2$ and $i\text{-C}_4\text{H}_9\text{O}_2$ self-reaction rate coefficients, and the $\text{C}_6\text{H}_{11}\text{O}_2$ and $i\text{-C}_4\text{H}_9\text{O}_2$ self-reaction rate coefficients. The agreement with expectations is therefore fortuitous.
- If I understand correctly, the analysis makes use of calculated steady-state concentrations. In the absence of NO, is there sufficient time for the slowly reacting peroxy radicals to reach steady-state within the reactor residence time? In particular for $t\text{-C}_4\text{H}_9\text{O}_2$, I estimate that this might require a residence time of hours; and several minutes for $c\text{-C}_6\text{H}_{11}\text{O}_2$. As a result, the actual concentrations may be much lower than the calculated steady state, leading to substantially underestimated rate coefficients for the added species reacting with the

continuously-present species. I also note that the individual rate coefficients for the cross reaction of these two slowly-reacting species in Table 1 cover a range of 11 – much more variable than for any of the other reactions. Might this be a reproducibility problem due to variations in the calculated steady-state vs. actual concentrations, and concentration gradients along the reactor?

- (vii) In Table S6A, a series of rate coefficients is presented for use in your analysis, attributed to ref. 18. I cannot find ref. 18, but some of these rate coefficients seem to be out of date – although I realise there is some variation in reported values. In particular, I think that for the reaction of NO with *t*-C₄H₉O₂ (and probably *c*-C₆H₁₁O₂) is about a factor of two too low, and that for the self-reaction of CH₃C(O)O₂ is more than a factor of two too high, when compared with the values currently recommended by the IUPAC Task Group (<http://iupac.pole-ether.fr/>) and other expert evaluations. The rate coefficient for the CH₃C(O)O₂ + HO₂ reaction is also too low by a factor of about 1.5 (i.e. it is based on the older FP-UV studies, as discussed above). I do not have a feel of how sensitive your results are to these rate coefficients but it would seem important to apply the prevailing recommendations.

I hope you find these comments and questions to be constructive and helpful, and thank you once again for your discussion comment.

References

Aschmann, S. M. and Atkinson, R.: Rate constants for the gas-phase reactions of alkanes with Cl atoms at 296 ± 2 K, *Int. J. Chem. Kinet.*, 27, 613-622, 1995.

Calvert, J. G., Orlando, J. J., Stockwell, W. R. and Wallington, T. J.: *The mechanisms of reactions influencing atmospheric ozone*, Oxford University Press, Oxford. ISBN 978-0-19-023301-0, 2015.

Choi, N., Pilling, M. J., Seakins, P. W. and Wang, L.: Studies of site selective hydrogen atom abstractions by Cl atoms from isobutane and propane by laser flash photolysis/IR diode laser spectroscopy, *Phys. Chem. Chem. Phys.*, 8, 2172-2178, 2006.

Groß, C. B. M., Dillon, T. J., Schuster, G., Lelieveld, J., and Crowley, J. N.: Direct kinetic study of OH and O₃ formation in the reaction of CH₃C(O)O₂ with HO₂, *J. Phys. Chem. A*, 118, 974–985, doi:10.1021/jp412380z, 2014.

Le Crâne, J. P., Rayez, M. T., Rayez, J. C. and Villenave, E.: *Phys. Chem. Chem. Phys.*, 8, 2163, 2006.

Nozière, B. and Hanson, D. R.: Speciated monitoring of gas-phase organic peroxy radicals by chemical ionization mass spectrometry: cross-reactions between CH₃O₂, CH₃(CO)O₂, (CH₃)₃CO₂, and *c*-C₆H₁₁O₂. *J. Phys. Chem. A*, 121, 8453-8464, 2017.

Villenave, E., Lesclaux, R., Seefeld, S., and Stockwell, W. R.: Kinetics and atmospheric implications of peroxy radical cross reactions involving the CH₃C(O)O₂ radical, *J. Geophys. Res.*, 103 (D19), 25273-25285, 1998.