About uncertainties on RO2 reaction rate constants

I thank the authors of the manuscript Jenkin et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2019-44 for their response.

It appears from this response that some points need to be clarified concerning the uncertainties on the RO2 reaction rate constants reported by different groups. These uncertainties are not smaller than the factor x5/5 reported in our 2017 paper, they just have not been properly discussed. I hope that the explanation below will convince you and the atmospheric and kinetic community that our rate constants deserve to be taken into account at least as much as those from other groups, since they were dismissed on the ground of large uncertainties on the RO2 calibrations, while other works did not even perform such calibrations or involve larger mechanistic assumptions.

1) UV absorbance methods
Methods based on monitoring RO2 by UV absorbance, while more direct than those based on stable products, are still indirect because the rate constants are not obtained directly from the experimental data (= by methods that are free of assumptions, such as measuring decay rates) but by fitting kinetic mechanisms to these data. These mechanisms always involve assumptions since they are only as valid as the knowledge at the time. This is **potentially the largest source of uncertainties with these methods, yet these uncertainties are never even discussed** because there is no way to quantify them. As you pointed out, most of the current knowledge on RO2 reactions is based on rate constants obtained by these methods in the mid-1990's. These works pre-date by a decade the discovery of the isomerizations in the isoprene system and other autoxidation reactions. Thus, obviously, they do not take these channels into account in their kinetic analyses. This is why I qualified these works as "old". Autoxidation is just an example and, while it concerns only a small number of the RO2 studied in the 1990's, there can always be more mechanistic surprises in the future. **Thus the mechanistic uncertainties on these data is real, even if not quantified**.

It is precisely because I was aware of these limitations (being a former member of the Bordeaux group myself) that I spent many years developing a better way to monitor RO2. **The whole point of our new technique is that**, **not only it does not require any mechanistic assumption** (the rate constants being measured directly from experimental decay rates), and is thus free from the corresponding uncertainties, **but it can also detect unexpected new channels**.

Beside the large - but unquantified- mechanistic uncertainties in the 1990's kinetic studies, those officially reported are not far from ours: Villenave et al., J. Geophys. Res., 1998, for instance, reports uncertainties by factors 1.6 to 1.9 on the cross-reactions, thus nearly x2/2 (or did I misunderstand ?). This seems a minimum for a study where 12 different species contribute to the absorbance and the kinetic mechanism includes 23 reactions !
This specific system is further discussed in point 4) below.

2) Mass spectrometric techniques (NO_3^- and NH_4^+ ions)
The uncertainties in the mass spectrometric systems (Berndt et al. 2015; 2018a; 2018b… and this is also probably true for similar works from the Helsinki group) **are not lower**, but only carefully eluded (as a matter of fact, only Berndt et al. 2015 are reporting uncertainties at all):
In chemical ionization techniques the detection sensitivity (= ratio signal over concentration) depends on the rate of the ion-analyte reaction, which, in principle, varies with different compounds (or RO2). Yet, in all the studies using NO_3^- or NH_4^+ ionization, the authors elude the problem by **assuming** that all these reactions are at collision limit, thus that the detection sensitivity is identical

for all the analytes, which conveniently avoids the need for time-consuming calibrations of the concentrations (and correspondingly increases the publication rate). Yet, this essential point is not clearly presented as an assumption in the papers. And **I am not aware of any validation for it, nor of any attempt to calibrate the RO2 concentrations**. At least for the NH_4+ systems used in the 2018 papers I recently had a verbal confirmation from the authors that “they have no idea of the concentration of RO2 in their system” because “there is no way to calibrate it”. In the absence of any calibration of the RO2 concentrations, an uncertainties factor of x10/10 on these concentrations can be easily assumed, as this is the range of variability observed between different compounds in proton transfer reactions (and there is no reason to assume this is very different with NO_3^- or NH_4^+ reactions). Therefore the resulting rate constants must carry the same x10/10 uncertainties. Of course, you are welcome to check all this with the authors themselves.

3) Uncertainties in the Noziere & Hanson 2017 paper

To my opinion, the factor x5/5 reported in our 2017 paper is overly conservative. Reporting such a large factor was essentially a request from my co-author because the calibrations of the RO2 concentrations had not been performed with the same method as previously (Hanson et al., Int. J. Mass. Spectrom., 2004). In particular, the quantities of NO added to titrate the RO2 were not measured directly but from the RO2 decay rate and my co-author was worried that mixing effects might have impacted the results. To lower that risk, I had performed the calibrations with various amounts of NO, and obtained the calibration factor from the slope ΔRO2/ΔNO, while potential mixing effects were expected to contribute to the intercept (mixing effects in 3 sLm bath gas not expected to change when adding various amounts of a trace compound).

The repeatability obtained in the results also support the fact that the x5/5 factor might be too conservative (one of the reviewers on our paper even pointed it out). In conclusion, **all the rate constants reported in our 2017 paper deserve to be taken into account by the community, at least as much as those reported by other groups**.

Concerning future calibrations, I am not planning more work on cross-reactions in the immediate future as I am currently studying other reactions. But I did perform recently a calibration of the RO2 in a similar flow system while monitoring NO with a photoluminescent NOx detector. For a series of primary RO2 (1-butylO2, 1-pentylO2 and 1-hexylO2) I obtained concentrations between 9 x 10(11) and 2.5 x 10(12) molec. cm-3. This seems to confirm the estimates in the 2017 papers, although these RO2 were produced by the direct photolysis of iodinated precursors rather than from Cl2. However, calibrating RO2 with NO is not straightforward, as it requires a “titration factor” taking into account the fact that each RO2 does not consume exactly one equivalent of NO. This factor can only be estimated from a kinetic model, with all the drawbacks expressed in point 1) above.

Therefore, it might be more accurate to calibrate the RO2 system with a PERCA in the future.

4) Discrepancies in the peroxyacetyl radical (“PA”) + t-butylO2 rate constant

Concerning the PA+ t-butylO2 reaction, it is difficult to be sure of which rate constant is the most accurate, as this is a complex system. PA produces large concentrations of CH3O2, which, in turn, reacts fast with PA.

In our work, this reaction was studied by maintaining t-butylO2 constant in the reactor and adding PA periodically (Fig 4A and 7D). Fig. 4A shows that the addition of PA (red curve) consumes some of the CH3O2 present (produced by the self-reaction of t-butylO2, black curve) so that the overall concentration of t-butylO2 (blue curve) increases from the net effect of being consumed by PA and having its reaction with CH3O2 suppressed. As there is initially much less CH3O2 present than tbutylO2 (slow self-reaction) **this qualitatively confirms that the rate constant of reaction of PA with t-butylO2 must be much smaller than that of PA with CH3O2, otherwise t-butylO2 should be consumed instead of CH3O2**. But this also indicates that the amounts of PA added were very small, otherwise the CH3O2 level should have increased upon PA addition. Thus, the t-butylO2 profile might not have been much impacted by the reaction with PA and the rate constant reported might actually contain large uncertainties. I need more time to look into this, but will make sure to communicate the conclusion once I am sure.

The UV-based study of Villenave et al. 1998 (which, indeed, I had missed) might also contain large uncertainties, as their Fig. 1 shows that neither PA nor t-butylO2 are the largest contributions to the absorbance, but rather the build-up of CH3O2. Their analysis might not be very sensitive to the PA + t-butylO2 reaction either, but perhaps more to CH3O2 + PA.