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Comment on acp-2021-758

Anonymous Referee #2

Referee comment on "Evaluation of the daytime tropospheric loss of 2-methylbutanal" by
María Asensio et al., Atmos. Chem. Phys. Discuss.,
<https://doi.org/10.5194/acp-2021-758-RC2>, 2021

Review "Evaluation of the daytime tropospheric loss of 2-methyl butanal" by Asensio et al.

This manuscript reports results from the study of an aliphatic aldehyde, 2-methylbutanal. The reported results include measurements of the UV absorption cross-sections of the aldehyde, reaction rate coefficients of the aldehyde with OH and Cl radicals, products observed from the chemistry as detected by FTIR, PTRMS, and GC-MS, and finally particulate matter formation results are reported. The authors include potential photolysis and oxidation mechanisms in the SI.

Overall, I find the UV absorption cross-sections and kinetic OH and Cl kinetic rate coefficients to be of high quality, useful for atmospheric research and appropriate for publication in the ACP journal. However, the product study analysis and reporting of SOA formation I find to be less useful, and in need of additional refinement if they are to be included in the main document. This manuscript reports a tremendous amount of work. However, more is not always better, and the paper would increase its impact potential if it were focus more on the results with higher certainty.

General comments:

Photolysis mechanism: more focus on this aspect could strengthen the paper. Simple calculations of the energetics of the possible decomposition pathways for atmospherically relevant photons may be helpful. Providing additional information to support the branching ratio constraints would be helpful. For example, the band used for quantification of butane (C-H stretch) overlaps highly with the precursor and likely, many products. Given this, how well is butane actually quantified? Is butane quantified by other methods?

It would be useful to include a figure of the photolysis lamp spectrum in the SI.

Product studies: The approach to product analysis described in the paper appears to assume RO₂+RO₂ radical chemistry. To the extent this is true, the results derived from these experiments may not be generally applicable to the atmosphere, where RO₂ reactions with NO and with HO₂ often dominate RO₂ reactivity. However, it is also often true in systems where primary RO₂ production greatly exceeds other primary radical production (eg, HO₂ and NO), that HO₂ chemistry remains important (due to substantial HO₂ generation from initial RO₂ + RO₂ reactions). HO₂ + RO₂ reactions often produce ROOH in high yield. What would be the fate of ROOH in your experimental system. Can ROOH be specifically detected with the applied instrumentation? Would ROOH decompose and be detected at other products in this system/instrumentation. What is the RO₂ lifetime in these experiments? What is the potential for autoxidation (RO₂ H-shift) within the reaction chambers? Within the atmosphere? A simple kinetic simulation of the chemistry occurring within reaction chambers may be highly useful for a better understanding of the RO₂ chemistry in these experiments. Suggest these questions should be discussed and clarified in the manuscript.

SOA studies: Related to the comment above – to be useful for modeling the atmospheric fate of these species, SOA formation needs to be quantified for well-known conditions (including, RO₂ fate [fraction reacting with RO₂, HO₂, and NO] and RO₂ lifetime [can autoxidation be important, RO₂ H-shift]) which relate to those found in the atmosphere. Differences in these pathways can substantially alter the formation of SOA, and as such, at a minimum one needs to carefully describe the experimental RO₂ fate when reporting an SOA yield. The quantification of particulate matter is a challenge, even, in large chambers, requiring careful correction for size dependent wall-loss, and correction for vapor-particle-wall partitioning of semi-volatile species. If these corrections have been done here this should be described in more detail. The fact that early nucleation occurs is interesting. It may be more fruitful to shift focus to this, describing potential mechanisms, and whether these may have atmospheric significance.

It may be helpful to add a Table to the SI for yields of the more certain products from photolysis and CI from each quantification method.

While not obtrusive to the point of obscuring understanding, the sentence structure could be improved in several places to improve clarity and readability (e.g. LN62-63, LN113-114)

Specific comments:

LN14: for CI rate coefficient should be ' $\times 10^{(-10)}$ '?

LN31: I'm not familiar with O₃ reactions with saturated aldehydes. Could you include more description and references? NO₃ radical is known to react with aldehydes, thru aldehydic-H abstraction. Might be useful to mention this in overview.

LN67: It would be useful to state the composition of diluent gas (and other places in manuscript)

LN85-98: Often, as a result of chemistry following radical formation from initial photon excitation, additional oxidants can be formed (eg, OH/HO₂) either directly or from photolysis of resulting products. These oxidants can also contribute to the loss of the starting material. Were any efforts made to constrain the impact such chemistry may have on these results?

LN94: insert 'large' before 'surface'?

LN115-139: It would be useful to state the volume (or gas residence time) of the LIF setup

LN177-188: It would be good to explicitly specify the diluent gas, reaction pressure, and temperature.

LN239-241: It may be clearer to write this section for wavelength region used for the photolysis expts (>290nm?). Are all three channels listed here accessible under these photon energies? DeltaG estimate?

LN249-250: Can you discuss this further? Why is the CO yield dependent on initial MB? This is may be telling you something worth digging into.

LN270-275: Can butane also be measured by the PTRMS or GC-MS? If so, it would be worthwhile to describe these results, as they would lend confidence to the FTIR quantification of butane.

Fig7: Is that CO₂ initial and 50 min spectra? Is this understood? Seems like there is also H₂O in the residual spectra? Is this understood? Can impact of OH chemistry in the Cl expts be quantified using this?

LN350-363 & Fig8: More discussion of how PTR signals for acetald and 2MB were deconvoluted is needed. Also, there should be some explanation for how PTR calibrations were conducted.

LN396: 'J' -->'H' ?

LN431: Probably more realistic to assume [Cl] scales with sun (J(MB)?) and then scale to constraint (1.3e5)? This will impact discussion LN448-449.

LN447-452: It would be useful to report the daily integrated loss pathways considered here for this (ie over day fraction 2MB lost to OH, Cl, photolysis).

Fig S1: State if units are log10 or loge A.

Table S1: State more precisely the wavelength intervals used. Eg. 1-nm integrated intervals with midpoint wavelength listed in table?

Fig S6: There seems to be some issues with x-axis alignment on this figure. Suggest these should either be perfectly aligned (ie automatically, using plotting program) or the numbers for each x-axis should be retained. For example, butane and acetaldehyde ticks to not line up with others (butane C-H band should be aligned with that of butanol). Are there CO2 bands in some of these spectra (eg butanone, acetald., butanol, and MGLX)? Also H2O in methylglyoxal? If so, probably worthwhile to point out these as impurities, not considered in fitting.