

***Interactive comment on* “Photooxidation of pinonaldehyde at ambient conditions investigated in the atmospheric simulation chamber SAPHIR” by Michael Rolletter et al.**

Anonymous Referee #1

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This paper reports results of experiments where pinonaldehyde, a product of atmospheric reactions of biogenic emissions, is photolyzed in a large outdoor environmental chamber in the presence and absence of an OH radical scavenger. The decay of pinonaldehyde, formation of formaldehyde, acetone, and ozone, and levels of OH and HO₂ were monitored during the irradiations. However, there were no data on more complex organic products that may give more direct information on the mechanisms. Although results of only one experiment of each type were reported so reproducibility was not tested, this laboratory has a reputation for high quality data in well characterized experiments, and these appear to be no exception. It was found that pinonaldehyde photolyzed significantly more rapidly butyraldehyde, which is what is assumed

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in MCM and other mechanisms for higher aldehydes. The product and radical levels observed were not consistent with MCM predictions even after the pinonaldehyde photolysis rate was adjusted, and a more complex mechanism proposed by Fantechi et al (2002) (FAN) gave somewhat better predictions in some respects and somewhat worse in others. No mechanism was presented that was consistent with all the data.

This paper makes a contribution to our understanding of this important biogenic compound that should ultimately improve our ability to model its atmospheric impacts, and should be published. The measurement of the photolysis rate is an important contribution. On the other hand, this work certainly does not resolve uncertainties concerning details of the reaction pathways and the products formed – tests against formaldehyde data and acetone measurements (or lack thereof) are not very definitive because of the many ways these small compounds could be formed. The problems fitting the radical data were examined in sensitivity calculations but not really resolved. Nevertheless, these results provide additional data that will be useful for understanding these mechanisms.

Although I recommend that this paper be accepted for publication, I have several comments and suggestions that the authors should consider before finalizing this paper.

Figure 1 shows how the major first-generation photolysis and OH reactions of pinonaldehyde are represented in the MCM and FAN models, and is the only place where the reader is informed of the structure of pinonaldehyde, which many readers won't know without looking it up, and of the various intermediates that are otherwise referenced in the text only with obscure MCM or FAN names. This figure is near the end of the manuscript in the review copy, but it needs to be at the very start of the published version so readers can more easily see the chemistry that is actually being discussed. Either that or have a very small figure near the beginning giving the structures being discussed.

Although the FAN mechanism shown on Figure 1 is an improvement over MCM in

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that it considers more of the possible processes, it has some omissions that were not adequately considered in the sensitivity calculations. The paper mentioned that new data indicate that some peroxy radicals undergo unimolecular H-shift reactions, which is overlooked in both MCM and FAN, and the did sensitivity calculations (S1) showing the effect of assuming all those formed in the OH reaction rapidly react forming HO₂. However, while the available data and estimates suggest that these H-shifts are fast for peroxy radicals with HCO- groups such as PINALO₂, FAN_D1, and Fan_G1, there are no sufficiently labile abstractable H atoms for such reactions of C₉₆CO₃, which is formed about 60% of the time in the FAN model, or for the C₉₆O₂ radical that it forms. In addition, the reactions subsequent to the initial H-shifts are estimated to form another peroxy radical that converts NO to NO₂, and it is not clear that this is included in the sensitivity calculation. If they did it was not stated, and they need to include a supplementary table giving the S1 mechanism, as they do with the FAN mechanism.

It is quite likely that the MCM and FAN mechanisms are underestimating radical input from photolyses of secondary products. If the dicarbonyl parent compound photolyzes faster than expected based on simpler monocarbonyls, that's likely to be true for the many dicarbonyl products as well. They found that increasing photolysis rates to those for glyoxal did not increase radical levels sufficiently, and they had to increase them to that of NO₂ (a rather extreme level that is not really reasonable) to get the radicals to the observed levels, and then it greatly overestimates initial HO₂ radicals (Model S2). However, if the H-shift isomerizations of peroxy radicals with -HCO groups are indeed as fast as expected, then it is possible that peroxy acids with additional carbonyl groups may well be formed in up to 50% yields. These bifunctional compounds probably photolyze more rapidly than simple peroxy acids, and maybe more rapidly than glyoxal. This possibility would be worth examining.

A major conclusion of this study is that "pinonaldehyde photolyzes faster than MCM predicts". That is true, but it is more to the point, and more meaningful to the photochemical community in general, to convey this as "pinonaldehyde photolyzes faster

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than simple aldehydes like butyraldehyde". This is because the MCM website indicates MCM assumes that all compounds like this photolyze as rapidly as butyraldehyde. The fact that this is not true has implications for all mechanisms and photochemistry in general.

I am a bit uncomfortable with using models constrained to fit measured O₃, NO, and NO₂ when evaluating a mechanism's ability to predict HO₂ radical levels. This is because the rapid photostationary state reactions involving O₃, NO, and NO₂ require that the total rate of all peroxy + NO reactions be approximately equal the differences between the rates of the fast photolysis of NO₂ and the fast reaction of O₃ with NO, which are much larger in magnitude than the peroxy rates. It seems to me that this might cause small measurement uncertainties in NO, NO₂ or O₃ to have large effects on artificial radical sources and sinks required to for this constraint to hold. It may be valid the way they did this, but more discussion may be needed. It would be more straightforward and understandable if they could constrain to as few measurements as possible when evaluating mechanisms, and preferably only using reaction conditions such as jNO₂. Why not just constrain just one of the reactant predictions, and let the others fall where the mechanism tells you?

The ratio of rate constants used in the model for the reactions of peroxy radicals with HO₂ vs. NO may also affect model predictions of HO₂. Has this been looked into? These rate constants have not been measured, and estimates based on rate constants for simpler radicals may be an oversimplification.

I have the following minor formatting comments on the figures: (1) Most of the figures are not suitable for presentation in black and white. (2) The species whose concentrations are being plotted should be shown more conspicuously. Right now, this information is only given in very tiny font on the reaction labels. (3) The FAN_a result is not shown in the top plot of Figure 6, probably because it is exactly the same as MCM_a. Perhaps it should be stated in the caption that they are the same. (4) On figure 8, the color shown for MCM on the legend (red) does not match the color on the plots (pink).

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