The authors thank you for dedicating your time to reviewing our work, and we greatly value the opportunity to discuss the results. Below, we present our point-by-point response to your comments.

Referee #6

The authors Aranda et al. have conducted a series of experiments examining the oxidation of a pair of saturated, functionalized carbonyl molecules. The experiments cover the three major relevant atmospheric oxidants (OH, Cl, and NO3 radicals) and include both relative-rate measurements and studies on major product formation to inform chemical mechanisms. The overall significance of different reactions and products is discussed in the context of general atmospheric chemistry. The authors also highlight some current unknowns regarding the chemistry of aldehydes, a significant and reactive class of volatile organic compounds. The authors have put a substantial amount of effort into these tasks and the interpretation of their data. I have several questions related to the oxidation mechanisms discussed in the paper. If these and minor comments are addressed, I believe the paper should be accepted for publication

I suggest the authors take care when discussing the Cl-initiated oxidation of 3,3-dimethyl butanal. Previous works studying the oxidation of aldehydes (Iwasaki et al., 2008; Rayez et al., 2011; Singh et al., 2009) observed a strong deactivating effect of the CHO group that extended over multiple carbons and did not fit well with SAR predictions; Singh et al. (2009) wrote "the substituent factor for -CHO is significantly less than one, and that the group has a deactivating effect over several carbon atoms along the alkyl chain." It is not clear to me whether the work of Carter (2021) used by the authors for estimating functional group factors accurately reflects these prior works. I therefore suggest that the authors evaluate the prior references mentioned here (or others, as relevant) and determine whether the 0.4 substituent factor, and the discussion in sections 3.1-3.2 and the proposed chemistry in Figure 8, are reasonable. It may not be feasible with the current experimental data, but experimental verification of SAR predictions for Cl reaction with aldehydes would be beneficial in understanding Cl/aldehyde chemistry.

The authors discuss major RO2 radical reaction channels in section 3.2. Can the authors make any estimate of the relative prevalence or importance of the different RO2 radical reaction partners (RO2, HO2, OH/Cl) during these experiments? Without some sort of estimate of RO2 reaction branching ratios, it is difficult to determine the significance of the different identified products and their associated proposed formation pathways. To put this another way, how realistic are the reaction conditions and calculated product yields?

The authors mention the clear loss of some primary products during later experiment times (Figure 4). Can the authors provide an estimate of when secondary chemistry and product formation may become relevant during each experiment? This could include oxidation or photolysis reactions of primary products. It is not currently clear whether primary products may be more or less reactive or photolabile than the parent molecules, which complicates the interpretation of the yield results and the variety of products identified through FTIR and GC-MS analysis.

Response of authors

The authors thank you for dedicating your time to reviewing our work, and we greatly value to reviewing our work, and we consider it very valuable to have the opportunity

to discuss the results. As we can confirm, the review of the manuscript has been very thorough, allowing us to correct not only typographical errors but also some data that had not been accurately transferred from the spreadsheets to the tables in the manuscript.

Below, we present our point-by-point response to your comments.

NOTE: It is important to note that, based on the suggestion of Referee #5, the authors have decided to restructure the entire Results and Discussion section regarding the reaction products. This involves changing the figures in both the manuscript and the supplementary material.

Regarding to comment about the SAR predictions for Cl reaction with aldehydes, the authors have used the value reported by Carter et al. (2021), as it is a review up to 2020 and is therefore considered to have taken into account the studies on aldehydes mentioned (Iwasaki et al., 2008; Rayez et al., 2011; Singh et al., 2009). The fact that the experimentally obtained rate constant for 33DMbutanal with Cl ($1.27x10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}) and the one estimated using the SAR method with a factor of 0.4 for the -CHO group ($k_{estimated}$ $=1.36x10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}) are very similar suggests that the value of 0.4 used for -CHO is appropriate. On the other hand, based on the similarity between the estimated and experimental rate constants, the authors have proposed the reaction mechanism for 3,3-dimethylbutanal.

The following paragraphs have been modified in the revised manuscript

Lines 265-266

'In all cases the estimated rate coefficients are very similar to the experimental values (see Table 1), indicating that the reactivity factors used for the estimations are well established'

Regarding the estimation of the importance of different RO2 reactions, initially in the proposed reaction mechanisms, all possible reactions of RO2 were included based on general atmospheric reactivity (Finlayson-Pitts and Pitts, 2000, Atkinson 2007), as we had no information to rule out any pathway. In the revised version of the manuscript, the RO2 + HO2 reaction has been included, which was initially omitted, considering it to be significant only in polluted atmospheres and to avoid overly complex mechanisms that are difficult to follow. On the other hand, in the revised version of the manuscript (lines 299-303), it is indicated that, based on the estimated rate constants for isomerization and decomposition process of RO radical (Vereecken and Peeters (2009, 2010), some pathways of the mechanism are ruled out. In this way, a more simplified mechanism has been proposed for 3,3-dimethylbutanone. In the case of the mechanism for 3,3-dimethylbutanal, only the isomerization has been excluded.

The following paragraphs have been modified in the revised manuscript

Lines 288-311

'It is well established (Atkinson, 2007) that alkyl radicals, formed in the initial step of these reactions, rapidly react with O2 to generate the corresponding peroxyradical (RO2·). These RO2 radicals can undergo various pathways. In the absence of NO, peroxyradicals primarily undergo two self-reaction processes: one leading to the formation of alkoxyradicals (RO2· + RO2· → 2RO· + O2), and the other producing two molecules, such as hydroxy compound

and carbonyl compound (RO2· + RO2· → hydroxy compound + carbonyl compound + O2). Another significant process is the reaction of RO2 with OH radicals and HO_2 radicals that undergoes different pathways (Bottorff et al., 2023; Berndt et al., 2022; Fittschen, 2019; Jenkin et al., 2019; Berndt et al., 2018; Winiberg et al., 2016).'

In the presence of NO, the RO2 radical may react to form alkoxyradicals and NO2 (RO2· + NO· → RO· + NO2) or nitrated compounds (RONO2), and in presence of large concentration of NO2, RO2 generates peroxynitrated compounds (ROONO2) (pathway less favoured). Under typical tropospheric conditions, alkoxyradicals can react with molecular oxygen (O2), undergo unimolecular decomposition or isomerize. The reaction of RO· radicals with O2 is only possible if the carbon atom bearing the radical contains at least one hydrogen atom. Additionally, in the presence of NO and NO2, alkoxyradicals can also form nitrated compounds (Atkinson, 2007).

The rate coefficients for unimolecular decomposition and isomerization processes have been estimated in this work, using the method by Vereecken and Peeters (2009, 2010). In the case of 33DMbutanone, the rate coefficients for isomerization were much lower than those for decomposition making isomerization products insignificant. The estimated decomposition rate coefficient to form acetone (1.7×10^{12} s^{-1}) was much higher than to obtain butane-2,3-dione (6×10^{3} s^{-1}). For 33DMbutanal the decomposition rate is four times higher than that for the isomerization process.

Taking all the above into account, and to facilitate the qualitative analysis of reaction products from the reaction of 33DMbutanone and 33DMbutanal with atmospheric oxidants, proposed reaction mechanisms are depicted in Schemes 1S and 2S in the supplementary material. The RO2 + HO2 reactions are excluded to avoid further complicating the mechanism for 33DMbutanal, as they are significant only in the absence of NOx, that is, in remote unpolluted atmospheres.'

Regarding to comment about secondary chemistry in the revised manuscript the next paragraphs have modified in order to give more information about the loss processes of some primary products and when secondary chemistry and product formation may be relevant.

Lines 370-382

'The trend of the acetone and HCHO profiles indicate that they are primary products, although the concentration of HCHO starts to decrease after 20 min of reaction, possibly due to secondary chemical reactions such as photolysis or by the reaction with the main oxidant. The profile of the nitrated compounds, especially PAN, shows a significant increase after 5 minutes of reaction, related to the rise in NO2 concentration in the medium after that time.

Fig. 4 shows an example of yield plots for the reactions of 33DMbutanone with Cl atoms in the presence of NO.

The yields of nitrated compounds were estimated from the slopes of the plots showing linear behavior (using the initial data) to avoid contributions from secondary chemistry. For PAN, the data used were from a Δ[33DMbutanone] of approximately 2 ppm (see Fig. 5S). In the case of HCHO, the yield has been recalculated using the formalism published by Tuazon et al., 1986.'

lines 530-533

'The trends of the concentration-time profiles of the quantified products for the reaction of 33DMbutanal with Cl atoms (Fig. 14S), suggest that they are primary products in the early stages (linear trend). However, it is observed that after a certain reaction time, the concentrations of 22DMpropanal and HCHO decrease. This decrease could be attributed to loss processes involving reactions with Cl atoms and/or photolysis.'

lines 541-543.

'The concentration plots of the products formed against the variation 33DMbutanal, used to obtain the yields, are shown in Fig. 15S. For of HCHO and 22DMpropanal, where the concentration decreases by react with the main oxidant, the yield has been recalculated using the formalism by Tuazon et al., 1986.'

Comments Minor Comments

General: I found some discussion of parent and product structures difficult to follow. I would suggest showing structures of parent molecules in Table 2 somewhere in the text as well as adding a label or number to some products or intermediates in Figures 7 and 8 to make referencing these structures within the text more clear.

Response of authors

Thank you for your suggestion. The structures are included in the tables of the supplementary material, where the names are also provided. To avoid overly crowded and large tables in the manuscript, the authors believe it is not necessary to include this information in Table 2 and Table 3. The names have been included in Figures 7 and 8 (Figures 6 and 8 in the revised manuscript).

Line 201: might the decrease in reaction rate when moving to 3,3-dimethyl butanal be due to the fact that many of the abstractable H are now primary, with a lower inherent reaction rate towards OH and Cl, rather than steric factors?

Response of authors

The authors agree with you, and indeed the decrease in the rate constant may also be related to the fact that many of the abstractable hydrogens are now primary. However, in the case of reactions with OH, where the structure of the compound has a much greater influence on the reaction rate than in reactions with Cl, the steric factor of an additional methyl group must be important.

Taking into account your suggestion, the following sentence has been included in the revised manuscript as follows:

Lines 223-224.

'The decrease in the rate coefficient may also be related to the fact that many of the abstractable hydrogens are now primary'

Line 311, Figure 7, and elsewhere: I'm not familiar with the "alkoxy nitrate" compounds the authors note as forming from reaction of NO or NO2 with alkoxy radicals (e.g., (Atkinson, 2007)). Can the authors provide more background on the formation of these molecules?

Response of authors

In the new figures of the revised manuscript, examples of the structures of these alkoxy nitrates (RONO2 or RONO) have been included.

Lines 489-491: Atkinson (2007) also wrote that "this ''prompt'' decomposition of alkoxy radicals formed from the exothermic RO2 + NO reaction appears to be important for alkoxy radicals with a barrier to decomposition of approximately 9 kcal mol^{-1} or less, with prompt decomposition being unimportant for alkoxy radicals with higher barriers to decomposition." If the authors assert that alkoxy radicals formed in this work undergo "prompt" decomposition, they must present work supporting this conclusion (for example, utilizing the methods proposed in the already cited work of Vereecken and Peeters, 2009).

Response of authors

This comment is responded above. This is the paragraphs that have been modified in the revised manuscript:

'The rate coefficients for unimolecular decomposition and isomerization processes have been estimated in this work, using the method by Vereecken and Peeters (2009, 2010). In the case of 33DMbutanone, the rate coefficients for isomerization were much lower than those for decomposition making isomerization products insignificant. The estimated decomposition rate coefficient to form acetone (1.7×10^{12} s^{-1}) was much higher than to obtain butane-2,3-dione (6×10^{3} s^{-1}). For 33DMbutanal the decomposition rate is four times higher than that for the isomerization process.'

Line 493: RO2 + Cl à RO is also a potential reaction (Maricq et al., 1994) that may be relevant to consider.

Response of authors

We consider the RO2 + Cl reaction forming RO to be irrelevant for the reactions of 3,3-dimethylbutanone and 3,3-dimethylbutanal, as the rate coefficients obtained in this our work are higher than or of the same order as the RO2 + Cl reaction (as reported in the study by Maricq et al., 1994). Furthermore, the formation of ClO/ClOOCl does not observe.

Figure 8: For channel III, might intramolecular hydrogen shifts occur from wither the initial RO2 or RO radicals? Based on prior estimates (Vereecken & Nozière, 2020; Vereecken & Peeters, 2010), these aldehydic H-shifts are expected to be relatively fast. Might such reactions contribute to the larger variety of product structures observed for Cl reaction compared to OH, given the greater importance of channel III for Cl reaction?

Response of authors

Indeed, these intramolecular hydrogen shifts from the initial RO2 or RO radicals could occur, but only the reactions that could explain the identified products (based on the IR spectra or their MS) in the different experiments are included. Not all reactions are included to avoid complex mechanisms.

Effectively the greater variety of products observed in the reaction with Cl compared to the reaction with OH can be attributed to the ability of Cl to initiate reactions through all three possible channels, leading to a wider range of products. In contrast, the reaction with OH is limited to proceeding predominantly through a single channel,

resulting in fewer product variations. No additional explanation has been included in the revised manuscript.

Technical comments

Line 265: "mayor" à major

OK

Line 561: "…spectrum of 22DMpropanoic [acid]."

OK

References

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Código de campo cambiado

Finally, we would like to thank the reviewer for the thorough work done to improve the submitted manuscript. With your suggestions and corrections, the quality is clearly higher.