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#5

General comments and main concerns:

The article "Reactivity study of 3,3-dimethylbutanal and 3,3-dimethylbutanone: Kinetic, reaction products, mechanisms and atmospheric implications" by Aranda et al., is written in line with several previous studies performed by this research group.

The manuscript consists of two parts related to kinetic and mechanistic investigations on the reaction of two carbonyls (one ketone and one aldehyde) with atmospheric oxidants (Cl, OH, and NO3). The manuscript comprises a first part including three kinetic studies of 33DMbutanal+Cl, and 33DMbutanone with CL and OH radicals and a second part dedicated to product studies performed with chlorine and hydroxyl radical for both carbonyl compounds and gas-phase product studies initiated by NO3 radicals for the reaction with the aldehyde.

The manuscript needs consistent English corrections and also needs to be restructured on the sections related to gas-phase product presentation. The structure of the manuscript is tangled and difficult to follow, especially for the gas-phase product section. I suggest a structure with subsections for results and discussion representative for each studied reaction.

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.

As you suggest the structure of reaction products has been restructured. Now in the revised manuscript the gas-phase product section has been divided in subsections for results and discussion representative for each studied reaction. This represents a significant change from the original manuscript, as the figures/tables in both the manuscript and the supplementary material have been modified.

One main concern is related to product studies where, despite the extensive degradation mechanisms shown in the article, the products tentatively quantified are formaldehyde, acetone, and 22DMpropanal. No other products could be really supported by the presented results.

The mechanisms should be redesigned in a much simpler form to emphasize the findings and to highlight the m/z for the compounds identified in the present study. The expected products in the dotted line in the mechanism should be supported by the identified m/z in

the mass spectra. Please add in the article, supportive information from mass spectra corresponding to chromatogram peaks.

Response of authors

The authors consider that, although it has only been possible to quantify acetone, formaldehyde, 2,2-dimethylpropanal, nitrate compounds, and PAN using the FTIR system, the reaction products identified using GC-TOFMS are noteworthy. These products are proposed based on qualitative analysis of mass spectra obtained with field ionization (which provides the molecular ion) and the fragmentation pattern analysis of mass spectra acquired with electron impact ionization. The authors consider that the expected products, (showed in Figures 6 and 8 in the revised manuscript), are supported by the m/z values identified in the mass spectra. Tables 2S and 3S present the mass spectra of all major chromatographic peaks as suggested.

So, we consider that this work is particularly significant as it provides, for the first time, the mass spectra of these compounds.

Other concern is related to PAN formation and organic nitrate formation which are mainly suggested to be formed by generally accepted mechanisms due to the concentrations of the reactants involved in the present study. Please discuss the formation of this compound in terms of interferences due to the secondary sources of PAN which could be formed, for example, PAN formation from acetone degradation and huge NOx concentration. This source would explain also the delay in the formation of PAN.

Response of authors

As can be seen in the concentration-time profiles and plots of the reaction products formed versus the consumption of the reactant, PAN is exclusively detected in the reaction of 33DMbutanone with Cl when there is no NO in the medium and the concentration of NO2 begins to be significant. If PAN formation were of secondary origin, for example, by the reaction of acetone, PAN should also have been detected in the experiments of the reaction of 33DMbutanal with Cl in the presence of NO. Therefore, we conclude that PAN is formed by the reaction of 33DMbutanone with Cl in the presence of NO2. In the revised manuscript the next paragraph has been included in lines 485-490 as follows:

'Considering that the formation of PAN can only be explained via channel II (hydrogen abstraction from the -CH_3 group of the tert-butyl group), which involves the decomposition of the initially formed alkoxy radical (2,2-dimethyl-3-oxobutan-1-yloxy radical), and that the plot of PAN concentration versus the variation in 33DMbutanone concentration shows a linear relationship with a slope close to one (indicating an estimated PAN yield of 100%, see Fig. 5S), it could be concluded that the percentage of Cl attack on the -CH_3 group of the tert-butyl group is nearly100%.'

To explain the delay in the formation of PAN, a stated has been added in the revised manuscript in lines 372-373 as follows

'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.'

The techniques employed in the present study can identify multiple other products present in the designed degradation mechanism. Could the authors reconsider the product

formation interpreting the mass spectrum of each peak in their study? IR spectra did not show an OH absorption band around 3600 cm-1 according to the proposed alcohol products?

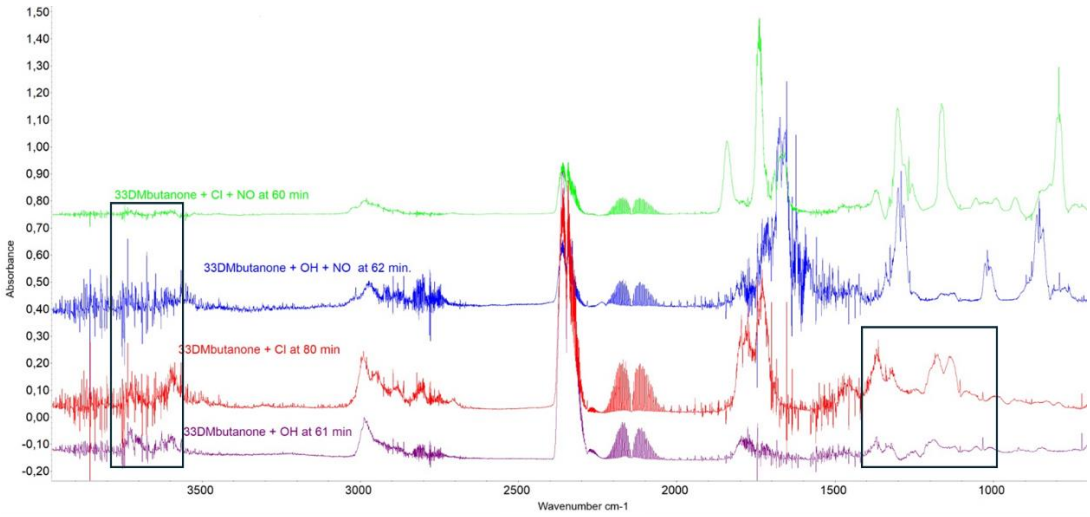
There are also reference spectra that could help to identify possible formation products (eg. Biacethyl, etc.).

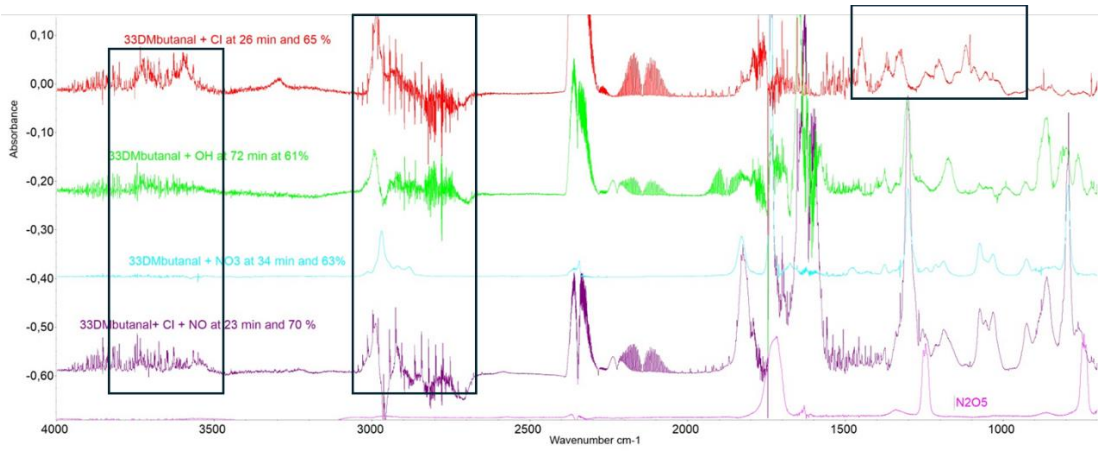
A statement at line 592 indicates the formation of formic acid "which was not quantified". Why do not provide all the possible information in the article? I suggest discussing the residual spectrum in terms of remaining IR features that are not allocated to the known products.

Response of authors

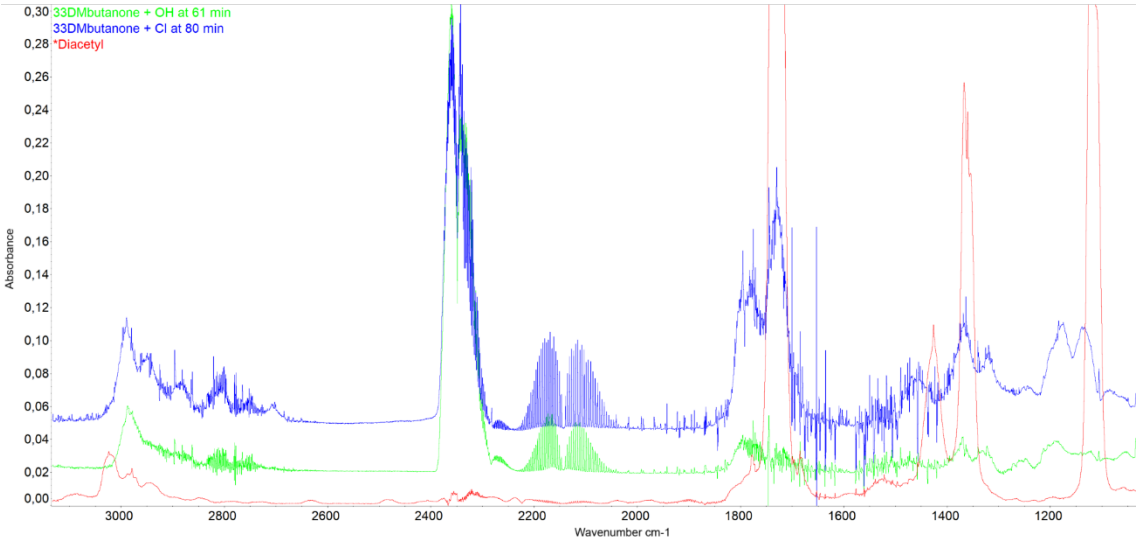
As previously mentioned, the assignment of reaction products in experiments conducted with the GC-TOFMS system has been based primarily on the analysis of mass spectra. Many of these compounds exhibit very similar IR bands that overlap, making their identification challenging. Additionally, it is believed that the quantities of these compounds are small, resulting in IR spectra with weak bands (very low absorbance).

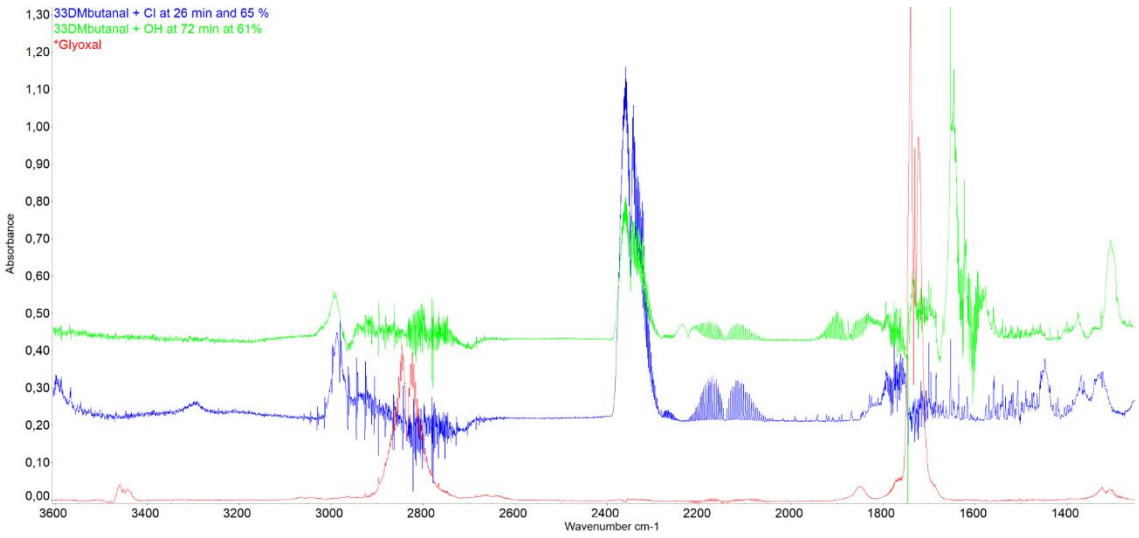
However, a review of the residual IR spectra from the reactions of 33DMbutanal and 33DMbutanone reveals a discernible absorption band around 3600, 3000, 1770 and 1200-1000 cm^{-1}. (The IR band at 3600 cm-1 is not present in the reaction of 33DMbutanal with the NO_3 radical and 33DMbutanone with Cl + NO).





The residual IR spectra have been compared with reference spectra of biacethyl in the case of the reactions with 33DMbutanone and with glyoxal for 33DMbutanal, with no characteristic IR bands of these compounds being clearly observed. Furthermore, as discussed in the manuscript, the formation of butane-2,3-dione (biacethyl) is less favored than the formation of acetone (lines 302 in the revised manuscript).





The residual spectra exhibit very low absorbance values, and the bands correspond to overlapping signals from different products. Therefore, we consider that these spectra are not sufficiently reliable to distinguish the reaction products.

Nevertheless, taking your suggestion into account, the following texts have been included in the revised manuscript:

Lines 351-360

'After removing the IR absorption bands of formaldehyde and acetone from the spectra in Fig. 2, the newly obtained residual spectra reveal the presence of IR absorption bands characteristic of various organic functional groups, such as carbonyl (-C(O) ~1745-1795 cm^{-1}) and hydroxyl (-OH, ~3600 cm^{-1}) (see Fig. 4S). As it can be seen, all the spectra show IR bands around 3725-3500 cm^{-1}, 3000-2750 cm^{-1} and 1780 cm^{-1}, indicating the formation of common reaction products in the reactions of 33DMbutanone with Cl and OH. Other different IR bands (1136, 1180, 1364 cm^{-1}) are also identified, which would suggest different reaction products. Additionally, the IR bands shown in Fig. 4S are consistent with the multifunctional products proposed in Scheme 1S. Confirmation of these compounds is not possible due to their unavailability as commercial standards and the absence of reference spectra in existing infrared databases. Furthermore, the low intensity of their IR bands, likely resulting from low concentrations in the medium, combined with band overlap, hinders their identification'.

Lines 383-385

Formic acid is mainly produced through secondary reactions when formaldehyde is present, as evidenced by typical secondary concentration profile time (see Fig. 9S).

Lines 525-529

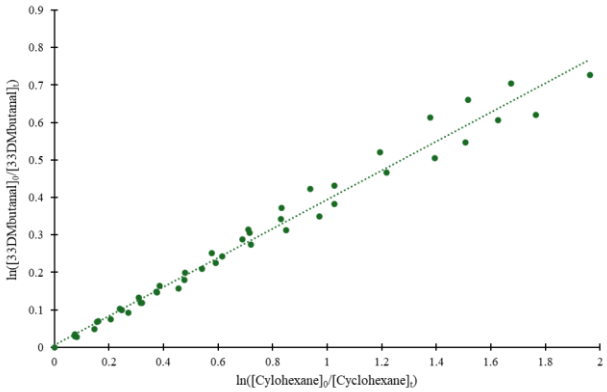
'After removing the IR absorption bands of the identified products in Fig. 11S, the residual spectra reveal the presence of IR absorption bands characteristic of carbonyl (~1700-1790 cm^{-1}), hydroxyl (~3600 and 1033 cm^{-1}) and organic acid/acyl chloride compound (~1800 cm^{-1}) (Fig. 12S). The amplified residual spectra of Fig. 12S (Fig.13S) shows clearly some IR absorption bands that appear at the same wavenumber indicating common reaction products. The IR band at 1105 cm^{-1} shown in Fig. 13S again indicates the formation of formic acid.'

Please include in the paper all the plots for all the reference compounds used in kinetic experiments for 33DMbutanal with Cl. The scientific community wants to see how well the linearity of the kinetic plots and which of the reference compounds worked better. Why the other kinetic plots are not properly represented?

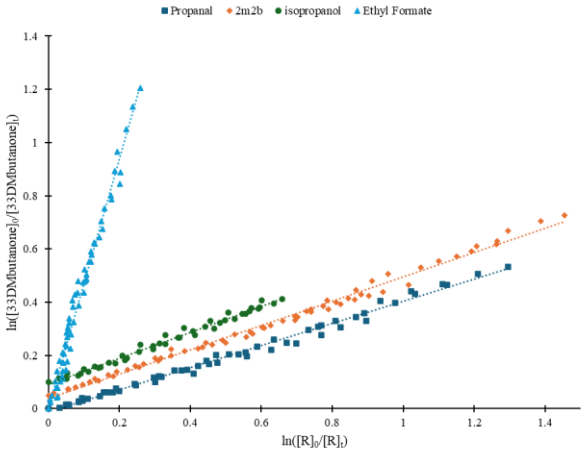
Response of authors

It is standard practice to include only an example of these plots in the manuscript and others in the supplementary material. However, following your suggestion, all the plots for all the reference compounds used in kinetic experiments have been included in the supplementary material of the revised manuscript.

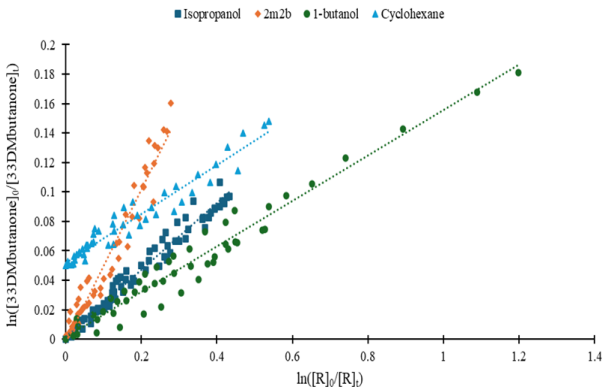
a)



b)



c)



'Figure 1S. Plot of Eq. (I) for the reaction of 33DMbutanal with Cl atoms using cyclohexane as reference compound (a) and for 33DMbutanone with Cl atoms (b) and OH radical (c) using different references compounds. In some cases, the plots have been displaced for clarity.'

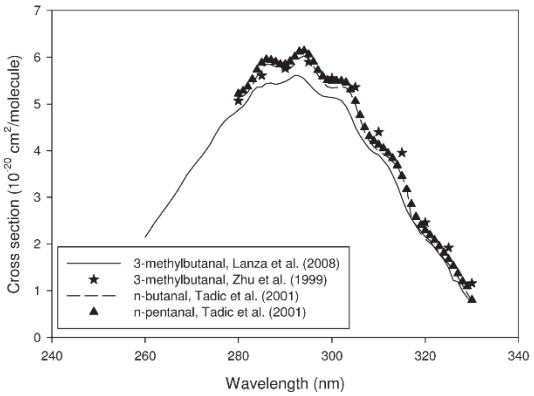
To indicate the good fit of the experimental data, the following sentence has been included in the revised manuscript:

Lines 183-186

'Plot of Eq. (I) depicting the reaction of 33DMbutanal with Cl atoms, using cyclohexane as a reference, is presented in Fig. 1Sa. Additionally, the Fig. 1S includes the plots for the reaction of 33DMbutanone with Cl atoms and OH radicals, along with all the reference compounds used. The plots show a linear fit with r^2 ? 0.99 and low origin intercept values, indicating the absence of secondary reactions.'

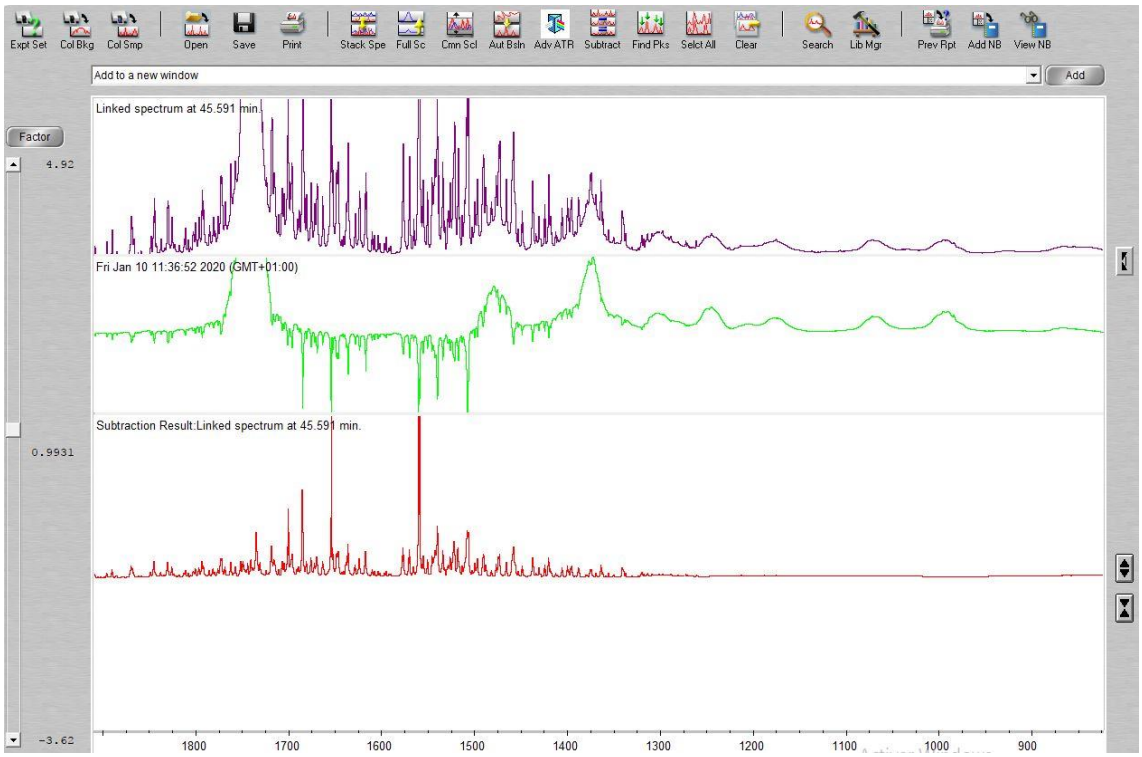
An important concern is related to the photolysis of 3,3 -Dimethylbutanal. Tadic et al., found significant photolysis for 3,3-Dimethylbutanal in the spectral range used in the present study. How do the authors comment on the missing correction for the photolysis in their kinetic and product studies? How significant is the photolysis? There is a competition between photolytic lifetime and reactive lifetime, how do you comment on that?

Effectively Tadic et al. (2012) conducted a study on the photolysis of 33DMbutanal using radiation in the range of 270 nm to 380 nm, observing that photolysis occurred. However, in our case, the radiation is limited to λ >360 nm. As demonstrated in the study by Lanza et al. (2008), the maximum absorption cross-section of 3-methylbutanal corresponds to 290 nm, decreasing sharply at wavelengths greater than 320 nm.



By analogy with 3-methylbutanal, 33DMbutanal is expected to exhibit similar behavior. This is the primary reason why, under our experimental conditions, 33DMbutanal does not undergo photolysis

I am sharing a screenshot below where it can be observed that the spectrum of 33BMbutanal at time zero and after 45 minutes of photolysis does not change by more than 3%. (subtraction factor 0.9931)



Therefore, we do not consider any further corrections to the manuscript necessary.

Specific comments:

Could authors add information about the concentration of the radical precursors?

Response of authors

As it is indicated in lines 141-146 of the revised manuscript, the concentration of atom/radical precursor is (in ppm) 17-22 for Cl_2, 16-20 for methyl nitrite, 30 for H_2O_2 and 14-25 for N_2O_5.

Table 1 – 33DMbutanal+Cl – the error for the second exp with cyclohexane is wrong.

Response of authors

Effectively the error is wrong. In the revised manuscript, the error has been corrected.

Please give an explanation to "d" in the table.

Response of authors

The table 1 has been modified in the revised manuscript and "d" is defined

Please comment in the text for the difference of 25% between the kcarbonyl values for the reaction of 33DMbutanal+Cl.

Response of authors

The authors consider this difference it is normal and it is not necessary to comment it in the text.

We really do not consider it necessary to make any additional comments in the text regarding this since this percentage can be considered as usual in the calculation of these rate constants and fallx within the range of experimental errors.

Could you explain the lowest kcarbonyl values for the reaction of 33DMbutanone+OH using 1-butanol and cyclohexane as reference compounds?

The following rate constants were recommended by McGillen database:

1-butanol + OH: 9.14e-12 cm3molec-1s-1

2-methyl-2-butanol + OH: 3.42e-12 cm3molec-1s-1

2-propanol + OH: 5.24e-12 cm3molec-1s-1

Why the study does not use these values as the authors mentioned in the article but uses other values as the kOH = 9.8±2.0 for 1-butanol for example?

Response of authors

The McGillen database 2020, has been reviewed, and indeed the recommended value for the rate constant of 1-butanol with OH is 9.14×10^{-12} cm^3 $molecule^{-1}$ s^{-1}. The data has been recalculated using this new value, and the modified data is presented in Table 1. It can be verified that the final value of the rate constant for 33DMbutanone with OH remains unchanged. In the other cases, the recommended value has been used (2-methyl-2-butanol + OH: $3.42x10^{-12}$ cm^3 $molec^{-1}$ s^{-1} and 2-propanol + OH: $5.24x10^{-12}$ cm^3 $molec^{-1}$ s^{-1}. See Table 1 of revised manuscript).

Please comment in the text for the difference of 50% between the kcarbonyl values for the reaction of 33DMbutanone+OH. 0.96 and 1.92 are completely unrealistic for this study.

Response of authors

Upon reviewing the data in Table 1, we identified an error in the reported rate coefficient for the reaction of 33DMbutanone with OH when 1-butanol was used as the reference compound. The corrected value was (1.80±0.37) instead of 0.96±0.11. Taking into account your suggestion to use the constant for 1-butanol as $9.14x10^{-12}$, the averaged value is 1.68 ± 0.26 cm^3 $molecule^{-1}$ s^{-1}.

In the revised manuscript, the weighted average of k obtained for 33DMbutanone+OH (presented in table 1) is $(1.25\pm0.05)\times10-12$ cm^3 $molecule^{-1}$ s^{-1}, closely aligns with the data reported by Mapelli et al. (2023) $(1.2\pm0.2)\times10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} and the recommended value from McGillen (2020) $(1.21\pm0.05)\times10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}.

Due to this difference, four reference compounds have been used, whereas it is common practice to use only two or three. However, to ensure the accuracy of the constant value, all data obtained using four reference compounds are provided. The average value obtained is similar to that reported by Mapelli and to the value recommended by McGillen.

Therefore, the authors believe that this result provides a reliable rate coefficient for the reaction of 33DMbutanone with Cl and OH and consider it unnecessary to include any comment in the text regarding the different data obtained for the individual rate coefficients for the reaction of 33DMbutanone with OH.

The reaction of acetylperoxy with HO2 could be better represented by a more recent paper: Winiberg, et al., 2016, Direct measurements of OH and other product yields from the HO2 + CH3C(O)O2 reaction, Atmos. Chem. Phys., 16, 4023–4042, https://doi.org/10.5194/acp-16-4023-2016, 2016. This could explain the formation of ozone, peroxides, and OH radicals. Please discuss the effect of OH radicals formed in the reaction with chlorine atoms on the formation products. The reactivity towards OH and chlorine could help with these discussions.

Response of authors

Thank you for the information, this reference has been included in the revised manuscript. In the study of Winiberg, et al., 2016 the experiments are conducted in the absence of NO and the RO_2 radical is different from those initially generated in the reactions of 33DMbutanal and 33DMbutanone. In no case under experimental conditions without NO, such as the reactions of 33DMbutanone with Cl and OH or 33DMbutanal with Cl, ozone has been observed. Furthermore, while the formation of the OH radical could play a significant role in the reaction with Cl, the authors consider that, given the rate constant for OH is an order of magnitude lower than that for Cl atoms, the products identified in our experiments are primarily attributed to the reaction with Cl. In the reaction of Cl in the absence of NO, it is possible that RO2 radicals react with OH generated but it is not possible to confirm the reaction product generated (RO2OH) using FTIR by the lack of reference spectrum.

The yields from nitrated gas-phase products are not very well represented. Could authors explain the curved shape?

Response of authors

We do not understand what do you mean by "not well represented."

In figure 4 of revised version of manuscript, the up curved plot is indicating that there are additional reactions that form nitrated compound, and the linear plots indicate that the nitrated compound are formed as main products.

The yield of nitrated compounds and PAN in the case of 33DMbutanone reaction, was obtained from linear trend. In the revised manuscript this is indicated as follows

Lines 378-380

'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).'

Please give more information about the error calculation for kinetic results and product yields.

Response of authors

The information about the error calculations for kinetic results is included in the foot of table 1 in the revised manuscript as follows:

The total absolute error σ(kcarbonyl) is a combination of the statistical errors from the regression analysis (σslope) and the quoted error in the value of the rate coefficient of the

reference compound (σR). The final values of the rate coefficients and the associated error were calculated as weighted average (Colmenar et al., 2020).

and the error calculation for product yields is now included in the foot of tables 3 and 4 as follows:

'The quoted error in the individual yield (2σ) is two times the statistical errors from the regression analysis (2 × σslope). The quoted error in the average yield (2σ) is two times the Standard deviation (2 × σ).'

Minor comments:

Please consider ";" between the cited reference citation in the article text body.

OK

Please revise the way used to include the cited literature in the article text body.

OK

In the introduction section, the information about the formation of 33DMbutanone as a product from d 3,3-dimethyl-2-butanol degradation is presented a couple of times.

Line 104. Please use only one literature-cited reference for the experimental details found in the previous publication. Multiple citations, in this case five, lead to an increase in self-citations and this is unwanted.

OK

Please avoid commas for Figure 1 and all the kinetic figures that are included in the article body and supplement.

OK

Line 185. Please use the fundamental atmospheric chemistry reference literature (Finlayson-Pitts book for example) to support the attempt related to faster reactions with chlorine radicals.

Response of authors

Some references have been included in line 205 of revised manuscript
'(Mellouki et al., 2015; Calvert et al., 2011; Atkinson, 2007).

Line 260 Please mention which SAR approach the authors considered

The SAR approach considered has been indicated in line 250-252 of the revised manuscript as follows:

'SAR (Structure-Activity Relationship) predictive methods (Carter et al., 2021; Calvert et al., 2011; Jenkin et al., 2018; Kerdouci et al., 2014; Kwok and Atkinson, 1995).'

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.