

**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 #1.

Introduction Part. While the article mentions the environmental and industrial sources of 3,3-dimethylbutanal and 3,3-dimethylbutanone, it lacks specific data on their typical concentrations and distributions in the actual atmospheric environment. It is better to add relevant background information to help readers better understand the importance of these compounds in the atmosphere.

**Response of authors.**

**Effectively, It would be relevant to indicate the data of concentrations of these compound present in the atmosphere. However, the literature review about this, indicates that these compounds are not emitted in large quantities, or they have not been measured. In the study by Mapelli et al 2023, on 3,3-dimethylbutanone, no data on concentrations found or measured in the atmosphere were reported.”**

2. Even if the authors use the same reference compound, the parallel experimental results will get a large error in the rate constant. Is this a reasonable margin of error? How does the author explain this error?

**Response of authors.**

**It cannot be considered surprising this degree of error. Yes, this margin of error is typical for these types of experiments where the rate coefficient is expressed in units of  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , especially when the kinetic method used to determine the rate coefficient is a relative method. In this approach, there is a systematic error associated with the subtraction process that cannot be precisely quantified.**

**This error can significantly affect slow reactions. This is the case for the reaction of 3,3-dimethylbutanone (33DMbutanone) with OH radicals, where the rate coefficient is on the order of  $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , making it a slow reaction compared to other OH reactions (typically  $k \sim 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ). Additionally, in the reaction with OH, where methyl nitrite is used as the OH radical precursor, an additional systematic error may arise due to the overlapping of IR bands from methyl nitrite and the reaction products with those of 33DMbutanone and reference compounds. This is why multiple reference compounds were used in this study.**

**Upon reviewing the data in Table 1, we have 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 correct value is  $(1.80 \pm 0.37)$ , which has already been corrected in Table 1.**

**As shown in Table 1, there are 13 rate coefficient measurements for the reaction of 33DMbutanone with OH. The final rate coefficient can be calculated using either a simple average or a weighted average. However, because these data correspond to different reference compounds and experiments conducted on different days, the authors have chosen to use the weighted average.**

The weighted average obtained is  $(1.25 \pm 0.05) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . This value closely aligns with the data reported by Mapelli et al. (2023)  $(1.2 \pm 0.2) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and the recommended value from McGillen (2020)  $(1.21 \pm 0.05) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Therefore, the authors believe that our result provides a reliable rate coefficient for the reaction of 33DMbutanone with OH.

3-How is the error calculated for each rate constant? Please elaborate.

**Response of authors.**

The total absolute error  $\sigma(k_{\text{carbonyl}})$  is a combination of the statistical errors from the regression analysis ( $\sigma_{\text{slope}}$ ) and the quoted error in the value of the rate coefficient of the reference compound ( $\sigma_R$ ).

$$\sigma(k_{\text{carbonyl}}) = \sqrt{(k_R * \sigma_{\text{slope}})^2 + (\text{slope} * \sigma_{k_R})^2}$$

where  $\text{slope}$  and  $\sigma_{\text{slope}}$  are the slope and the associated error, and  $k_R$  and  $\sigma_{k_R}$  are the reference coefficient and its error. The final values of the rate coefficients and the associated error were calculated as a weighted average.

I have to mention that when working with different reference compounds it is necessary to consider the error associated with averaging the results obtained with each of them. To do this, we work with weighted mean and standard deviation values with the following equation:

$$\bar{x} = \frac{\sum_{i=1}^N w_i x_i}{\sum_{i=1}^N w_i}$$

Where  $x_i$  are the obtained rate coefficients and  $w_i$  is the associated weight given by:  $w_i = \frac{1}{\sigma^2}$

The standard deviation associated with the weighted average is given by:

$$\sigma = \sqrt{\frac{1}{\sum_{i=1}^N w_i}}$$

We have not considered it necessary to provide all the details of the error calculation in this article since it has already been extensively explained in previous articles, (Colmenar et al. 2020 (<https://doi.org/10.5194/acp-20-699-2020>) Aranda et al. 2024 <https://doi.org/10.1016/j.atmosenv.2024.120420>)

4. The clarity of Figures 2 and 3 is not enough. Please adjust the image resolution to make the picture more visible.

**Response of authors.**

We will attempt to obtain figures with higher resolution and quality. However, in the case of Figure 2, since there are so many spectra together, it has been difficult to improve the quality while maintaining the full spectrum (from  $800 \text{ cm}^{-1}$  to  $3000 \text{ cm}^{-1}$ ).

5. Is the peak time of each product compared with the standard peak time of the national standard?

**Response of authors.**

**We would need to clarify what we mean by the term 'standard' we are referring to a commercial compound, not a national standard. To avoid confusion, the manuscript will be updated by replacing the word "standard" with "commercial compound."**

6. The mechanism diagrams in Figures 7 and 8 are quite confusing and recommend readjustment.

**Response of authors.**

**We do not really understand what do you mean with the term 'readjustment'. The proposed mechanism corresponds to the possible attack routes of the atmospheric oxidant with the organic molecule and the subsequent evolution to the products. Please, could you please specify what you mean by 'readjustment'?**

7. The author has repeatedly mentioned that these aldehydes may contribute to the production of SOA, so does the author consider supplementing the SOA experiment in this system to better evaluate its contribution to SOA?

**Response of authors.**

**The authors indeed find it highly interesting to conduct studies aimed at determining SOA generation. Currently, the instrumentation required for these experiments, specifically an Aerosol Mass Spectrometer, is an equipment recently acquired but that is not available for use in our laboratories in the near future, it is part of an ongoing project, after a process of calibrating and optimizing this experimental system.**

8. Combined with SAR prediction, the authors point out that methyl groups adjacent to tert-butyl groups are the main reaction path, especially in the oxidation of OH radicals and Cl atoms, but many studies have pointed out that aldehyde groups are the most important and possibly the only core reaction path in aldehydes. How do the authors consider this problem?

**Response of authors.**

**It may be that this explanation is not clearly conveyed in the manuscript. What we aim to express is that for 33DMbutanone (ketone compound), the SAR method (see Table S1 in the supplementary material) and the results of this study, indicate that the reaction predominantly initiates with the oxidant (atomic chlorine/hydroxyl radical) abstraction of the hydrogen from the methyl group adjacent to the tert-butyl group. In contrast, for the reaction of 33DMbutanal (aldehyde compound), the hydrogen abstraction depends on the specific oxidant. For the reaction with atomic chlorine, the hydrogen abstraction can occur from any group (with a similar percentage of attack on the CH<sub>3</sub>-, CH<sub>2</sub>-, and C(O)H groups). For NO<sub>3</sub>, hydrogen abstraction primarily occurs at the aldehydic hydrogen (63%), followed by the hydrogen in the CH<sub>2</sub> group (37%). For the OH radical, 94% of the abstraction occurs at the aldehydic hydrogen.**

**In this regard, if the referee considers it not sufficiently clear, the text in the manuscript will be revised in the final version.**

**We want to indicate that, in the scheme shown in Figure 8, we have detected an error in the percentage for Channel I of the nitrate radical reaction which has already been corrected.**

9. In Section 3.1 Kinetic study, the author points out that some wall losses, photolysis losses, etc. can be ignored. Please give specific experimental results and present them in pictures to intuitively understand the wall losses.

#### Response of authors.

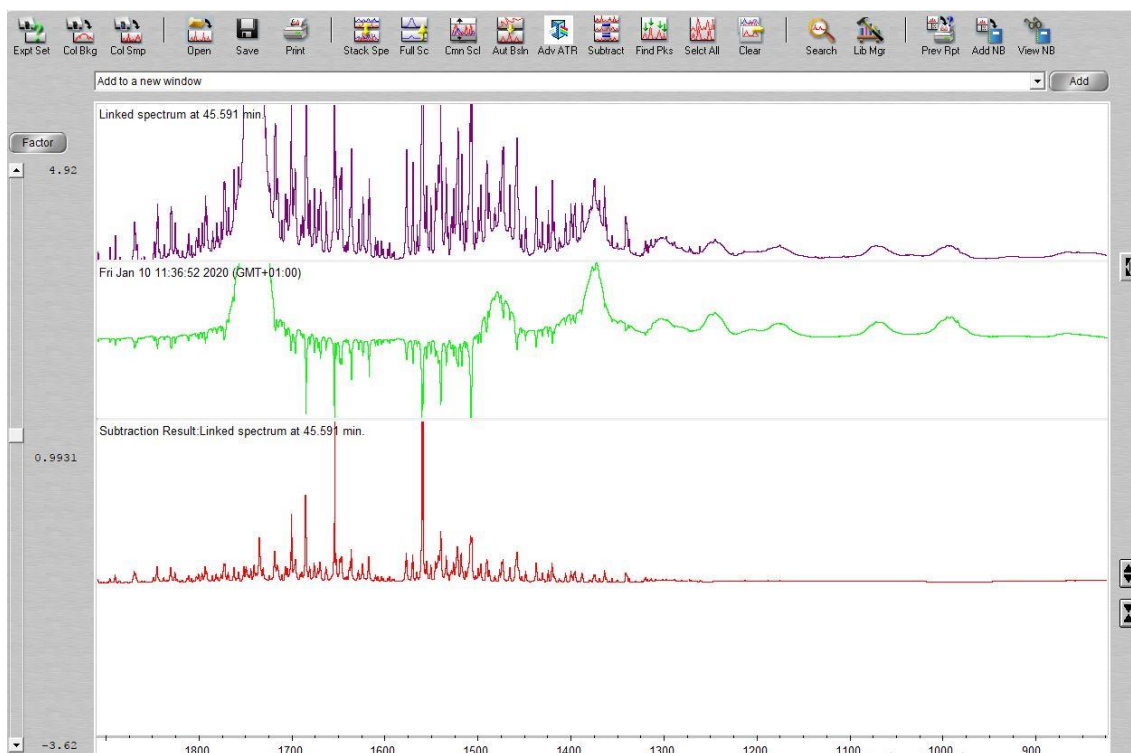
The methodology used for the kinetic study involved a series of preliminary experiments to determine the loss processes due to wall adsorption, photolysis, etc. The authors considered these loss processes negligible when the percentage variation in the reactant concentration was less than 3%.

To determine these losses using FTIR, the procedure involved comparing the initial spectrum of the reactant with the spectrum recorded after a long period (45 minutes, which is the typical time range for the kinetic study of 33DMbutanal and 33DMbutanone). If the variation was less than 3%, the authors deemed these processes insignificant and concluded that they did not need to be accounted for in the kinetic study.

Only in cases where the comparison showed a variation greater than 3%, the rate coefficients for these loss processes were determined using the equation:

$$\ln([\text{reactant}]_0/[\text{reactant}]_t)=kt$$

For the study of 33DMbutanal and 33DMbutanone, the percentage variation in concentration was less than 3% in all cases. Therefore, the loss coefficients were not calculated, and we do not have any graphs of the mentioned equation. However, as an example, 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)



Since the preliminary experiments conducted for the kinetic study of **33BM**butanone and **33DM**butanal showed that the loss processes of these reactants (including the reference compounds) are negligible, the authors believe it is unnecessary to provide further information on this matter.

However, if the referee considers it necessary, we will include the following sentence in the manuscript revised *“To determine these loss processes, the initial spectrum of the reactants was compared with the spectrum recorded after a long period (45 minutes, which is the typical time range for the kinetic study of 33DMbutanal and 33DMbutanone)”* ..