

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

Referee #2

The manuscript describes results from laboratory based experiments to elucidate the gas phase atmospheric degradation chemistry of two VOC, namely 3,3-dimethylbutanal (henceforth DMBal in this review) and 3,3-dimethylbutanone (DMBone). There is much novel and valuable data presented here, but some improvements in presentation and discussion are required.

The introduction sets out the likely atmospheric sources and sinks of the two VOC, and outlines previous work. The experimental section is a little lacking in detail. For example, it may be that the photochemistry used to generate OH from CH<sub>3</sub>ONO is familiar to the authors, but it was not to this reviewer (nor many readers). If you are not going to elaborate here, at least include a reference to a literature paper describing these details. Further, I am not familiar with lamps of output 350 nm. Please describe.

#### **Response of authors.**

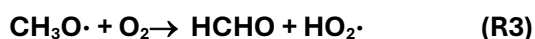
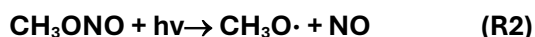
**The authors acknowledge that certain details about the experimental process are missing. However, we believe that the manuscript is already sufficiently extensive and further elaboration on aspects described in the literature (Finlayson-Pitts and Pitts 2000). Nevertheless, if the reviewer deems it necessary, the next information will be included in the final version:**

**“The oxidants were generated by photolysis or decomposition of a precursor (Finlayson-Pitts and Pitts 2000).**

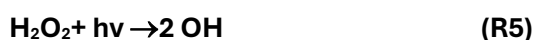
**The generation of chlorine atoms was achieved through the photolysis of Cl<sub>2</sub> using radiation emitted by actinic lamps ( $\lambda_{\text{max}} = 360 \text{ nm}$ ).**



**Hydroxyl radicals (OH) were generated by the photolysis of methyl nitrite (CH<sub>3</sub>ONO) in air in the presence of NO, following the reaction sequence below:**



**Some experiments have been carried out using H<sub>2</sub>O<sub>2</sub> as precursor of OH and UV radiation ( $\lambda=254 \text{ nm}$ ) in a Quartz gas cell reactor.**



**Nitrate radicals (NO<sub>3</sub>) were generated through the thermal decomposition of dinitrogen pentoxide (N<sub>2</sub>O<sub>5</sub>) at room temperature, according to the following equilibrium**



(R6)”

There is a wealth of data presented in the results section, useful both for rate coefficient determinations and for product yields. Data presented in plots (e.g. Fig. 1) appear to be of high quality. My main concern regarding this manuscript concerns the data presented in Table 1, and the associated discussion. The data for DBBal + Cl looks good, both as presented in Fig. 1 and in Table 1. However, for determinations of  $k$  for the other two reactions, there appears to be an unusually wide spread of results. For DMBone + Cl, these values (in  $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) range from 3.03 to 5.22. The results obtained using 2-methyl-2-butanol as a reference VOC all cluster at the lower end of this range of results, whereas results using other reference compounds tend to agree on  $k \sim 5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . These observations are surely worthy of comment in the following text, together with some analysis of the provenance of the reference  $k$ -data. Is the data on 2-methyl-2-butanol + Cl (or any other of the reference reactions) well established? All worth a few more sentences, though to conclude on this reaction, if no prior studies were available then results from this work represent a considerable contribution to our understanding of atmospheric chemistry.

More concerning is kinetic data in Table 1 on DMBone + OH (Table 1). Results from this work range from  $k / 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} = (0.96 \pm 0.11)$  to  $(1.92 \pm 0.59)$ , exactly a factor of two, considerably larger than I would expect from a relative rate study.

There is no clear sense here that the reference reactions are responsible for this inconsistency. Nor (if the data quality in Fig. 1 is in any way exemplary), was this likely a result of random noise from experiment to experiment. So, having ruled out two potential problems, we should consider other sources of error. Was there another experimental factor exerting a malign influence on the data? I note that we cannot tell from Table 1 whether experiments were conducted at 254 nm (where photolytic effects may be serious) or 350 nm, where the more complex precursor chemistry may introduce other secondary effect. Details such as precursors used should be included in Table 1. The uncertainties quoted for each experiment indicate that data quality could be quite varied; were all datasets nonetheless proportional in appearance – all having intercepts of zero and no evident curvature? Perhaps all such plots should be included in the S.I. Were there any difficulties in differentiating FTIR peaks of DMBone from precursors or products? An overall weighted average yielded  $(1.25 \pm 0.05) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The surprisingly small (4%) uncertainty in  $k$  does not appear to reflect the inconsistencies encountered from one experimental determination to the next. There is more analysis needed and more discussion around the above points required to justify the closing statement from line 179 “These data are in good agreement with the values obtained in this study, thereby contributing to the accurate determination of the rate coefficients.”

#### **Response of authors.**

**When the FTIR system is used to determine the rate coefficient, a systematic error associated with the subtraction process arises, which cannot be precisely quantified. To minimize this systematic error, it is important to avoid overlapping of IR bands from the radical precursor, reference compounds, and reaction products. In many cases, it is challenging to find a reference compound whose characteristic IR bands do not**

overlap with those of the organic compound (in our case, 3,3-dimethylbutanal and 3,3-dimethylbutanone).

Additionally, the slower the reactions, the smaller the variations in the absorbance of the characteristic IR bands of the reacting compounds, making the subtraction factors determined at time  $t$  and  $t'$  very similar. In such cases, small changes in determining the subtraction factor can significantly influence the calculation of the relative rate coefficient ( $k_{\text{carbonyl}}/k_{\text{Reference}}$ ) and therefore in the calculation of  $k_{\text{carbonyl}}$ . For this reason, four reference compounds were used in the reactions of 33DMbutanone to determine the rate coefficient ( $k_{\text{carbonyl}}$ ) as accurately as possible.

As shown in Table 1, there are 13 rate coefficients measurements for reaction of 33DMbutanone with Cl and OH.

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 is  $(1.80 \pm 0.37)$  instead of  $0.96 \pm 0.11$ . It has been modified in Table 1 in a revised manuscript.

The final rate coefficient can be calculated using either a normal 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 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

$$\text{by: } w_i = \frac{1}{\sigma^2}$$

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

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

Regarding your question about the rate coefficients of all reference compounds, these are the corresponding to the database of McGillen et al 2020 (<https://essd.copernicus.org/articles/12/1203/2020/>)

In the case of Cl reaction the weighted average obtained is  $(4.22 \pm 0.27) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The rate coefficient obtained for Cl atoms is very similar to recommended value from McGillen (2020)  $(4.48 \pm 0.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

In the case of OH reaction the weighted average obtained is  $(1.25 \pm 0.05) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , again 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 Cl and OH.

Regarding the comment on secondary reactions, such as the photolysis of 3,3-dimethylbutanal and 3,3-dimethylbutanone when irradiated at  $\lambda_{\text{max}}=360 \text{ nm}$  (254 nm was not used in kinetic experiments), or the reaction between carbonyl compounds and radical precursors ( $\text{Cl}_2$  or  $\text{CH}_3\text{ONO}$ ), it should be noted that preliminary experiments were conducted to evaluate these processes. The results of these experiments demonstrated that such contributions are negligible, since the variation in the concentration of the reactants (carbonyl compounds and references compounds) at time zero and 45 minutes is less than 3%.

Moreover, if these processes were significant, the plot of the equation used to determine the  $k_{\text{carbonyl}}/k_{\text{reference}}$  ratio would exhibit curvature or a significant origin intercept. In our experiments, the plots showed linear fit with  $r^2 \sim 0.99$  and low origin intercept values, indicating that these secondary processes do not affect the results.

The authors will consider including the representations in the supplementary material as suggested by the reviewer. However, given that there are numerous graphs, resulting in a large amount of information we have made a selection. All the information will be available on demand.

There follows good discussion of k results, both in terms of the reactivity of different oxidants, of different functional groups (aldehyde and ketone) and of the impacts of structural changes within the VOC on reactivity. However, I found the absence of any comparison with one of the most recent and sophisticated SAR formulations surprising. The authors should compare results obtained here with those calculated using Jenkin et al. (2018) [doi.org/10.5194/acp-18-9297-2018](https://doi.org/10.5194/acp-18-9297-2018)

#### Response of authors.

As indicated, the rate constant estimated for the reaction of 3,3-dimethylbutanone and 3,3-dimethylbutanal with OH radicals was calculated using the EPA's EPI Suite™ software (<https://www.epa.gov/tsca-screening-tools/epi-suitetm-estimation-program-interface>), specifically the AOPWIN™ model within EPI Suite™. This model estimates the gas-phase reaction rate for interactions between hydroxyl radicals (the most prevalent atmospheric oxidant) and a given chemical. The software version used is updated as of 2023. The  $k_{\text{estimated}}$  ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) were  $22.12 \times 10^{-12}$  for 33DMbutanal and  $1.69 \times 10^{-12}$  for 33DMbutanone.

For the reaction of 33DMbutanone with OH, the rate constant was also estimated based on the values from Jenkin et al. (2018), obtaining a value of  $1.45 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . However, we considered that using the software was sufficient.

**Thank you for the suggestion.**

The product studies for both reactions appear commendably detailed. Methods appear sound. My only concern here was the unidentified problem with the DMBone kinetic data (see above). This may have derived from FTIR retrievals. Might this propagate into errors in product yields?

**Response of authors.**

**Could the reviewer please specify or clarify their question? I am not entirely sure what they are referring to.**

There follows a discussion of atmospheric implications. The points raised here all seem reasonable, as do the various estimates of lifetimes and POCP. One point to note would be that photolysis lifetimes were estimated elsewhere based upon measured spectra, but that no quantum yield data was available. There are consequently large uncertainties in the rate of photolysis for either of these VOC.

**Response of authors.**

**For 3,3-dimethylbutanal (33DMbutanal), the photolysis rate coefficient is indeed an estimated value based on absorption cross-section data for 3-methylbutanal as reported by Lanza et al. (2008), since no data is available for 33DMbutanal. Therefore, we assume that the photolysis rate constant for 33DMbutanal may have a significant uncertainty.**

**In contrast, for 3,3-dimethylbutanone (33DMbutanone), the photolysis rate constant is derived from the data provided by Mapelli et al. (2023), who determined quantum yields and effective absorption cross-sections. Consequently, this value does not carry significant uncertainty**

Typos / minor concerns:

should be an italic “k” throughout the manuscript;

**Ok, all “k” will be changed an italic “k” throughout the manuscript;**

Table 1 header is confusing. It states that k is in units of  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , but in fact the k values throughout the table are in different units of  $10^{-10}$ ,  $10^{-11}$  or  $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , depending on which reaction is being reported. I suggest that the most sensible way to report this is to list all k values in one consistent set of units, e.g.  $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . At the very least, remove the misleading statement “k in units of  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ” from the table header.

**Ok, the suggested changes will be taken into account in a revised manuscript**

Similar comments re. k values and powers of ten for Table 2.

**Ok, the suggested changes will be taken into account in a revised manuscript**

Line 166 “an” to “and”

**Ok, the suggested changes will be taken into account in a revised manuscript**