egusphere-2024-3241

Title: Reactivity study of 3,3-dimethylbutanal and 3,3-dimethylbutanone: Kinetic, reaction products, mechanisms and atmospheric implications

Author(s): Inmaculada Aranda et al.

Public justification (visible to the public if the article is accepted and published):

Dear Dr Pilar Martin,

Thank you for providing a revised document with your responses to the reviewers' comments.

As you can see below, the reviewers still feel that the manuscript requires substantial improvement.

Report# 2: The manuscript improved addressing the provided suggestions and comments. A significant part of the manuscript has been restructured. This represents a substantial change from the original manuscript. The results and discussion section adds new information on the interpretation of FTIR and MS data. Proofs of the IR and MS data were included in the supplementary information files. Also, the kinetic data has been added to the SI. However, some minor revisions need to be applied before publication.

Question: Please add a statement in the text to explain the scattering of points in Fig S1 c.

Response of author: A paragraph has been added in the manuscript to explain the scattering of points in Fig S1 c. Although we consider that the data presented in Fig. S1c. do not show a greater dispersion than usual in this type of kinetic studies with slow reaction rates, the presence of methyl nitrite could also affect the analysis. It should be noted that the values of the rate constants presented in Table 1 for each reference compound correspond to the average value of the constants obtained in each of the experiments performed, but Graph 1S shows all the data together as an example, and although it shows dispersion for the reasons previously mentioned, it is not the graph used to calculate the rate constant. In any case, in accordance with your suggestion, we have decided to include a paragraph in the article, which is the following:

Pag 6, line 187: *"the dispersion of the data observed in the ·OH reaction with 33DMbutanone (Fig. 1Sc) is due to the complexity of the analysis, especially for slow reactions, and the overlapping of the bands of the precursor (methyl nitrite)."*

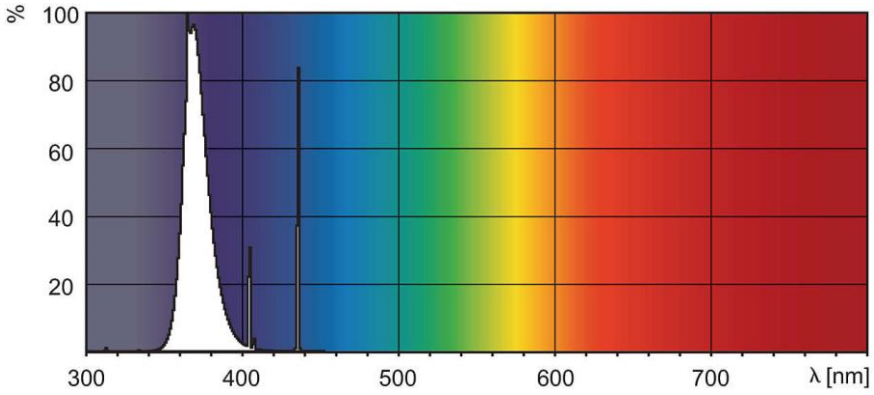
Question: There is still unresolved concern related to the photolysis of 33DMbutanal. The answer is not accepted in the way presented by the authors, however, the test presented by the authors could be mentioned in the text to explain somehow that even though there is a possibility of photolysis, this was tested and found not to affect the results. The authors mentioned "radiation emitted by actinic lamps (λmax = 360 nm)", and this is in contradiction with the answer "the radiation is limited to λ >360 nm". Actinic lamps emit light in a range from around 290 to 450 nm with a maximum of 360nm. There

is a range of light that could induce the photodegradation of 33DMbutanal. Tadic et al., suggested in their article that "It is obvious that in case of … 3,3-dimethylbutanal photolytic and reactive lifetimes are very similar, and that those two removal processes compete among each other".

Response to the comments: Firstly, respecting to: 'Actinic lamps emit light in a range from around 290 to 450 nm with a maximum of 360nm. There is a range of light that could induce the photodegradation of 33DMbutanal. Tadic et al., suggested in their article that "It is obvious that in case of … 3,3-dimethylbutanal photolytic and reactive lifetimes are very similar, and that those two removal processes compete among each other'.

We must answer that **this is not the case in our experiments.** As demonstrated by the emission spectrum of the lamps used (Philips Actinic BL TL-K 40W/10-R, Wavelength Range: 340-400 nm, Peak at 365 nm, see below) and the results of our photolysis experiments, 3,3-dimethylbutanal does not undergo photolysis under our experimental conditions**.** That is, the radiation used to generate atomic chlorine and the OH radical does not induce photolysis of 3,3-dimethylbutanal as it has been explicated in the manuscript. Naturally, when determining the atmospheric lifetime to evaluate its implications, we must account for the fact that the radiation reaching the troposphere is energetic enough for the photolysis process to be comparable to the loss caused by the reaction with the OH radical, as explained in the manuscript.

We show here the emission Spectrum of the lamps used in our experiments. Philips Actinic BL TL-K 40W/10-R. Wavelength Range: 340-400 nm. Peak at 365 nm



As indicated in the manuscript (line 168-170), the possible photolysis of 3,3-dimethylbutanal is negligible under the conditions used in our experiments. Therefore, we do not consider it necessary to add more information on this matter in the manuscript.

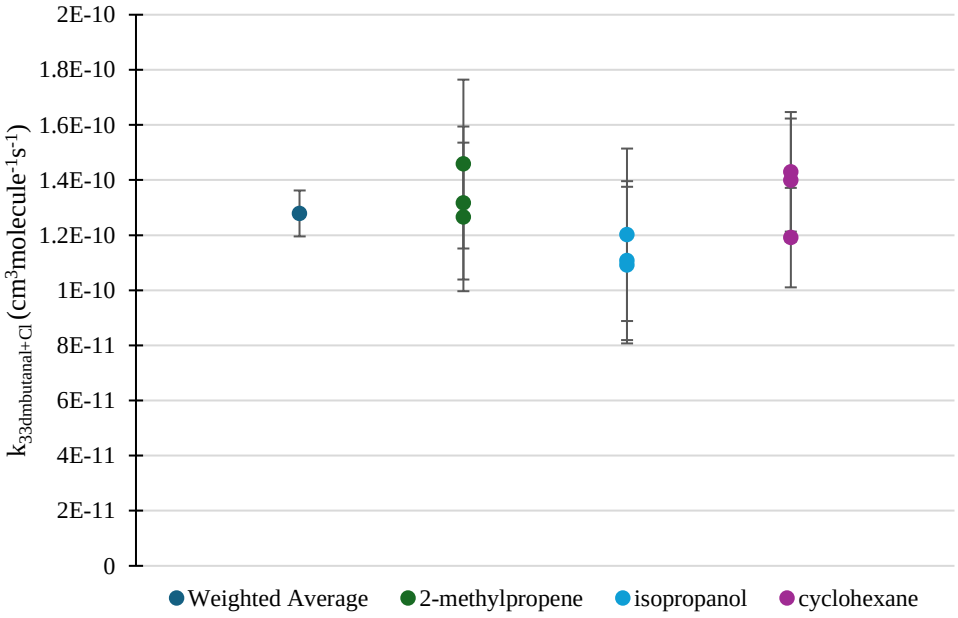
Authors' response to the comment 'The authors mentioned "radiation emitted by actinic lamps (λmax = 360 nm)", and this is in contradiction with the answer "the radiation is limited to λ >360 nm'.

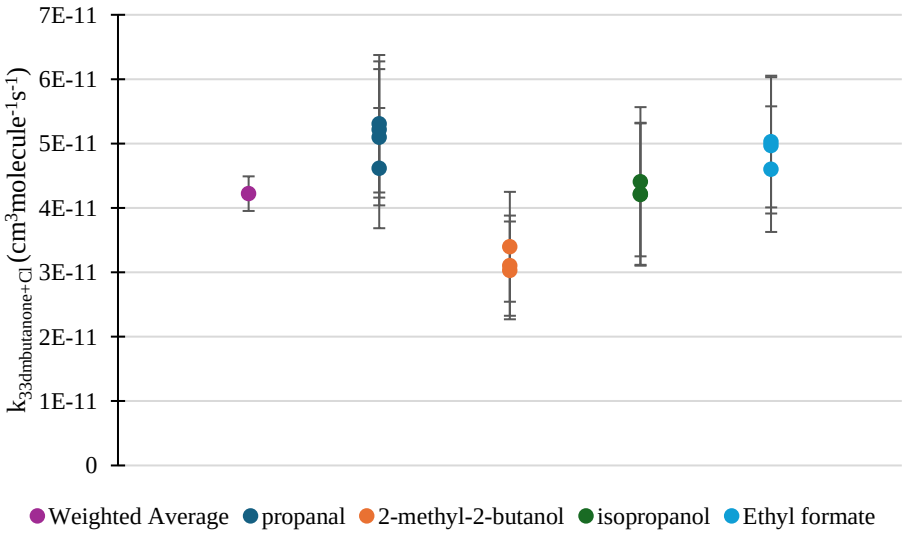
Answer: The previous response we made to the referee could not be entirely appropriate, and we apologize for that. In fact, we did not mean to imply that the radiation was limited to wavelengths greater than 360 nm. As confirmed by the emission spectrum of **our lamps** (attached photo), the emission range is 340-400 nm, with a peak wavelength of 365 nm. To be rigorous, we will also change the maximum value from 360 nm to 365 nm in the manuscript (line 124).

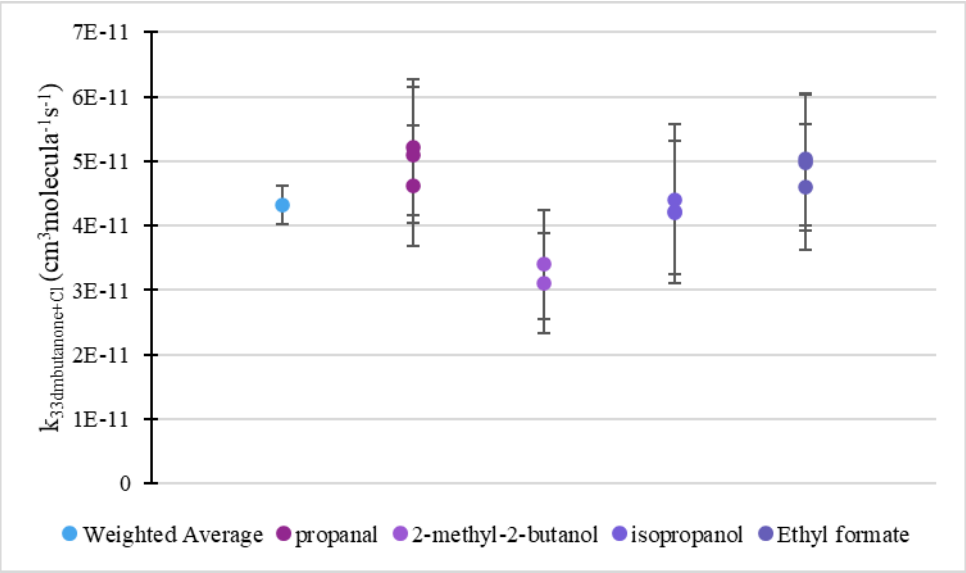
-Question: Another unresolved comment: "Please comment in the text for the difference of 25% between the kcarbonyl values for the reaction of 33DMbutanal+Cl." This aspect is even more annoying for the reaction with OH radical where the difference is dropping to 50%. Please add a statement in the text to explain such scattering.

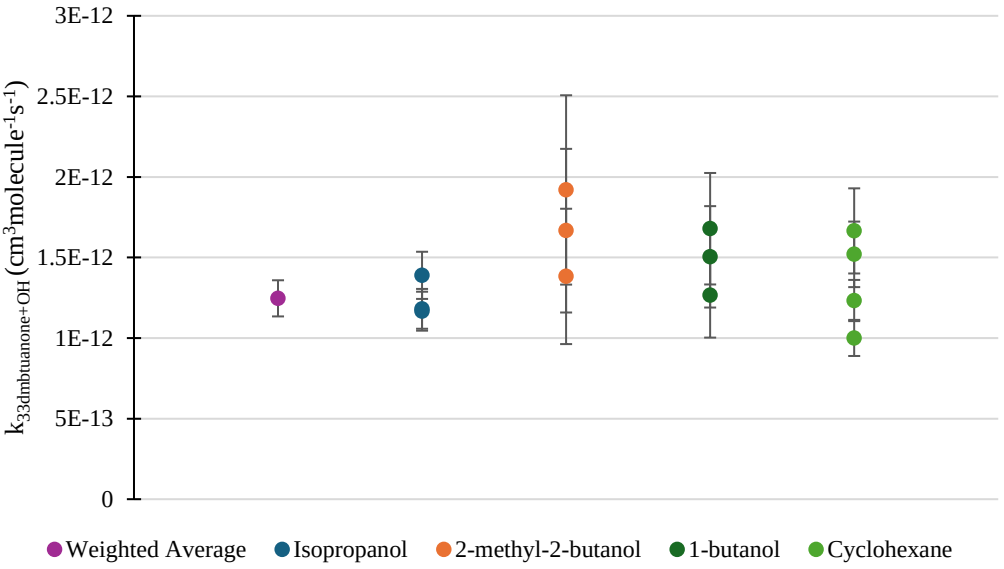
Response of authors: We have included a short explanation of the fact (line 199). "*Upon examining the rate coefficients and their associated uncertainties, it is evident that most of the experimental values fall within the expected error margins. Furthermore, the 50% difference observed between the rate coefficient values obtained for the reaction of 33DMbutanone with the OH radical is considered usual, given the level of analytical complexity, particularly in the case of slow reactions".* This is because variations in determining the subtraction factor significantly influence the constant's value.

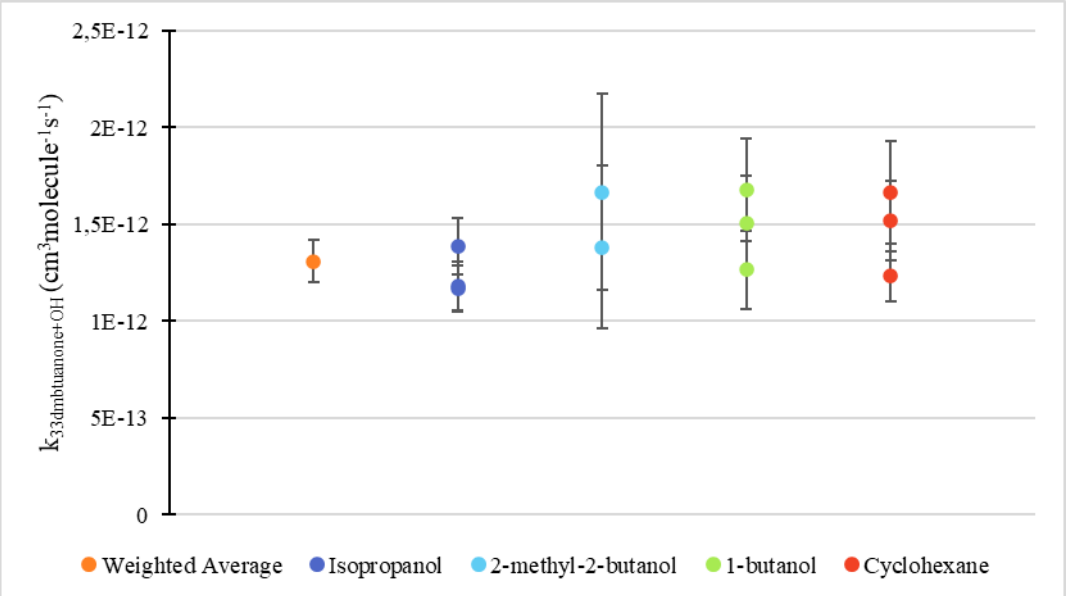
Thus, this can be verified in the following graphs, which show the error range of the obtained values. These graphs are not included in the manuscript.






7E-11
6E-11
5E-11
4E-11
3E-11
2E-11
1E-11
0
$k_{33dmbutanone+Cl}$ ($cm^3molecula^{-1}s^{-1}$)
Weighted Average
propanal
2-methyl-2-butanol
isopropanol
Ethyl formate


3E-12
2.5E-12
2E-12
1.5E-12
1E-12
5E-13
0
$k_{33dmbtuanone+OH}$ ($cm^3molecule^{-1}s^{-1}$)
Weighted Average
Isopropanol
2-methyl-2-butanol
1-butanol
Cyclohexane


2,5E-12
2E-12
1,5E-12
1E-12
5E-13
0
$k_{33dmbtuanone+OH}$ ($cm^3molecule^{-1}s^{-1}$)
Weighted Average
Isopropanol
2-methyl-2-butanol
1-butanol
Cyclohexane

Report 3: There remain inconsistencies in presentation (see below). Some of the kinetic data remains unusually scattered, though the presentation and explanatory text around these has been improved. Also heartening to see the products sections has been substantially revised.

Response of authors. As previously responded to Report #2, We have included a short explanation of the fact (line 199): "*Upon examining the rate coefficients and their associated uncertainties, it is evident that most of the experimental values fall within the expected error margins. Furthermore, the 50% difference observed between the rate coefficient values obtained for the reaction of 33DMbutanone with the OH radical is considered usual, given the level of analytical complexity, particularly in the case of slow reactions".*

Question: There remain inconsistencies in presentation throughout the manuscript, with muddling of units, parentheses etc., and whether dots are used to denote radical species or not.

Response of authors. The manuscript has been revised again eliminating the inconsistencies, muddling of units, denoting radical species, parentheses etc.,

Report #1: The revised manuscript is technically sound, but the reason the author chose 3,3-dimethylbutanal and 3,3-dimethylbutanone to research is still unclear, as the authors stated these compounds are not emitted in large quantities or not measured in the atmosphere, so if these compounds could play an important role in the tropospheric chemistry? So the related description in the manuscript should be revised.

Response of authors

The authors firmly believe that the work carried out is fully justified, as explained in the introduction. These two compounds have been identified as reaction products in the atmospheric degradation of alcohols (Colmenar et al., 2020).

Colmenar, I., Martín, P., Cabanas, B., Salgado, S., Tapia, A., Aranda, I.: Atmospheric fate of a series of saturated alcohols: kinetic and mechanistic study, Atmos. Chem. Phys. 20, 699–720. https://doi.org/10.5194/acp-20-699-2020, 2020.

Additionally, 33DMButanal could be an intermediate in the synthesis of neotame, a sweetener. Industrially, 33DMButanone is produced for use in fungicides, herbicides, and pesticides and could also serve as a solvent substitute for hazardous solvents like toluene, due to its low toxicity and good solvation characteristics.

We have included this sentence in the manuscript: (line 60) "*Although there are no atmospheric concentration measurements for these compounds, their current and potential uses justify the need to understand their atmospheric reactivity and degradation processes*."

Indeed, several studies have already addressed the determination of rate constants with OH and NO_3 radicals and photolysis under atmospheric conditions. Our work further contributes new data on the reactivity not only with these oxidants $\cdot OH$ and $NO_3\cdot$ but also with Cl atoms. Moreover, the research presented in this article helps to better understand the atmospheric chemistry of carbonyl compounds in general.

Therefore, we do not consider it necessary to introduce more modifications into the article**.**

Finally, we thank the reviewers for their thorough work, which undoubtedly further improves this article.