

## Review on the paper egusphere-2024-3241 by Aranda et al.

This paper deals with the kinetics and mechanisms of two carbonyl compounds (3,3-dimethylbutanone and 3,3-dimethylbutanal) with OH, Cl and NO<sub>3</sub>. The kinetics of 33DMbutanal with Cl atoms at ambient temperature are determined for the first time, while for the other kinetics (33DMbutanone with Cl atoms and OH radicals), values were already reported in the literature. A set of reaction products has been identified, with a (semi)quantification for a few of them.

My main concern is that many statements consist of suggestions that are not (fully) supported by results. Some of the conclusive remarks are not really convincing. The kinetics present scattering in the results that needs to be clarified.

Overall, the manuscript is quite long and there are many typos that need to be corrected (I reported only a few below).

### Comments

Line 34: it is stated that "large carbonyl compounds can influence on climate change if they are strong infrared light absorbers by altering the Earth's radiation balance": I don't agree: the atmospheric concentrations of carbonyls are too small to influence the climate by IR light absorption.

3.1 Kinetic study: did you check that the reaction of the compound (resp. the reference) with the oxidant did not form products absorbing at the selected IR bands for the reference (resp. for the compound)?

Why not showing all the relative kinetic plots (in Supplementary Material)?

Schemes S1 & S2: HO<sub>2</sub> radicals are formed in the mechanisms (through RO+O<sub>2</sub> for example): why not including the RO<sub>2</sub>+HO<sub>2</sub> reactions in the mechanisms (see also line 606)? Especially for secondary and even more tertiary RO<sub>2</sub>, where RO<sub>2</sub>+RO<sub>2</sub> rate constants are very low... Besides, these mechanisms could be advantageously simplified, by removing low reactivity channels (for example RC(O)O radicals mainly decompose into R+CO<sub>2</sub>, (CH<sub>3</sub>)<sub>3</sub>CO<sub>2</sub>+(CH<sub>3</sub>)<sub>3</sub>CO<sub>2</sub> is negligible, etc.). What about direct photolysis of α-dicarbonyls, which has been shown to be significant?

Table 1: there are significant discrepancies between the k values obtained using the different reference compounds, especially with 33DMbutanone+OH (from 0.96 to 1.92) and with 33DMbutanone+Cl (from 3.03 to 5.30). This need to be discussed. How well known are the reference rate constants?

Line 321: Figure 2: what do you mean with "64 % of the conversion and a 29% respectively"? What are the experimental conditions of the experiments? Could you indicate the concentrations of the references? This figure is difficult to read (small size, bright colours, IR spectra mixed).

Line 333: it is stated that "Additionally, IR bands of N<sub>2</sub>O<sub>5</sub> (precursor of NO<sub>3</sub>) have been observed in the reaction with Cl atoms": referring to Figure S2, we cannot see any N<sub>2</sub>O<sub>5</sub> bands appearing in the product spectra...

Line 365: "the concentrations of acetone and nitrated compounds increase more than expected": what are actually the expected trends??

Figure 3S: what are the differences with Figure 4 (a) and (b)??

Figure 5S: OH reaction in absence of NO: this is from H<sub>2</sub>O<sub>2</sub> photolysis, right? Did you carry out OH reaction in presence of NO (as seems from line 118)? Is there a yield plot also?

Figure 5: comparing (a) and (b): why are the plots of nitrated compounds curved in one case (a) and linear in the other case (b)?

Figure 7S: how do you explain the shift on the x-axis?

Table 3: how did you calculate the uncertainties for the average yields? Why so large differences with those in Table 4??

Lines 421-423: "reaction of 33DMbutanone with Cl atoms in the presence of NO the total carbon is 95% (not accounting for nitrated compounds),": how is it possible to get almost 100% carbon balance without taking into account nitrated compounds (that seem to be significant from Table 3)?

Table 4: for "33DMbutanal + NO<sub>3</sub>": no yields are reported: could the authors calculate upper limits (based on their sensitivity)? Especially since acetone is detected by GC... Why is the yield of nitrated compounds exactly = 100%??

Tables 3 & 4: calculation of the carbon budget: I suggest explaining it in the main text, not in the notes of the Tables, since it is not very clear as now...

Lines 424-426: from Figure S9, it is said that formic acid and hydroxyacetone were observed. While this seems to be valid of formic acid, I cannot see any features for hydroxyacetone... Besides, formic acid is often observed in such experiments when formaldehyde is present; it may be formed from secondary wall reactions of CH<sub>2</sub>O...

Figure 12S: "generated chromatograms for the 33DMbutanone + OH +NO at different reaction times": what are these reaction times? It is noted "8 min" for all last 3 chromatograms... What do you mean with "generated"?

Line 460: "a little peak that appear together with the peak of air, that could correspond to acetone.": why not calibrating directly with pure acetone instead of "creating a chromatogram using a specific tool"??

Lines 462-467: this descriptive part concerning the "specific tool" for creating chromatograms is absolutely unclear. Which software? What about reliability? What is the advantage for acetone compared to direct calibration?

Lines 492-493: "the possible reaction of RO<sub>2</sub> with OH radical": could you estimate the contribution of these reactions relative to RO<sub>2</sub> + RO<sub>2</sub>?

Line 508: PAN is known to be unstable at high temperature: how can you attribute the peak at 5.59 min to PAN, knowing that the SPME fiber is heated at 250°C in the GC injector? See also lines 569-570.

Lines 512-514: PAN is formed after a series of almost 12 successive reactions (scheme 1S): how can you affirm that a PAN yield of 100% is consistent with the SAR estimated branching ratio of 98% for channel II??

Line 543: isomerization of oxy-3,3-dimethylbutyryl radical: is this "new" pathway supported by literature studies? Because decomposition of such oxy acyl radicals (into alkyl + CO<sub>2</sub>) is considered to be extremely fast. I cannot see this suggested reaction on Figure 8, why? Indeed, another pathway was suggested farther (lines 602-607). Why then concluding (lines 696-698) that "The positive

identification of 33DMbutanoic acid implies a pathway in the reaction mechanisms of 33DMbutanal, that initially have not been considered.”?

Lines 545-549: mass spectrum of 33DMbutanoic acid compared to mass spectrum of the peak at 9.56 min: you indicated that these 2 spectra match well (“correspond”): could you support this by showing the comparison in Supp Mat?

Lines 550-552: Figure 18S is not convincing...

Lines 558-561: mass spectrum of 22DMpropanoic acid compared to mass spectrum of the peak at 8.23 min: you indicated that these 2 spectra match well (“correspond”): could you support this by showing the comparison in Supp Mat?

Lines 582-583: I don’t understand how you conclude that acetone comes mainly from channel I *because* the yields are similar... this may be fortuitous?

Line 596: “100% of the reacted 33DMbutanal forms nitrated compounds”: this is not demonstrated; this is only suggested because no other compounds were detected.

Lines 636-638: photolysis rates: it should be specified if the photolysis quantum yield has been taken as 1.

Lines 692-693: the conclusion that “the results suggest that the RO<sub>2</sub> + OH· reaction in the unpolluted atmosphere could be significant.” is bold, because it is only based on the difference of acetone yields between Cl and OH systems...

### **Minor comments/Typos**

Line 30: established

Line 36: remove ‘;’ at the end of the sentence, before the closing bracket

Citations of references are not homogeneous through the MS; please check (“XX et al., XXX” with point and comma).

Lines 129-130: remove capital letters for the compound’s names (same thing lines 136-139)

Line 150: “the losses of the reactants...”

Line 151: the loss of < 3% is over how much time?

Table 1: note d is not explained. Notes a,b,c: the statement “k<sub>carbonyl</sub> and k<sub>R</sub> is given in 10<sup>-10</sup>, 10<sup>-11</sup>, 10<sup>-12</sup>, respectively” is not clear: we have 2 subjects (k<sub>carbonyl</sub> and k<sub>R</sub>) and 3 possibilities (10<sup>-10</sup>, 10<sup>-11</sup>, 10<sup>-12</sup>)!

Lines 181 & 182: use “x” instead of “x” (check all the MS)

Line 182: the statement “This is the general trend observed in the atmospheric chemistry for the oxidation reactions of organic compounds; k<sub>Cl</sub>>k<sub>OH</sub>>k<sub>NO<sub>3</sub></sub>” needs at least one reference.

Consistency between Table 1 and 2: the uncertainties in k<sub>Cl</sub> for 33DMbutanal (this work) are not the same. Same for k<sub>OH</sub> for 33DMbutanone.

Line 210: please homogenize the naming of 3-methylbutan-2-one all through the MS (see Table 2 where it is noted 3-methylbutanone).

Line 217: what is the "atmospheric radical"?

Line 222: "more favoured than H atom"

Line 224: "33DMbutanone"

Line 232: "double bond"

Line 238: "coefficients"

Line 241: "kestimated=22.12x10-12": please keep only 3 significant figures and write in scientific style

Line 245: "factors"

Line 254: "Schemes"

Line 265: "major"

Line 271-272: the sentence is not clear

Line 276: "neutral compounds": you mean "closed-shell"?

Line 286: "establish"

Line 303: "Colmenar et al., 2018"

Figures 3S & 5S, caption: "reacted"

Lines 391-396: Table 3 caption is reported twice.

Table 3: GS-TOFMS, Reaction products: "Hydroxy-2,3-butanedione"

Notes in Table 3: why using note (1) and \* instead of continuing with "h"? Same comment for Table 4.

Table 4: "33DMbutanal + OH": "24.9±0.8"

Line 409: "products identified"

Line 419: "only"

Line 429: "GC-MSTOF": sometimes you write "GC-TOFMS": please be consistent!

Line 431: "The yields should be considered with caution": but no yields are reported for GC!!

Lines 438-439: already said in lines 434-437.

Figure 6: (a) and (b) look almost exactly the same while they are reported to be "33DMbutanone + Cl atoms (a) in the absence of NO and FI mode, (b) in the presence of NO"? How can you say that "(a) present more peaks than ... (b)" (line 446)?

Line 447: "This indicates that the presence of NO influences the reaction mechanism.": this is true but not very new...

Line 456: "In some cases": which cases?

Line 483: "can see that": no subject in the sentence

Lines 484-485: not consistent: "the reaction products generated is different" and "similar compounds seem to be formed"