**Response to the anonymous referee #2**

In the following, the referee's comments (RC) are reproduced (black) along with our replies AC (blue) and changes made to the text (red) in the revised manuscript.

**Title: Atmospheric fate of a series of Methyl Saturated Alcohols (MSA): Kinetic and Mechanistic study**

**General comments:** This paper reports the experimental studies on the reactions of Cl atoms, OH radicals and NO3 with MSA using Relative rate method using FTIR and GC-TOFMS as analytical tools. They have carried out the product analysis at room temperature in presence of synthetic air and reported the products obtained for the title reactions.

**RC**

**Recommendation: This work is good and carried out systematically but, of routine nature not suitable to ACP and can be published in more specific journals related to kinetics. However, the authors may consider the following suggestion to improve the quality of the Paper, if they wish to submit to another specific journal.**

AC:

The authors, before deciding to send the work to the ACP, have evaluated if the work could be framed within any of the themes of the journal finding that the work is effectively framed in the thematic areas and activities presented in this journal:

-Subject area: gases. Effectively, our work focuses on gas phase reactions

-Research activity: Laboratory study. Our study is an experimental work carried out in the laboratory.

-Altitude range. The studied reactions have an interest at the troposphere level since the compounds under study are emitted to the troposphere by different processes, and taking into account the possible future use of these compounds as additives to the fuels, this use could cause significant troposphere emissions.

-Sciences focus. Our work corresponds clearly to the field of the Chemistry.

Therefore, we consider that our work is perfectly publishable in the ACP. It presents the first study of reaction products with proposals of reaction mechanisms that provides a valuable information on the reactivity in the troposphere of compounds of atmospheric interest such as are the alcohols. Alcohols are being object of study by the scientific community and our work provides the first data about the atmospheric reactivity of a series of alcohols that in a future could be used as fuel. Furthermore, our work helps to the scientific community in particular and to the society in general to understand the behavior and implications of alcohols in the atmosphere. The authors know that there are other journals where this work can be published but we consider that ACP is the best for two reasons mainly:

1-This journal allows more extensive works than others, since it does not limit the number of pages. In our case, this fact is important since the work involves discussing a lot of experimental results.

2-It is a journal of wide diffusion in the environmental field with open access and not exclusive of kinetics. The publication of our work in a specific journal of kinetic would imply that

diffusion of our results was more restricted.

**Major issues regarding the manuscripts:**

**1-RC:** The manuscript is difficult to read and understand, confusing in many places, careful reading should be done throughout.

**AC:** The manuscript has been reread. Some sentences or paragraphs in the kinetic discussion section have been rewritten in order to better understand of work presented. All modifications have been indicated in the new version of manuscript.

**2-RC:** In the abstract, "$(2.70 \pm 0.55) \times 10^{-10}$ and $(5.57 \pm 0.66) \times 10^{-12}$ for reaction of 3,3-dimethyl- 1-butanol with Cl and OH radical respectively and $(1.21 \pm 0.37) \times 10^{-10}$ and $(10.51 \pm 0.81) \times 10^{-12}$ for reaction of 3,3-dimethyl-2-butanol with Cl and OH radical respectively". – sentence should be rewritten.

**AC**: This sentence been rewritten. We have added the following text:

"Rate coefficients (in $cm^3$ $molecule^{-1}$ $s^{-1}$ unit) measured at ~ 298 K and atmospheric pressure (720 ± 20 Torr) were as follows: $k_1$ (E-4-methyl-cyclohexanol + Cl) = $(3.70 \pm 0.16) \times 10^{-10}$, $k_2$ (E-4-methyl-cyclohexanol + OH) = $(1.87 \pm 0.14) \times 10^{-11}$, $k_3$ (E-4-methyl-cyclohexanol + $NO_3$) = $(2.69 \pm 0.37) \times 10^{-15}$, $k_4$ (3,3-dimethyl-1-butanol + Cl) = $(2.69 \pm 0.16) \times 10^{-10}$, $k_5$ (3,3-dimethyl-1-butanol + OH) = $(5.33 \pm 0.16) \times 10^{-12}$, $k_6$ (3,3-dimethyl-2-butanol + Cl) = $(1.21 \pm 0.07) \times 10^{-10}$ and $k_7$ (3,3-dimethyl-2-butanol + OH) = $(10.50 \pm 0.25) \times 10^{-12}$ "

**3-RC**: In page nº.2; "Therefore, previously to the massive use, it is necessary to study the reactivity of the large alcohols in atmospheric conditions, in order to establish and to evaluate their atmospheric impact". – the atmospheric conditions may vary depends upon the altitude hence temperature dependent and pressure dependent studies need to be done in order to get the complete atmospheric impact.

**AC:** We agree with the referee that reactions must be evaluated in the temperature range typical of the Troposphere, but it is not possible in our case because our experimental system does not allow us to work at different temperatures. We are working in a modification of the reactors to do these experiments in a near future. In the case of the effect of pressure on rate coefficients, the literature data about kinetic studies of this kind of reactions, show not significant influence on the rate coefficients, in the typical range of atmospheric pressure. Kinetic studies about Oxygenated Volatile Organic Compounds in which it is used absolute method (that works in different ranges of pressures) and relative method (that works at atmospheric pressure) the rate coefficients obtained are similar taking into account the experimental errors. For this reason, the most of the reactions of atmospheric interest are evaluated only at atmospheric pressure (https://kinetics.nist.gov/kinetics/index.jsp).

The authors with this phrase, do not mean that with our results the atmospheric implications of alcohols are perfectly established, but help to establish these implications. The authors know that more experiments should be carried out to obtain a complete knowledge of the atmospheric implications of these alcohols, as indicated in the conclusion section. A phrase indicating the need to perform the kinetic study at typical atmospheric temperatures in order to obtain more

information of the reaction mechanism and can extrapolate the data of rate coefficients to other typical atmospheric conditions, could be added in the conclusion section.

"...However, kinetic experiments in the tropospheric temperature range are necessary to obtain more information about the reaction mechanism and extrapolate the data of rate coefficients to other typical atmospheric conditions and thus be able to better establish the atmospheric impact of the alcohols."

**4-RC:** What are the limits for photolysis and wall effect limits? Is there any preliminary reaction carried out to check secondary chemistry for the title reactions? Explain.

**AC**: As it is indicated in the main text (kinetic study section), previous to the kinetic study, it is habitual to carry out a series of experiments in order to establish the possible secondary reactions. In the case of MSA, the next experiments were done.

-Checking dark reactions of MSA together with the reference compounds.

-Checking the reaction of MSA and refence compounds with $Cl_2$, $CH_3ONO$, NO and $NO_2$.

-Checking the photolysis of MSA and reference compounds.

In all cases, these experiments showed insignificant loss processes of reactants.

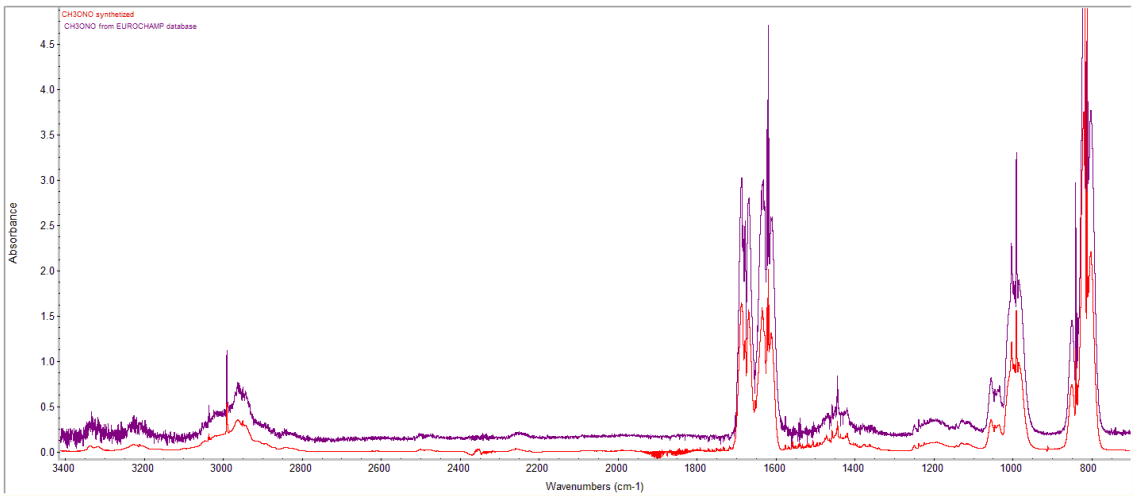
**5 RC**: Page 4, "Kinetic measurements were performed at room temperature 298 K) and atmospheric pressure ~ (720 Torr)" – Authors have stated the pressure at which the reactions were carried out is 720 Torr throughout the main text but, in the abstract it is stated as 740 Torr. It is advised to check the values.

**AC:** The experiments on Teflon® reactor were done at atmospheric pressure that each day could variated between 700 and 710 Torr. The experiments on Pyrex® reactor were done at pressure between 710 and 740 Torr. In the new version of the manuscript, all data of pressure have been changed by 720 ± 20 Torr.

**6 RC**: CH3ONO was synthesized in the laboratory – give the procedure and specify the purity of the prepared compound with NMR, IR etc.

**AC:** The procedure of synthesis of $CH_3ONO$ is the same that the described by Taylor et al 1980 and we consider that it is not necessary to give details of the synthesis procedure in order to not extent more the manuscript. When the $CH_3ONO$ is synthetized, an IR spectrum is done and it is compared with the $CH_3ONO$ reference spectrum of database. In all cases a high purity is observed.

An example of IR spectrum of $CH_3ONO$ synthetized and reference spectrum from Eurochamp 2020 database (https://data.eurochamp.org/data-access/ir-spectra/) is showed in the figure above.




**7-RC:** Page 5, "During the reaction process in the 50 L Pyrex® glass chamber, the identification of products was made using the FTIR analysis but, at the same time, a sample was taken and analyzed in the SPME/GC-TOFMS system". - is quite confusing and should be rephrased for better understanding for the readers.

**AC:** This sentence will be rewritten.

"In some experiments carried out in the 50 L Pyrex® reactor, a simultaneous identification of products was performed using both detection techniques. For that, one sample of mixing reaction was taken from this reactor using the SPME and subsequent analyzed with GC-TOFMS"

**8 RC**: Page 5, "To obtain the yield percentage of carbon, the yield obtained is multiplied by 100 and by the ratio of carbons between the product and the MSA from which it comes".

– not clear.

**AC**: This sentence will be removed in the new version of manuscript and a footnote in the table 6 will be included indicating how the total carbon has been calculated.

$$Total\ Carbon\ (\%) = \sum_{1}^{i} \left( \frac{nº\ of\ carbon\ of\ product_i}{nº\ of\ carbon\ of\ MSA} \times molar\ yield_i(\%) \right)$$

**9-RC**: Authors are advised to use the recommended rate coefficients for all the reference reactions for better reliability of the rate coefficients.

**AC:** The authors know that is convenient to use the recommended rate coefficients for all the reference compounds, but in some cases it was not possible to use reference compounds with a recommended rate coefficient, because their IR bands overlapped with the IR bands of MSA or because there was no other reference compound with rate coefficients similar to the MSA. So we had to use reference compounds whose rate coefficients were well established but not as well as recommended compounds. In order to assure the rate coefficients determined, different reference compounds were used.

**10-RC:** Page 7, "This behavior could be explained for the different size and electronic properties of each oxidant that make the Cl atom the most reactive (value of k in the limit of collision) but also less selective than OH and NO3 radicals". – needs more explanation.

AC: More explanation has been included in the manuscript.

"This behavior could be explained considering the geometry and the electronic density of each oxidant, together with the kinetic Collision Theory. As Cl atom has spherical distribution of its density, for the collision any orientation is adequate, in addition the Cl atoms presents less steric hindrance. Then, comparatively the Cl reaction is less selective and faster with values for the rate coefficients, k, in the collision limit. However, the OH radical presents an asymmetric electron density located mostly over its oxygen atom. Therefore, for the OH reaction the oxygen of OH radical, must be specific oriented to the hydrogen of the MSA that will be abstracted. The electronic density of nitrate radical is distributed around the three oxygens which implies several appropriate orientations. However, as the nitrate radical has a non-linear structure, the steric hindrance is much bigger than for the OH and it reduces the reactivity of $NO_3$ in relation to those of OH radical."

**11-RC:** Page 7, "In the case of 3,3-dimethylbutanols, there is…… of the structure of the organic compound on the reactivity (SAR Method, Kwok and Atkinson, 1995)". -Rewrite the sentence.

**AC:** Taking in account your suggestion and the suggestion of referee #1, this part of the kinetic discussion has been rewritten in order to more clarity. In the new version of manuscript, the next sentences appear:

"The activating effect of hydroxyl group of the alcohols was quantified by different authors (Kwok and Atkinson 1995; Kerdouci et al, 2010, Calvert et al. 2011) taking into account the available kinetic data reported in bibliography, obtaining the factor of reactivity for the hydroxyl group, F(-OH)). This factor of reactivity is different for each oxidant, 1.18 for Cl reaction, 2.35 for reaction with OH (Calvert et al. 2011) and 18 for $NO_3$ reaction (Kerdouci et al., 2010). There are no data of rate coefficients for the reactions of the homologous alkanes of the MSA studied in this work with $NO_3$ radical, and therefore it is not possible to check out the effect of hydroxyl group in the reactivity of $NO_3$ reaction. However, according to the factor of reactivity obtained by Kerdouci et al. (2010) for the reactions of alcohols with $NO_3$, this effect is higher than the corresponding to Cl and OH reactions."

**12-RC**: Page 7, "The activating effect of the length chain in the reactivity is being more marked in the Cl reaction than in the case of OH and NO3 reactions". Why? Proper explanation should be given. Sentence is very confusing.

**AC:** To clarify, this sentence will be rewritten as follows:

"The activating effect of the length chain in the reactivity of alcohols is more evident in Cl reactions than OH reactions (See Table S1). Furthermore, if the rate coefficients of 3-methyl-1-butanol (3M1ButOH) and 3,3DM1ButOH with Cl and OH reactions are compared, it can be observed a slight increase of rate coefficient for Cl reaction ($k_{3M1BuOH+Cl}$ = 25.0 × $10^{-11}$; $k_{3,3DM1ButOH+Cl}$ = 26.9 × $10^{-11}$) and an important decrease of the rate coefficient for OH reactions ($k_{3M1BuOH+OH}$ = 14 × $10^{-12}$; $k_{3,3DM1ButOH+OH}$ = 5.33 × $10^{-12}$). This behavior could be explained by the different order of reactivity between the oxidants. For Cl atom, more reactive (k order of $10^{-}$

$^{10}$ $cm^3$ $molecule^{-1}$ $s^{-1}$) but less selective, an increase of the length chain or in the number of methyl groups implies more hydrogens available to be abstracted and therefore an increase of the rate coefficient. However, for OH radicals, less reactive and more selective, the attack for H-abstraction will be carried out in a specific place, so an increase of the chain has not a significative effect to the reactivity, even the presence of a second methyl group disfavor the reaction probably due to the steric hindrance near to the attack position."

**13-RC**: Page 8, "In general, the SAR method applied to alcohols predicts better rate coefficients for Cl atoms and OH radical than for NO3 radical, especially for primary alcohols". – But the value of the kexp/kSAR for the reaction of 3,3DM1ButOH with NO3 is found out to be 3.29. Please give the explanation for this discrepancy.

**AC:** As it is indicated in the section of reaction product study, the reason of the discrepancy could be the fact that the SAR method developed for $NO_3$ reaction by Kerdouci et al. does not consider the effect of the factor -$CH_2$-OH in the reactivity. Moreover, the authors of this SAR method (Kerdouci et al. 2010, 2014) indicate the smaller predictive ability of this SAR method for saturated alcohols with $NO_3$ due to the lack of experimental data.

**14-RC**: Page 8, "….and in some cases due to heterogeneous reactions with the walls of the gas cell". – contradicting statement - check the experimental method given!

AC: In this case the heterogeneous reactions, it refers to reactions of the precursors with the Pyrex walls of gas cell. In the text an annotation will be included. It is the following:

"..and in some cases are due to heterogeneous reactions of these precursors with the walls of the gas cell'

**15-RC:** Page 10, why no exploration on OH + NO and NO2 + NO3??

AC: We don't understand exactly what you mean with this question. Our experimental procedure does not allow us to carry out experiments in absence of NO in the case of OH reactions and in absence of $NO_2$ in the case of $NO_3$ reaction.

**16-RC:** "The kinetic and product study confirms that the atmospheric degradation mechanism 1 for methyl saturated alcohols and possibly for the rest of unstudied saturated alcohols, proceeds mainly by abstraction of the hydrogen atom bonded to carbon instead hydrogen atoms bonded to oxygen atom of the alcohol group". – This is a known fact and should be removed from the conclusion.

AC: This assumption has been included in the document because we would like to remark that effectively our results support, confirm, the general reactivity of alcohols.

In the new version of manuscript, the first and second conclusions have been reorganized as follows.

"The kinetic and product study support that: 1 -The atmospheric degradation mechanism for MSA, and possibly for the rest of unstudied saturated alcohols, proceeds by abstraction of the hydrogen atom bonded to a carbon instead of hydrogen atoms bonded to the oxygen atom of the alcohol group. 2 -The reaction mechanism in the H-abstraction process depends on the oxidant.

Chlorine atoms abstract any type of alkyl hydrogen from saturated alcohols with a high percentage, compared to the hydroxyl radical and the nitrate radical. OH and $NO_3$ radicals abstract mainly the hydrogen in the α position, if the saturated alcohols are secondary. For primary alcohols, the abstraction of a hydrogen in β position could be also important in the reaction with $NO_3$ radical. Therefore, more kinetic studies for $NO_3$ radical with primary alcohols are necessary to update the SAR method developed by Kerdouci et al., and to quantify the effect of the OH group in β position, ($-CH_2OH$)."

However, if the reviewers consider this sentence unnecessary could be eliminated of the conclusions.

**17-RC**: Main text and Table 2 values – The given reasons are different. Please clarify.
AC: The main text and table 2 have been checked. This table has been modified as the referee #1 suggests. In the new version of manuscript this section has been modified.

"…The estimated rate coefficients, $k_{log}$, according with Eq (2) and Eq (3), and the ratios ($k_{exp}/k_{log}$), are also shown in Table 2. This estimation method obtains slightly better rate coefficient for 3,3DM1ButOH + $NO_3$ reaction ($k_{exp}/k_{log}$. = 1.53) than SAR ($k_{exp}/k_{SAR}$ = 3.24). However, for Cl reactions the ratios $k_{exp}/k_{log}$ are in the range of 0.6-1.97, indicating that the Eq (2) predicts worse the rate coefficients than SAR method. Again, this fact could be due to the different mechanism reaction in the H-abstraction process for Cl and OH reactions. Such as it has been indicated above to apply these relationships both oxidants must react according to the same mechanism...."

**18-RC**: Since 2-butanol is not a suitable reference authors could have been chosen another reference for their studies.
AC: We suppose that you want to say 1-butanol.
As it has been explained above in question 9, it is difficult to find reference compounds with the necessary characteristic to be used in these experiments.

**19-RC:** In Table 1, it seems like authors have taken the average of deviation values obtained in individual rate coefficients (column 4). It is advised to carry out the proper analysis of the errors by standard error propagation method. (For reference see *Chem. Phys. Lett*. 2013, 590, 221-226 and *New J. Chem*. 2017, 41, 7491-7505).
AC: By suggestion of referee #1 the data of Table 1 have been revised. The analysis of data have been done as it is explained in the main text and footnote of Table 1 of the new manuscript version.

"The ratios of the rate coefficients, $k_{MSA}/k_R$, the absolute rate coefficients and the weighted average are shown in Table 1. The error of $k_{MSA}/k_R$ are given by 2 times the statistical deviation calculated from the least-square fit of the plot of Eq. (1). The uncertainties for rate coefficients of MSA ($\sigma_{kMSA}$) were calculated from the uncertainty of slope of plots ($\sigma_{slope}$) and the uncertainty of the reference ($\sigma_{kR}$) by using the propagation of uncertainties. The average value of the rate coefficient obtained with different reference compounds and its associated error were obtained by weighted average."

**20-RC**: Why the effect of the bath gas on the rate coefficients were not explored?

AC: The effect of the bath gas on the rate coefficients were explored in a previous study (Cabañas et al. 2005). The results of the rate coefficients in $N_2$ and air where similar, considering the experimental error. So, we always use $N_2$ as bath gas (except to the OH reaction because it is necessary $O_2$ to generate the OH) because it is less expensive than air.