

**Manuscript Number: ACP-2019-662**

**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 NO<sub>3</sub> 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.

**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.**

**Major issues regarding the manuscripts:**

1. The manuscript is difficult to read and understand, confusing in many places, careful reading should be done throughout.
2. 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.
3. 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.

4. 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.
5. 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.
6. CH<sub>3</sub>ONO was synthesized in the laboratory – give the procedure and specify the purity of the prepared compound with NMR, IR etc.
7. 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.
8. Page 5, “To obtain the yield in 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.
9. Authors are advised to use the recommended rate coefficients for all the reference reactions for better reliability of the rate coefficients.
10. 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 NO<sub>3</sub> radicals”. – needs more explanation.
11. 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.

12. 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 NO<sub>3</sub> reactions”. Why? Proper explanation should be given. Sentence is very confusing.
13. Page 8, “In general, the SAR method applied to alcohols predicts better rate coefficients for Cl atoms and OH radical than for NO<sub>3</sub> radical, especially for primary alcohols”. – But the value of the  $k_{\text{exp}}/k_{\text{SAR}}$  for the reaction of 3,3DM1ButOH with NO<sub>3</sub> is found out to be 3.29. Please give the explanation for this discrepancy.
14. Page 8, “...and in some cases due to heterogeneous reactions with the walls of the gas cell”. – contradicting statement - check the experimental method given!
15. Page 10, why no exploration on OH + NO and NO<sub>2</sub> + NO<sub>3</sub>??
16. “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.
17. Main text and Table 2 values – The given reasons are different. Please clarify.
18. Since 2-butanol is not a suitable reference authors could have been chosen another reference for their studies.
19. 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).
20. Why the effect of the bath gas on the rate coefficients were not explored?