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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Atmospheric fate of a series of Methyl Saturated Alcohols (MSA): Kinetic and Mechanistic study" *by* Inmaculada Colmenar et al.

Inmaculada Colmenar et al.

mariapilar.martin@uclm.es

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RC: Colmenar et al. have presented in this paper an extensive study of the atmospheric chemistry of some long-chain saturated alcohols. The manuscript contains kinetic studies involving relative rate method as well as reaction product analysis for reaction with the main atmospheric oxidants. These long-chain alcohols might have potential future use in biofuels and therefore it is essential to understand the atmospheric fate of these chemicals in advance. The material of this manuscript is relevant for publication in ACP although there are scopes for improvement in terms of presentation of data and explanation of results in certain areas of the current version of the manuscript. The

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quality of some data is questionable and there are several typographical errors. Therefore, I recommend publishing this paper in ACP after revision considering the following issues listed below. AC: We thank the referee for the interest shown on our work and the comments and suggestions. Specific comments:

RC: (i) Sec. 2.1 Kinetic experiments: The description of the experimental details for relative kinetic measurements involving FTIR is inadequate and some points are not clear. Is it an in situ or an ex-situ experiment? Is the White optics located inside the reaction chamber? If White absorption cell is a different cell then was there a facility for circulation of reaction mixture between the reaction chamber and the absorption cell? Are the actinic lamps located inside or outside of the reactor? I would recommend providing a schematic diagram of the whole set-up which will clarify all these issues. This would be extremely helpful for the readers to visualize and understand the whole setup. AC: Due to extensive number of results presented in this article, the authors have considered to omit certain aspects related to the description of the experimental system and procedure, since all this information is widely described in previous works of our research group (Tapia et al 2011. https://doi.org/10.5194/acp-11-3227-2011; Martin et al. 2013. https://doi.org/10.1016/j.atmosenv.2013.01.041). We suggest consulting these references for more information. However, and according with the your comment we have decided to extent the description of the experimental system in the manuscript AC: In the case of the methods of estimation rate coefficients. A brief explanation of the SAR method together with the calculations developed to estimate rate coefficients will be included in the supplementary material.

RC:(ii) Kinetic study: All the terms used in Table 1 should be described in this section (P 6, L 17, after the introduction of Table 1). AC: Table 1 has been modified. See comment to the question (x). In addition, the following description that shows how errors have been calculated will be included in the main text. “The ratios of the rate coefficients, kMSA/kR, the absolute rate coefficients and the weighted average are shown in Table 1. The error of kMSA/kR are given by 2 times the statistical deviation calculated from

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the least-square fit of the plot of Eq. (1). The uncertainties for rate coefficients of MSA (sigmakMSA) were calculated from the uncertainty of slope of plots (ïĄşslope) and the uncertainty of the reference (sigmakR) 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."

RC: (iii) P 7, L 13: "the factor of hydroxyl: : :" – define this factor. AC: P7 the lines 12 and 13 where appears "the factor of hydroxyl: : :" have been rewritten for more clarity. "SAR method has quantified this effect for each functional group of an organic compound establishing a series of factor of reactivity (F(X)) (See A1 supplementary material). In the case of.."

RC:(iv) P 7, L 23 – 27: this portion is not clear. Please explain. AC: This paragraph has been rewritten for more clarity. "As can be seen in Table S1, in the case of the Cl atoms reactions, the rate coefficients for primary alcohols (1-propanol, 1-butanol, 1-pentanol, 3-methyl-1-butanol and 3,3-dimethyl-1-butanol), are higher than the ones of the secondary alcohols (2-propanol, 2-butanol, 2-pentanol, 3-methyl-2-butanol and 3,3-dimethyl-2-butanol). This fact could be due to the more quantity of hydrogens activated in alfa position, while in the case of OH and NO3 radicals seems to be more important the formation of the most stable radical than the number of hydrogen in alfa position."

RC: (v) Sec 3.1.1 Estimation of rate coefficients: The title for this section should be modified. The method used for the estimation of rate coefficient should be mentioned in the title. AC: We have considered that it should be a generic title and not particularize, due to the fact that the estimation has been done using two different methods.

RC:(vi) P 7, L 39: When you first introduce SAR, write its full form. Also, since a lot of discussions has been made on SAR, it would be helpful to briefly describe the basics of SAR method in this section. AC: It is true that the first time SAR appears, it must be indicated to which the acronyms correspond. This will be corrected. An explication will be made in supplementary information (S1) in order to not do more extensive the

manuscript.

RC: (vii) P 9, L 27-28: All the IR bands mentioned here are not labelled in Fig. S2. Also, the font size for the labels is too small. AC: All IR bands mentioned in the main text (P9, Line 27-28) are labelled in the different spectra of Fig. S2. (Fig. S3 in the next version of supplementary materials) We have found an error of IR bands, P9 line 28, appears 1260 cm-1 but must be aprox 1660 cm-1. This IR band is labelled in Fig. S2 in the green spectrum (1652.7 cm-1). The size of the labels will be increased in the next version of the manuscript.

RC:(viii) P 10, L 8: "It should be noted that these data should be taken with caution, since they could imply many sources of error" – Please discuss all possible sources of error. AC: The two experimental systems used involve different sources of error: -Errors in the process of introducing the reagents into the gas cell or Teflon bags, (by dragging the compound into a carrier gas stream). -Error in measuring the amount of sample when injected with a micro syringe. -In the case of the experiments carried out in the FTIR, the fact that the reagents and products have similar absorption bands makes the subtraction process difficult to perform. In addition small variations in the subtraction factor can have a lot of influence on the yields of the reaction products. -In the SPME-GCTOFMS system there are systematic errors in the sampling process by the operator (off-line process). Furthermore, all the compounds present in the reaction mixture (reagents and products) compete differently for adsorbing on the fiber.

RC:(ix) P 10, L 21-24: The large difference between the yields of E-4-methylcyclohexanone obtained using the SPME/GC-TOFMS and FTIR is surprising. The authors argued that the difference in reactor volume could be the reason behind. This is not clear to me. Please explain in details. AC:We consider that the difference in yields is due to the procedure used in the different reactors for the study of the reactions with the nitrate radical. In the case of the experiments in the Teflon reactor, the volume of 150 L allows us to make small additions of the precursor (N2O5) until the final concentration indicated in Table 3. Consequently, when small precursor

amounts are added, the concentration of inorganic nitrated compounds (NO3, NO2, HNO3) in the reaction mixture is smaller than doing only one addition in excess, which is what is done in the Pyrex glass reactor, where since the initial time of reaction, there are high concentrations of these nitrated compounds. In this way, the formation of nitrated organic compounds (confirmed in the FTIR experiments) is being favoured in the 50 L reactor versus the formation of 4-methylcyclohexanone. In the new version of manuscript the paragraph of P10 lines 22-26 has been modified. "...could be due to the different way to add the precursor in both reactors (small aliquots of N2O5 in the Teflon® gas bag of 150L versus only one large addition in the Pyrex® glass gas cell). This procedure causes a lower initial concentration of inorganic species nitrated (NO3, NO2, HNO3) in reactor of 150 L than in reactor of 50 L, favouring the formation of carbonyl compounds instead of nitrated organic compounds"

RC:(x) Table 1: The terms used in the table are not described either in the main text or in the legend of the table. What are the quantities listed in column 4 and 5? The values listed in Column 4 appear to be average of the values presented in Column 3, yet the same notation for the two columns was used. The uncertainties for some values are extremely high (sometimes close to 50 % !!) which is unacceptable. A detailed discussion on the possible sources and high values of the uncertainties should be presented in the text. AC:The data in table 1 have been reviewed (Table 1 attached in supplemet). Absolute constants and their errors have been recalculated. It was found that in certain cases different criteria had been applied in the process of defining errors (sigma or 2sigma) and a mistake was also found when applying the error propagation formula. Thus, table 1 has been modified. A column has been included with the data of the relative rate coefficients and their errors (2sigma, standard deviation of the linear adjustment by least squares) and we have decided to leave only one column with the average value of absolute rate coefficient, calculated using the weighted arithmetic mean. Thus it can be verified that the experimental data (kMSA/kR) do not show large deviations. The errors of the absolute rate coefficients have been obtained

taking into account the errors associated with the reference rate coefficients and the slope using the propagation of errors. For that reason, those data obtained using a reference rate coefficient with large error show larger uncertainties. On the other hand, it is important to indicate that it is usual to find similar error values in the field of gas phase radical atmospheric chemistry, especially when the method used is the relative one. https://kinetics.nist.gov/kinetics/index.jsp Likewise, all terms presented in the table have been described in the legend.

RC:(xi) Table 6: Total C balance for some reactions (particularly for Cl reactions) is extremely low. Please explain. AC:Table 6 has been revised and it has been observed that there were some erroneous data in the calculation of the carbon balance, although it is practically similar to the initial one. The very low values of the total balance of C are explained because, as observed in the residual spectra, after eliminating all known compound bands, there are still absorption bands of compounds that couldn't be identify or quantify, since they are not commercial. These compounds could correspond to the hydroxycarbonyls and dialcohols compounds shown in the different reaction schemes.

RC:Technical issues: The language in some parts of the manuscript could be improved. I've noticed some typos and other technical issues throughout the manuscript which are listed below. I have not thoroughly checked for technical issues in supplementary material and I'd request the authors to review this section again. (i) Title: Some words of the title are written in title case while other words are not. Consistency should be maintained. (ii) Abstract: P1 L13 – is the full stop at the end of this line valid? It looks like the sentence is continuing in the next line. P1, L20: when you first introduce HCOH, write its full chemical name. (iii) P2, L25: Change "Others" to "Other". (iv) P3, L23: the rate coefficient for the reaction with MSA is termed as kS here while in equation (1) it is termed as kMSA. Please, correct. Also, define kS and kR here. (v) P4, L5: equation (1) is written in Roman (I). Please change. (vi) P4, L5: 1st and 2nd brackets are wrongly placed for both the terms. (vii) In many

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places, hydrogen “subtraction” is written instead of “abstraction”. (viii) P6, L30: add “for MSA” after “: : : NO3 are higher”. (ix) P7, L2: write the full word “molecule”, not the abbreviation “molec” in the unit. (x) P7, L10: change “not” to “no”. (xi) P8, L1: “develop” can be changed to “developed”. (xii) P8, L19-20: check Units. (xiii) P8, L23-24: These values could be included in Table 2. (xiv) P8, L36: “Bands that are due: : :” – sentence is incomplete. (xv) P9, L15: “of Fig. 3” can be changed to “in Fig. 3”. (xvi) P11, L4 (and in other places): “stablish” can be replaced by “establish”. (xvii) P14, L22: change “MSA have not a” to “MSA do not have a”. (xviii) Table 2: “Ratio” – “R” is capital in one place and small in the other two places. (xviv) Fig.1 B): Left axis – correct problem with 1st and 3rd brackets. (xvv) Fig2. Title: change “4-methylcyclohexanona” to “4-methylcyclohexanone”. (xvvi) Fig3. Picture quality is poor. Axis fonts are not readable. (xvvii) Fig.4: the unit of x-axis missing. Describe the terms used in both the axis. (xviii) Fig7 & 8: the dot sign of radical is missing in some places. AC:All suggestions indicated in technical issues will be taken into account and modified in the manuscript.

Please also note the supplement to this comment:
https://www.atmos-chem-phys-discuss.net/acp-2019-662/acp-2019-662-AC1-supplement.pdf

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