

Response to the anonymous referee #1

Taking in account the comments of referee#2 some modifications have been realized with respect the first replies. So, the authors have been considered submit again the author comments to the referee #1

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.

comment of Anonymous Referee #1

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 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 to your comment we have decided to extent the description of the experimental system in the manuscript

“The experimental systems are described in previous works (Tapia et al 2011, Martin et al. 2013) and only a brief description is shown here. Kinetic measurements were performed at room temperature (~ 298 K) and atmospheric pressure (720 ± 20 Torr) by employing two separated experimental set-ups: 1) -A FTIR system formed by 50 L Pyrex[®] glass reactor couple to the Fourier Transform Infrared Radiation spectrometer as a detection technique (“on line” analysis). Inside of Pyrex[®] glass reactor there is a multi-reflexion system with three mirrors that allows an infrared radiation path of 2.8-200 meters. This reactor is known as white cell (Saturn Series Multi-Pass cell). The FTIR spectrometer (Thermo Nicolet 6700) is equipped with a KBr beam

splitter and liquid nitrogen-cooled MCT. Typically, for each spectrum, 60 interferograms were co-added over 98 s and approximately 30-40 spectra were recorded per experiment with a spectral resolution of 1 cm⁻¹. 2) -Teflon[®] gas bag reactor of 500 L with Solid Phase Micro Extraction fiber (SPME) as a pre-concentration sample method, followed by analysis on a Gas Chromatography-Mass Spectrometry system with a Time of Flight analyzer (SPME/GC-TOFMS) (AccuTOF GCv, Jeol) (“off line” analysis). Samples were collected by exposing a 50/30 mm DVB/CAR/PDMS Solid Phase Micro Extraction fiber (SPME, SUPELCO) for 5 min during the reaction and then thermally desorbed for 15 min at 250 °C in the heated GC injection port. A capillary column (30 m × 0.3 mm id × 1.0 mm film thickness, Tracsil TRB-1701, Teknokroma) was used to separate the compounds. The chromatographic conditions used for the analysis were as follows: injector, 250 °C; interface, 250 °C; oven initial temperature, 40 °C for 4 min; ramp, 30 °C min⁻¹ to 120 °C, held for 6 min; second ramp, 30 °C min⁻¹ to 200 °C, held for 3 min.

In each independent experiment, the reactants are injected into the reactors from a vacuum line by dragging with a stream of carrier gas used in the reaction. Both reactors are inside of a metallic housing in which walls there is a rack of actinic lamps (Philips, TL-40W, Actinic BL, λ_{max} = 360 nm). A scheme of the experimental systems is shown in Fig. S1 of supplementary material.

The kinetic experiments, for the Cl and OH reactions, were performed FTIR system. A spectral subtraction procedure was used to derive the concentrations of reactant and reference compounds at time t=0 and time t. The reaction of NO₃ with 4MCHexOH was studied using a Teflon[®] reactor of 500 L in order to minimize the wall deposition and dilution effects of consecutive additions of N₂O₅. Chlorine atoms and OH radicals were obtained by photolysis of Cl₂ in N₂ and methyl nitrite in the presence of NO in air. Methyl nitrite, CH₃ONO, was synthesized in the laboratory as described elsewhere (Taylor et al., 1980).”

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 have been 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 have been included in the main text.

“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 ($\sigma_{k_{MSA}}$) were calculated from the uncertainty of slope of plots (σ_{slope}) and the uncertainty of the reference (σ_{k_R}) 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: Taking in account your suggestion and the suggestion of referee #2, this part of the kinetic discussion has been rewritten/reorganized 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 NO₃ 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 NO₃ radical, and therefore it is not possible to check out the effect of hydroxyl group in the reactivity of NO₃ reaction. However, according to the factor of reactivity obtained by Kerdouci et al. (2010) for the reactions of alcohols with NO₃, this effect is higher than the corresponding to Cl and OH reactions.”

RC: (iv) P 7, L 23 – 27: this portion is not clear. Please explain.

AC: Taking in account your suggestions and the suggestions of referee #2, the kinetic discussion section has been rewritten in order to more clarity. In the new version of manuscript, the next sentence appear:

“In addition, as can be seen in Table S1, the position of hydroxyl group has a different effect depending on the oxidant. In the case of the Cl atom 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) contrary to the OH and NO₃ radical reactions. This fact indicates that in the reaction of Cl atoms the formation of the most stable radical seems to have less importance in the reactivity than the number of hydrogens in α position available to be abstracted.”

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 (S2) 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 new version of supplementary materials). We have found an error of IR bands, P9 line 28, appears 1260 cm⁻¹ but must be ~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 new 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 molecular 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 molecular 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 (N_2O_5) until the final concentration indicated in Table 3. Consequently, when small precursor amounts are added, the concentration of inorganic nitrated compounds (NO_3 , NO_2 , HNO_3) 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 favored in the 50 L reactor versus the formation of 4-methylcyclohexanone.

In the new version of manuscript the next paragraph is included.

“...could be due to the different way to add the precursor in both reactors (small aliquots of N_2O_5 in the Teflon® reactor of 150L versus only one large addition in the Pyrex® reactor). This procedure causes a lower initial concentration of nitrated inorganic species (NO_3 , NO_2 , HNO_3) in reactor of 150 L than in reactor of 50 L, favoring 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. Absolute rate coefficients and their errors have been recalculated. It was found that in certain cases different criteria had been applied in the process of defining errors (σ or 2σ) 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 (2σ , 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 (k_{MSA}/k_R) 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.

Table 1. Rate coefficient ratios, absolute rate coefficients and average rate coefficients for the reactions of a series of MSA with Cl atoms and OH and NO₃ radicals at 298 K and ~720 ± 20 Torr of pressure. Rate coefficients, k, in cm³ molecule⁻¹ s⁻¹.

Reaction	Reference	(k _{MSA} /k _R)±2σ	(k _{MSA} ±2σ) ^a /10 ⁻¹⁰	(\bar{k}_{MSA} ±2σ) ^b /10 ⁻¹⁰
3,3DM1ButOH + Cl	1-butene	0.85 ± 0.03	2.89 ± 0.42	2.69 ± 0.16
		0.79 ± 0.02	2.68 ± 0.38	
		0.76 ± 0.02	2.58 ± 0.37	
	Propene	1.18 ± 0.02	2.63 ± 0.37	
		1.21 ± 0.03	2.70 ± 0.38	
		1.22 ± 0.03	2.71 ± 0.38	
3,3DM2ButOH + Cl	1-butene	0.42 ± 0.01	1.42 ± 0.21	1.21 ± 0.07
		0.35 ± 0.01	1.17 ± 0.17	
		0.41 ± 0.01	1.38 ± 0.20	
	Propene	0.48 ± 0.01	1.08 ± 0.15	
		0.50 ± 0.02	1.12 ± 0.16	
		0.56 ± 0.03	1.26 ± 0.19	
4MCHexOH + Cl	2-methylpropene	1.08 ± 0.03	3.69 ± 0.32	3.70 ± 0.16
		1.16 ± 0.02	3.95 ± 0.33	
		0.98 ± 0.05	3.35 ± 0.32	
	1-butene	1.14 ± 0.03	3.86 ± 0.56	
		1.12 ± 0.03	3.78 ± 0.55	
		1.15 ± 0.04	3.90 ± 0.57	
Reaction	Reference	(k _{MSA} /k _R)±2σ	(k _{MSA} ±2σ)/10 ⁻¹²	\bar{k}_{MSA} ±2σ /10 ⁻¹²
3,3DM1BuOH + OH	Isopropanol	1.00 ± 0.04	5.09 ± 0.20	5.33 ± 0.16
		1.13 ± 0.09	5.78 ± 0.47	
		1.12 ± 0.08	5.72 ± 0.40	
	2-methyl-2- Butanol	1.60 ± 0.09	5.78 ± 1.01	
		1.57 ± 0.08	5.65 ± 1.00	
		1.61 ± 0.09	5.79 ± 1.02	
3,3DM2BuOH + OH	Isopropanol	2.33 ± 0.09	11.90 ± 0.48	10.50 ± 0.25
		2.05 ± 0.08	10.50 ± 0.45	
		1.95 ± 0.08	9.95 ± 0.43	
	2-methyl-2- butanol	2.39 ± 0.09	8.61 ± 1.50	
		2.92 ± 0.09	10.50 ± 1.78	
		2.25 ± 0.09	8.12 ± 1.34	
4MCHexOH + OH	Propene	0.64 ± 0.01	17.10 ± 2.59	18.70 ± 1.42
		0.76 ± 0.03	20.30 ± 3.19	
		0.76 ± 0.02	20.40 ± 3.10	
	Cyclohexene	0.27 ± 0.01	18.20 ± 4.55	
		0.27 ± 0.01	18.40 ± 4.62	
		0.27 ± 0.01	18.00 ± 4.46	
Reaction	Reference	(k _{MSA} /k _R)±2σ	(k _{NO3} ±2σ)/10 ⁻¹⁵	\bar{k}_{NO3} ±2σ /10 ⁻¹⁵
4MCHexOH + NO ₃	1-butanol	1.08 ± 0.12	3.39 ± 1.11	2.69 ± 0.37
		1.81 ± 0.15	5.70 ± 1.82	
		0.79 ± 0.07	2.51 ± 0.80	
	2-ethyl-1-hexanol	0.71 ± 0.10	2.08 ± 0.72	
		1.00 ± 0.10	2.93 ± 0.96	
		0.86 ± 0.08	2.52 ± 0.82	

^aThe uncertainties for rate coefficients of MSA (σ_{KMSA}) were calculated from the uncertainty of slope of plots (σ_{slope}) and the uncertainty of the reference (σ_{KR}) by using the propagation of uncertainties. ^bWeighted average according to the equation $(w_1k_1 + w_2k_2 + \dots)/(w_1 + w_2 + \dots)$; ($w_i = 1/\sigma_i^2$). The uncertainty of weighted average (σ) was given by $(1/w_1 + 1/w_2 + \dots)^{-0.5}$

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 ones. The very low values of the total balance of C could be explained because, as it is observed in the residual spectra, after eliminating all bands of the known compounds, 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.

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.

RC:(i) Title: Some words of the title are written in title case while other words are not. Consistency should be maintained.

AC: This has been corrected.

RC:(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.

AC: By suggestion of referee#2 this part of abstract has been modified. In the new version of manuscript, the next sentences appear:

“Rate coefficients (in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ unit) measured at $\sim 298\text{K}$ 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) = $(10.50 \pm 0.25) \times 10^{-12}$.”

RC: P1, L20: when you first introduce HCOH, write its full chemical name.

AC: This has been corrected.

RC: (iii) P2, L25: Change “Others” to “Other”.

AC: This has been corrected.

(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.

AC: This has been corrected.

(v) P4, L5: equation (1) is written in Roman (I). Please change.

AC: This has been corrected.

(vi) P4, L5: 1st and 2nd brackets are wrongly placed for both the terms.

AC: This has been corrected.

(vii) In many places, hydrogen “subtraction” is written instead of “abstraction”.

AC: The text has been revised and we have decided to use the term “subtract” to the analysis procedure of FTIR spectra and “abstract” to indicate the elimination of an hydrogen of MSA by the oxidants.

RC: (viii) P6, L30: add “for MSA” after “: : : NO_3 are higher”.

AC: This has been corrected.

RC: (ix) P7, L2: write the full word “molecule”, not the abbreviation “molec” in the unit.

AC: This has been corrected.

RC: (x) P7, L10: change “not” to “no”.

AC: This has been corrected.

RC:(xi) P8, L1: “develop” can be changed to “developed”.

AC: This has been corrected.

RC: (xii) P8, L19-20: check Units.

AC: The units have been checked

RC: (xiii) P8, L23-24: These values could be included in Table 2.

AC: These values and the ratio of k_{exp}/k_{log} have been included in Table 2 in the new version of the manuscript.

RC: (xiv) P8, L36: “Bands that are due: :” – sentence is incomplete.

AC: This has been corrected.

RC: (xv) P9, L15: “of Fig. 3” can be changed to “in Fig. 3”.

AC: This has been changed.

RC: (xvi) P11, L4 (and in other places): “stablish” can be replaced by “establish”.

AC: All words have been replaced.

RC: (xvii) P14, L22: change “MSA have not a” to “MSA do not have a”.

AC: This has been changed.

RC: (xviii) Table 2: “Ratio” – “R” is capital in one place and small in the other two places.

AC: This has been changed.

RC: (xviii) Fig.1 B): Left axis – correct problem with 1st and 3rd brackets.

AC: This has been corrected.

RC: (xv) Fig2. Title: change “4-methylcyclohexanona” to “4-methylcyclohexanone”.

AC: This has been corrected.

RC: (xvii) Fig3. Picture quality is poor. Axis fonts are not readable.

AC: The Fig.3 has been replaced.

RC: (xviii) Fig.4: the unit of x-axis missing. Describe the terms used in both the axis.

AC: This has been corrected.

RC: (xviii) Fig7 & 8: the dot sign of radical is missing in some places.

AC: The figures 5, 7 and 8 have been checked. All dot signs of the radicals have been included and their size have been increased.