

## 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 ( $\sim 298$  K) and atmospheric pressure ( $720 \pm 20$  Torr) by employing two separated experimental set-ups: 1) -A FTIR system formed by 50 L Pyrex<sup>®</sup> glass reactor couple to the Fourier Transform Infrared Radiation spectrometer as a detection technique (“on line” analysis). Inside of Pyrex<sup>®</sup> 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<sup>-1</sup>. 2) -Teflon<sup>®</sup> 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<sup>-1</sup> to 120 °C, held for 6 min; second ramp, 30 °C min<sup>-1</sup> 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<sub>max</sub> = 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 NO<sub>3</sub> with 4MCHexOH was studied using a Teflon<sup>®</sup> reactor of 500 L in order to minimize the wall deposition and dilution effects of consecutive additions of N<sub>2</sub>O<sub>5</sub>. Chlorine atoms and OH radicals were obtained by photolysis of Cl<sub>2</sub> in N<sub>2</sub> and methyl nitrite in the presence of NO in air. Methyl nitrite, CH<sub>3</sub>ONO, 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 ( $\sigma_{slope}$ ) and the uncertainty of the reference ( $\sigma_{k_R}$ ) 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 NO<sub>3</sub> 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<sub>3</sub> radical, and therefore it is not possible to check out the effect of hydroxyl group in the reactivity of NO<sub>3</sub> reaction. However, according to the factor of reactivity obtained by Kerdouci et al. (2010) for the reactions of alcohols with NO<sub>3</sub>, 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 NO<sub>3</sub> 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  $\alpha$  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<sup>-1</sup> but must be ~1660 cm<sup>-1</sup>. This IR band is labelled in Fig. S2 in the green spectrum (1652.7 cm<sup>-1</sup>).

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 ( $\sigma$  or  $2\sigma$ ) 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 ( $2\sigma$ , 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 NO<sub>3</sub> radicals at 298 K and ~720 ± 20 Torr of pressure. Rate coefficients, k, in cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

Reaction	Reference	(k <sub>MSA</sub> /k <sub>R</sub> )±2σ	(k <sub>MSA</sub> ±2σ) <sup>a</sup> /10 <sup>-10</sup>	( $\bar{k}_{MSA}$ ±2σ) <sup>b</sup> /10 <sup>-10</sup>
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 <sub>MSA</sub> /k <sub>R</sub> )±2σ	(k <sub>MSA</sub> ±2σ)/10 <sup>-12</sup>	$\bar{k}_{MSA}$ ±2σ /10 <sup>-12</sup>
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 <sub>MSA</sub> /k <sub>R</sub> )±2σ	(k <sub>NO3</sub> ±2σ)/10 <sup>-15</sup>	$\bar{k}_{NO3}$ ±2σ /10 <sup>-15</sup>
4MCHexOH + NO <sub>3</sub>	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	

<sup>a</sup>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. <sup>b</sup>Weighted 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 ( $\sigma$ ) 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 ( $720 \pm 20$  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 +  $\text{NO}_3$ ) =  $(2.69 \pm 0.37) \times 10^{-15}$ ,  $k_4$  (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 “: : :  $\text{NO}_3$  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.



## 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 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.

#### **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  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  unit) measured at  $\sim 298 \text{ K}$  and atmospheric pressure ( $720 \pm 20 \text{ Torr}$ ) 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 +  $\text{NO}_3$ ) =  $(2.69 \pm 0.37) \times 10^{-15}$ ,  $k_4$  (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 n°.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 reference compounds with Cl<sub>2</sub>, CH<sub>3</sub>ONO, NO and NO<sub>2</sub>.

-Checking the photolysis of MSA and reference compounds.

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

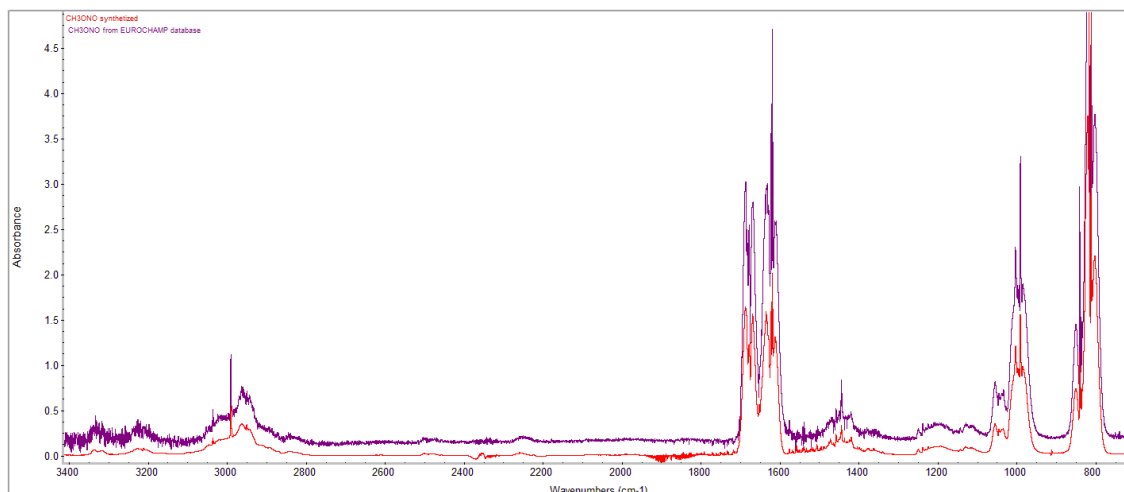
**5 RC:** Page 4, “Kinetic measurements were performed at room temperature 298 K) and atmospheric pressure ~ (720 Torr)” – Authors have stated the pressure at which the reactions were carried out is 720 Torr throughout the main text but, in the abstract it is stated as 740 Torr. It is advised to check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

**AC:** The experiments on Teflon® reactor were done at atmospheric pressure that each day could varied 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:** 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.

**AC:** The procedure of synthesis of CH<sub>3</sub>ONO 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<sub>3</sub>ONO is synthesized, an IR spectrum is done and it is compared with the CH<sub>3</sub>ONO reference spectrum of database. In all cases a high purity is observed.

An example of IR spectrum of CH<sub>3</sub>ONO synthesized 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.

$$Total\ Carbon\ (\%) = \sum_1^i \left( \frac{n^{\circ}\ of\ carbon\ of\ product_i}{n^{\circ}\ of\ carbon\ of\ MSA} \times molar\ yield_i(\%) \right)$$

**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 NO<sub>3</sub> 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  $\text{NO}_3$  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,  $F(-\text{OH})$ ). 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  $\text{NO}_3$  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  $\text{NO}_3$  radical, and therefore it is not possible to check out the effect of hydroxyl group in the reactivity of  $\text{NO}_3$  reaction. However, according to the factor of reactivity obtained by Kerdouci et al. (2010) for the reactions of alcohols with  $\text{NO}_3$ , 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  $\text{NO}_3$  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 ( $k_{3\text{M1ButOH}+\text{Cl}} = 25.0 \times 10^{-11}$ ;  $k_{3,3\text{DM1ButOH}+\text{Cl}} = 26.9 \times 10^{-11}$ ) and an important decrease of the rate coefficient for OH reactions ( $k_{3\text{M1ButOH}+\text{OH}} = 14 \times 10^{-12}$ ;  $k_{3,3\text{DM1ButOH}+\text{OH}} = 5.33 \times 10^{-12}$ ). This behavior could be explained by the different order of reactivity between the oxidants. For Cl atom, more reactive ( $k$  order of  $10^{-11}$ )

$10^3 \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) 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 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.

**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<sub>3</sub> reaction by Kerdouci et al. does not consider the effect of the factor -CH<sub>2</sub>-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<sub>3</sub> 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 NO<sub>2</sub> + NO<sub>3</sub>??

**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<sub>2</sub> in the case of NO<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub> radical. Therefore, more kinetic studies for NO<sub>3</sub> 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<sub>2</sub>OH).”

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<sub>3</sub> 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 ( $\sigma_{k_{MSA}}$ ) were calculated from the uncertainty of slope of plots ( $\sigma_{slope}$ ) and the uncertainty of the reference ( $\sigma_{k_R}$ ) 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.”

**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<sub>2</sub> and air were similar, considering the experimental error. So, we always use N<sub>2</sub> as bath gas (except to the OH reaction because it is necessary O<sub>2</sub> to generate the OH) because it is less expensive than air.



Relevant changes.

The pages and lines correspond with the modified manuscript.

- Pag. 1. Lines 10. The keywords have been included
- Pag 1. Lines 13-17. This paragraph has been included.
- Pag 3. Lines 19-20. The figure has been modified.
- Pag. 4 lines 11-37. The description of the experimental systems has been modified including more details respects to the initial version of manuscript.
- Pag. 5 Lines 10-13. The sentence has been rewritten.
- Pag. 6 lines 25-31. More information about the uncertainty's treatment has been included.
- Pag. 7 lines 11 to pag 9 line 24. The discussion of kinetic data has been rewritten to a better understanding.
- Pag. 7 lines 30-32. These lines have been eliminated and an equation for calculation of Carbon balance has been included as a footnote in Table 6.
- Pag. 11. Lines 16-20. This paragraph has been included to explain better the different yields of E-4-methylcyclohexanone obtained for both experimental systems.
- Pag. 15. Lines 24-32. Two conclusions have been reorganized in one.
- Pag 16. Lines 24-27. A new paragraph has been included.
- Pag.20 Lines 1-3. A reference has been included.
- Pag. 21. Lines 19-21. A reference has been included.
- Pag. 23. Table 1. Has been modified including the data of relative rate coefficients, eliminating the column 4 of the initial Table 1 and recalculating the errors of average value of the rate coefficient using the weighted average
- Pag. 24 Table 2. Has been modified including more data.
- Pag. 30 to Pag 37. The figures 1, 2,3,4,5,6,7,8, have been modified slightly with a better resolution in some case or to include some missed element in other.

# Atmospheric fate of a series of Methyl Saturated Alcohols

## (MSA): kKinetic and mMechanistic study

Inmaculada Colmenar<sup>1,2</sup>, Pilar Martín<sup>1,2</sup>, Beatriz Cabañas<sup>1,2</sup>, Sagrario Salgado<sup>1,2</sup>, Araceli Tapia<sup>1,2</sup>, Inmaculada Aranda<sup>1,2</sup>

<sup>1</sup>Universidad de Castilla La Mancha, Departamento de Química Física, Facultad de Ciencias y Tecnologías Químicas, Avda. Camilo José Cela S/N, 13071 Ciudad Real, Spain

<sup>2</sup>Universidad de Castilla La Mancha, Instituto de Combustión y Contaminación Atmosférica (ICCA), Camino Moledores S/N, 13071 Ciudad Real, Spain

Correspondence to: Pilar Martín ([mariapilar.martin@uclm.es](mailto:mariapilar.martin@uclm.es))

**Keywords.** Methyl saturated alcohols; additives; biofuel; atmospheric reactivity.

**Abstract.** The atmospheric fate of a series of Methyl Saturated Alcohols (MSA) has been evaluated through the kinetic and reaction product studies with the main atmospheric oxidants. Rate coefficients (in  $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$  unit) measured at  $\sim 298\text{K}$  and atmospheric pressure ( $7240 \pm 20$  Torr) were as follows:  $k_1$  (E-4-methyl-cyclohexanol + Cl) =  $(3.704 \pm 0.1653) \times 10^{-10}$ ,  $k_2$  (E-4-methyl-cyclohexanol + OH) =  $(1.8794 \pm 0.1465) \times 10^{-11}$ , and  $k_3$  (E-4-methyl-cyclohexanol +  $\text{NO}_3$ ) =  $(2.6992 \pm 0.37138) \times 10^{-15}$ , for reaction of E-4-methyl-cyclohexanol with Cl, OH and  $\text{NO}_3$ , respectively.  $k_4$  (3,3-dimethyl-1-butanol + Cl) =  $(2.6970 \pm 0.1655) \times 10^{-10}$ ,  $k_5$  (3,3-dimethyl-1-butanol + OH) =  $(5.3357 \pm 0.166) \times 10^{-12}$ ,  $k_6$  (3,3-dimethyl-2-butanol + Cl) =  $(1.21 \pm 0.037) \times 10^{-10}$  and  $k_7$  (3,3-dimethyl-2-butanol + OH) =  $(10.504 \pm 0.2581) \times 10^{-12}$ , for reaction of 3,3-dimethyl-2-butanol with Cl and OH radical respectively. The main detected products were 4-methylcyclohexanone, 3,3-dimethylbutanal and 3,3-dimethyl-2-butanone for the reactions of E-4-methyl-cyclohexanol, 3,3-dimethyl-1-butanol and 3,3-dimethyl-2-butanol respectively with the three oxidants. A tentative estimation of molecular yields has been done obtaining the following ranges (25-60) % for 4-methylcyclohexanone, (40-60) % for 3,3-dimethylbutanal and (40-80) % for 3,3-dimethyl-2-butanone. Other products such as formaldehyde, HCOH, 2,2-dimethylpropanal and acetone have been identified in the reaction of 3,3-dimethyl-1-butanol and 3,3-dimethyl-2-butanol. The yields of these products indicate a hydrogen abstraction mechanism at different sites of the alkyl chain in the case of Cl reaction and a predominant site in the case of OH and  $\text{NO}_3$  reactions, confirming supported the predictions of Structure Activity Relationships by (SAR) methods prediction.

Tropospheric lifetimes ( $\tau$ ) of these MSA have been calculated using the experimental rate coefficients. Lifetimes are in the range of 0.6-2 days for OH reactions, 7-13 days for  $\text{NO}_3$  radical reactions and 1-3 months for Cl atoms. In coastal areas the lifetime due to the reaction with Cl decreases to hours. The global tropospheric lifetimes calculated, and the polyfunctional compounds detected as reaction products in this work, imply that the Methyl Saturated Alcohols could contribute to ozone and nitrated compound formation at local, but also regional and even to global scale. Therefore, the use of large saturated alcohols as additives in biofuels must be taken with caution.

1

2

## 1 **1. Introduction**

2 Multitude of scientific studies about combustion emissions confirms that fossil fuels, especially diesel fuel, are the  
3 main responsible for air pollution. The loss of air quality and its consequences on health as well as global warming  
4 are some of the most important problems caused by air pollution ([www.iea.org](http://www.iea.org)). These consequences have led  
5 governments to set restrictive limits for the presence of certain pollutants in the atmosphere, such is the case of  
6 particulate matter (PM) (EURO 6) ~~and This has led~~ to develop biofuels (Sikarwara et al., 2017) as alternative to  
7 conventional ones.

8 Biodiesels are obtained from a transesterification process of animal or vegetable oils origin. Also, the fermentation  
9 of vegetal biomass gives methanol and / or ethanol (bioethanol). These lower alcohols have been used as fuels  
10 showing advantages as the reduction of the smoke, due to the presence of OH group that increases the oxygen  
11 content during the combustion process (Ren et al., 2008; Lapuerta et al., 2010; Sarathy et al., 2014; Sikarwara et  
12 al., 2017). However several studies have shown certain complications in the use of lower alcohols due to their low  
13 cetane number, high latent heat of vaporization and high resistance to auto-ignition (Karabektas and Hosoz, 2009).  
14 In order to avoid or to minimize these limitations, alcohol-diesel blends and alcohol-diesel emulsions have been  
15 used in diesel engines (Ozsezen et al., 2011). Other alternative is the use of longer alcohols (propanol, n-butanol,  
16 isobutanol and n-pentanol) with superior fuel properties than lower alcohols mixed with diesel fuel (Cheung, et al.  
17 2014; Kumar and Saravanan, 2016).

18 The fact that the use of high alcohols is a good alternative to conventional fuels could suppose an important  
19 presence of these alcohols in the atmosphere. Therefore, previously to the massive use, it is necessary to study the  
20 reactivity of the large alcohols in atmospheric conditions, in order to establish and to evaluate their atmospheric  
21 impact.

22 Alcohols are present in the atmosphere from a wide variety of anthropogenic and biogenic sources (Calvert et al.,  
23 2011). Methanol, ethanol and isopropanol are some of the main alcohols detected in urban areas such as Osaka  
24 and Sao Paulo cities (Nguyen et al., 2001) with concentrations between 5.8-8.2 ppbv and 34.1-176.3 ppbv  
25 respectively. Other alcohols such as E-4-methylcyclohexanol, have been identified in the exhaust gas emissions  
26 of burning fuel blends containing 7 % v/v (B7) and 20 % v/v (B20) of soy bean/palm biodiesel (84 % / 16 %)  
27 (Lopes et al., 2014). 3,3-dimethyl-1-butanol is a glass forming material, used as a chemical intermediate in organic  
28 syntheses ([www.capotchem.com](http://www.capotchem.com)). 3,3-dimethyl-2-butanol is a potential precursor for prohibited chemical  
29 weapons such as soman, a nerve agent (Murty et al., 2010). It is also used in conversion of ribose- and glucose-  
30 binding proteins into receptors for pinacolyl methyl phosphonic acid (Allert et al. 2004).

31 In the case of smaller alcohols, the knowledge of its reactivity is well established indicating that the degradation  
32 mechanism of saturated alcohols is mainly initiated by the H-abstraction from C-H bond. The H-abstraction from  
33 the OH group seems to be less favored (Grosjean et al., 1997, [Calvert et al., 2011](#)). According to literature  
34 (Atkinson and Arey, 2003; Atkinson et al., 2006; Calvert et al., 2011; Caravan et al., 2015; Mellouki et al, 2015),  
35 the main degradation route of saturated alcohols in the atmosphere is the reaction with OH radicals during ~~day~~  
36 ~~time~~ ~~medaytime~~. Kinetics with chlorine atoms are expected to be high, therefore reactions with Cl could also be an  
37 important degradation route, especially in coastal areas where concentration peaks of chlorine can be found.  
38 Reactions with ozone ( $k \leq 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) and nitrate radical ( $\sim 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) are too low to  
39 have a significant contribution to ~~their~~ degradation. However, the determination of the rate coefficients and the

1 reaction products of alcohols with the nitrate radical are also necessary to better understand the general reactivity  
2 of alcohols in the atmosphere since the reactions with this radical are a source of OH during the night-time  
3 (Finlayson-Pitts and Pitts, 2000).

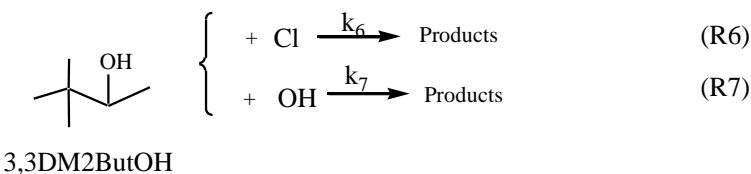
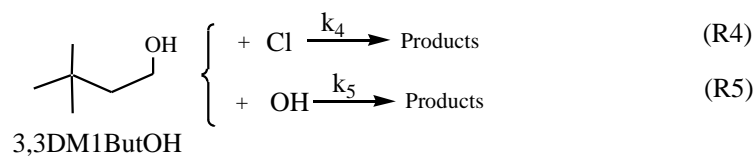
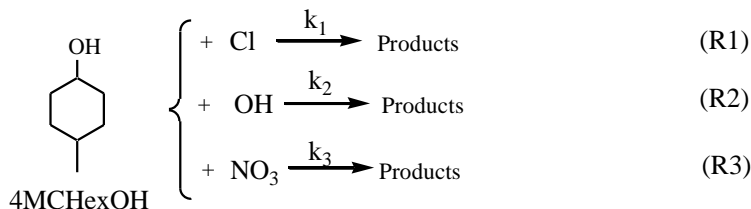
4 Although in the last years some studies about reactivity of large alcohols have been made ([Andersen et al. 2010](#);  
5 Ballesteros et al., 2007; [Hurley et al., 2009](#); [Andersen et al. 2010](#); Calvert et al, 2011; [Hurley et al., 2009](#); Moreno  
6 et al., 2012, 2014, Mellouki et al, 2015) the kinetic and mechanistic database is still scarce. In the case of the 3,3-  
7 dimethyl-1-butanol and 3,3-dimethyl-2-butanol (derives from 1-butanol, 2-butanol) there is a lack of information  
8 with respect to regarding the diurnal reactivity (Moreno et al., 2014; Mellouki et al., 2015). Regarding to cyclic  
9 alcohols, only data concerning the reactivity of chlorine atoms and OH radicals for cyclohexanol (Bradley et al.,  
10 2001; Ceacero-Vega et al., 2012) and OH for cyclopentanol (Wallington et al., 1988) have been reported.

11 Therefore, in the present work, the study of gas phase reactions of some Methyl Saturated Alcohols (MSA): E-4-  
12 methylcyclohexanol (4MCHexOH), 3,3-dimethyl-1-butanol (3,3DM1ButOH) and 3,3-dimethyl-2-butanol  
13 (3,3DM2ButOH) with the main atmospheric oxidants has been done in order to complete the kinetic and  
14 mechanism database, to improve our knowledge of the atmospheric chemistry of alcohols in special saturated  
15 alcohols, and to assess their a chemical's environmental chemical impact.

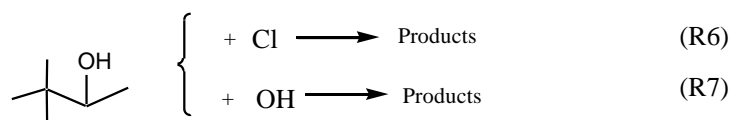
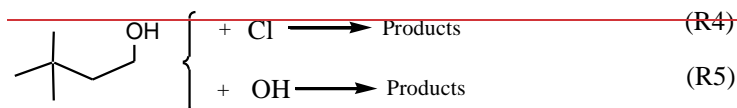
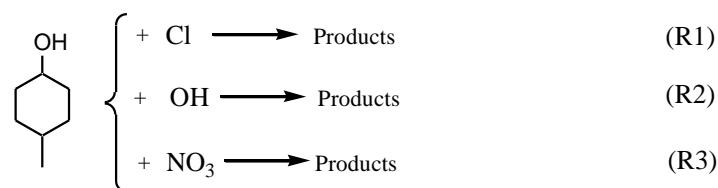
## 16 2. Experimental Section

### 17 2.1 Kinetic experiments

18 The reactions of a series of Methyl Saturated Alcohols (MSA) with the main atmospheric oxidants have been  
19 studied:



20



Rate coefficients were determined using a relative rate method. This method relies on the assumption that the organic compound (MSA) and the reference compound (R), are removed solely by their reactions with the oxidants (Ox: OH, NO<sub>3</sub> radicals and Cl atoms):



Where  $k_{\text{MSA}}$  and  $k_{\text{R}}$  are the rate coefficients of the MSA and the reference compound respectively.

On the assumption that the MSA and the reference compound are only consumed by reaction with the oxidant, the kinetic treatment for the reactions expressed by R8 and R9 gives yields the following relationship;

$$\ln \left( \frac{[\text{MSA}]_0}{[\text{MSA}]_t} \right) = \frac{k_{\text{MSA}}}{k_{\text{R}}} \ln \left( \frac{[\text{R}]_0}{[\text{R}]_t} \right) \quad (1)$$

where [MSA]<sub>0</sub>, [R]<sub>0</sub>, [MSA]<sub>t</sub>, and [R]<sub>t</sub> are the initial concentrations and those at time *t* for the Methyl Saturated Alcohol and the Reference compound, respectively. Two reference compounds with each oxidant were used to assure that the reference compound does not have any influence on overall rate coefficient.

According to Eq (1), a plot of  $\ln([\text{MSA}]_0/[\text{MSA}]_t)$  versus  $\ln([\text{R}]_0/[\text{R}]_t)$  should be a straight line that passes through the origin. The slope of this plot gives the ratio of rate coefficients  $k_{\text{MSA}}/k_{\text{R}}$ . Therefore the value of  $k_{\text{MSA}}$  can be obtained if the rate coefficient  $k_{\text{R}}$  of the reference compound is known.

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<sup>-1</sup>. 2) - A 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

1 GCv, Jeol) (“off line” analysis). Samples were collected by exposing a 50/30 mm DVB/CAR/PDMS Solid Phase  
2 Micro Extraction fiber (SPME, SUPELCO) for 5 min during the reaction and then thermally desorbed for 15 min  
3 at 250 °C in the heated GC injection port. A capillary column (30 m × 0.3 mm id × 1.0 mm film thickness, Tracsil  
4 TRB-1701, Teknokroma) was used to separate the compounds. The chromatographic conditions used for the  
5 analysis were as follows: injector, 250 °C; interface, 250 °C; oven initial temperature, 40 °C for 4 min; ramp, 30  
6 °C min<sup>-1</sup> to 120 °C, held for 6 min; second ramp, 30 °C min<sup>-1</sup> to 200 °C, held for 3 min.

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

11 The kinetic experiments, for the Cl and OH reactions, were performed in the FTIR system. A spectral subtraction  
12 procedure was used to derive the concentrations of reactant and reference compounds at time  $t = 0$  and time  $t$ . The  
13 reaction of NO<sub>3</sub> with 4MCHexOH was studied using a Teflon® reactor of 500 L in order to minimize the wall  
14 deposition and dilution effects of consecutive additions of N<sub>2</sub>O<sub>5</sub>. Chlorine atoms and OH radicals were obtained  
15 by photolysis of Cl<sub>2</sub> in N<sub>2</sub> and methyl nitrite in the presence of NO in air. Methyl nitrite, CH<sub>3</sub>ONO, was synthesized  
16 in the laboratory as described elsewhere (Taylor et al., 1980).

17 ~~Kinetic measurements were performed at room temperature (~298 K) and atmospheric pressure (~720 Torr) by~~  
18 ~~employing two experimental set-ups: All kinetic experiments, for the Cl and OH reactions, were performed using~~  
19 ~~a 50 L Pyrex® glass reaction chamber with a White cell that allowed a long pathlength up to 200 m coupled to a~~  
20 ~~FTIR spectrometer (Thermo Nicolet 5700) equipped with a KBr beam splitter and liquid nitrogen cooled MCT~~  
21 ~~detector, as a detection technique. Typically, for each spectrum, 60 interferograms were co-added over 98 s and~~  
22 ~~approximately 30–40 spectra were recorded per kinetic experiment with a spectral resolution of 1 cm<sup>-1</sup>. A spectral~~  
23 ~~subtraction procedure was used to derive the concentrations of reactant and reference compounds at time  $t=0$  and~~  
24 ~~time  $t$ . Chlorine atoms were obtained by photolysis of Cl<sub>2</sub> at a wavelength of 360 nm using 8 actinic lamps. OH~~  
25 ~~radicals were produced by photolysis of Methyl nitrite, CH<sub>3</sub>ONO, in the presence of NO in air. CH<sub>3</sub>ONO was~~  
26 ~~synthesized in the laboratory as described elsewhere (Taylor et al., 1980).~~

27 ~~The reaction of NO<sub>3</sub> with 4MCHexOH was studied using a bigger reactor, a 150 L or 500 L Teflon® in order to~~  
28 ~~minimize the wall deposition and dilution effects of the consecutive additions of N<sub>2</sub>O<sub>5</sub>. Solid Phase Micro~~  
29 ~~Extraction fiber (SPME) as a pre-concentration sample method, followed by analysis on a Gas Chromatography–~~  
30 ~~Mass Spectrometry system with a Time of Flight analyzer (SPME/GC-TOFMS) (AccuTOF GCv, Jeol) was used.~~  
31 ~~Samples were collected by exposing a 50/30 mm DVB/CAR/PDMS Solid Phase Micro Extraction fiber (SPME,~~  
32 ~~SUPELCO) for 5 min during the reaction and then thermally desorbed for 15 min at 250 °C in the heated GC~~  
33 ~~injection port. A capillary column (30 m × 0.3 mm id × 1.0 mm film thickness, Tracsil TRB-1701, Teknokroma)~~  
34 ~~was used to separate the compounds. The chromatographic conditions used for the analysis were as follows:~~  
35 ~~injector, 250 °C; interface, 250 °C; oven initial temperature, 40 °C for 4 min; ramp, 30 °C min<sup>-1</sup> to 120 °C, held for~~  
36 ~~6 min, second ramp, 30 °C min<sup>-1</sup> to 200 °C, held for 3 min. Nitrate radicals were generated in situ in the dark by~~  
37 ~~the thermal decomposition of N<sub>2</sub>O<sub>5</sub> (Atkinson et al., 1984, 1988). N<sub>2</sub>O<sub>5</sub> was obtained mixing O<sub>3</sub> with excess of~~  
38 ~~NO<sub>2</sub> (Scott and Davidson, 1958). Previously to the kinetic experiments a series of tests in dark and photolysis~~  
39 ~~conditions were carried out to evaluate secondary reactions such as wall depositions and photo-degradation~~  
40 ~~processes of reactants.~~

1 Range concentrations of reactants employed were as follows: 2-16 ppm of 4MCHexOH, 3-9 ppm of  
2 3,3DM1ButOH and 3,3DM2ButOH, 9-30 ppm of Cl<sub>2</sub>, 4-13 ppm of 1-butene and 2-methylpropene, 7-14 ppm of  
3 propene and cyclohexene, 5-7 ppm of isopropanol, 3-5 ppm of 2-methyl-2-butanol, 26-55 ppm of CH<sub>3</sub>ONO, 20-  
4 60 ppm of NO, 3-4 ppm of 2-ethyl-1-hexanol, 4-5 ppm of 1-butanol. For reactions of 4MCHexOH with nitrate  
5 radicals a number of 2-5 additions of N<sub>2</sub>O<sub>5</sub> with concentrations between 8-36 ppm were made per each experiment.  
6 N<sub>2</sub> and synthetic air were used as bath gases for Cl, NO<sub>3</sub> and OH reactions, respectively.

## 7 2.2 Product experiments

8 The product study was carried out at room temperature (~298 K) and at a pressure of (720 ± 20) Torr of synthetic  
9 air employing the two experimental detection set-ups mentioned above, FTIR at a pressure of (~720 ± 1) Torr of  
10 synthetic air and SPME/GC-TOFMS at atmospheric pressure. In some experiments carried out During the reaction  
11 process in the 50 L Pyrex® reactor, glass chamber a simultaneous identification of products was performed using  
12 both detection techniques. For that, one sample of mixing reaction was taken from this reactor using the SPME  
13 and subsequent analyzed with GC-TOFMS. the identification of products was made using the FTIR analysis but,  
14 at the same time, a sample was taken and analyzed in the SPME/GC-TOFMS system. In addition, independent  
15 experiments using SPME/GC-TOFMS technique in a 1450/5000 L Teflon® reactor were developed. Products  
16 analyses were carried out using the same procedure as for the kinetic experiments, without the reference  
17 compound, and employing synthetic air as bath gas. In this occasion the heating of the oven was changed slightly  
18 in order to get a better separation and to detect the products generated. The temperature ramps of the oven  
19 employed in the chromatograph were: 40 °C for 4 min; ramp, 25 °C min<sup>-1</sup> to 120 °C, held for 10 min; second ramp,  
20 25 °C min<sup>-1</sup> to 200 °C, held for 4 min.

21 The qualitative analysis in the FTIR experiments was carried out using the FTIR library that provides the FTIR  
22 spectrophotometer (Aldrich vapor phase sample library, <https://www.thermofisher.com/search/browse/results?customGroup=Spectral+Libraries>) and/or the FTIR  
23 database of Eurochamp (<https://data.eurochamp.org/data-access/spectra/>).

24 For the SPME/GC-TOFMS experiments, the NIST webbook (<https://webbook.nist.gov/chemistry/>) and the Mass  
25 Spectra database of the instrument were used to identify the products. Calibrated FTIR spectra and SPME/GC-  
26 TOFMS chromatograms of authentic samples were used to quantification in those cases where the product was  
27 commercially available.

28 The molecular yields of the reaction products were estimated from the slopes of plots of the concentration of  
29 formed product versus the amounts of MSA (Δ[MSA]) consumed. To obtain the yield in percentage of carbon, the  
30 yield obtained is multiplied by 100 and by the ratio of carbons between the product and the MSA from which it  
31 comes.

32 In the cases Sometimes, where it was observed an important loss of the reaction product could be taken on by  
33 reaction of the oxidant and/or by photolytic process, the concentration of the product was corrected using the  
34 formulism of Tuazon et al. (1986) (See S1 in supplementary material). Range concentrations of reactants  
35 employed were as follows: 2-14 ppm of MSA, 8-31 ppm of Cl<sub>2</sub>, 12-57 ppm of NO, 19-66 ppm of  
36 CH<sub>3</sub>ONO methylnitrite and 6-36 ppm of N<sub>2</sub>O<sub>5</sub>.

38



1 Chemicals used were as follows: 4MCHexOH (97 %, Aldrich), 3,3DM1ButOH and 3,3DM2ButOH (98 %,  
2 Aldrich); 1-butene, propene, 2-methyl-2-butanol, isopropanol, 2-methylpropene, 4-methylcyclohexanone and  
3 cyclohexene ( $\geq 99$  %, Aldrich), 2-ethyl-1-hexanol ( $\geq 99$  %, Fluka), 1-butanol (99.8 %, Aldrich), 3,3-  
4 dimethylbutanal (95 %, Aldrich) and 3,3-dimethyl-2-butanone (98 %, Aldrich), NO (99 %, Praxair), Cl<sub>2</sub> ( $\rightarrow 99.8$   
5 %, Praxair), synthetic Air (Praxair Ultrahigh purity 99.999 %), N<sub>2</sub> (99.999 %, Praxair). For N<sub>2</sub>O<sub>5</sub> synthesis, N<sub>2</sub>O<sub>4</sub>  
6 were used ( $>99.5$  %) from Fluka, P<sub>2</sub>O<sub>5</sub> (98 %, such as desiccant) from Fluka and O<sub>3</sub> synthesized by a generator  
7 model TRCE-5000, 5 g<sub>O<sub>3</sub></sub> h<sup>-1</sup> OZOGAS.

### 8 9 **3. Results and discussion**

#### 10 11 **3.1 Kinetic study**

12 Preliminary test experiments indicated that dark heterogeneous reactions and photolytic losses of MSA can be  
13 considered negligible in our experimental conditions ( $k \sim 10^{-6} \text{ s}^{-1}$ ). As mentioned above, the kinetic study of Cl  
14 atoms and OH radical with the MSA organics was carried out at room temperature ( $\sim 298 \text{ K}$ ) and at  $-720 \pm 20$  Torr  
15 of N<sub>2</sub> gas and synthetic air respectively. Nitrate radical experiments were performed ~~at room temperature and~~  
16 ~~atmospheric pressure~~ using N<sub>2</sub> gas in a 500 L Teflon reactor bag and employing the system SPME/GC-TOFMS. A  
17 number of injections of the unreacted mixture were carried out in order to determine the associated precision with  
18 the sampling method to be used in the error analysis (Brauers and Finlayson-Pitts, 1997). The standard deviations  
19 ( $\sigma$ ) were as follows: 3.7 % for 4MCHexOH, 1.7 % for 1-butanol and 3.5 % for 2-ethyl-1-hexanol. Figure 1 shows  
20 examples of the kinetic data plotted according to Eq (1) for the reactions of MSA with different atmospheric  
21 oxidants.

22 A good correlation was obtained with an intercept close to zero, which indicates the absence of other secondary  
23 processes. From the slopes of the plots ( $k_{MSA}/k_R$ ) and ~~known~~ knowing the values ~~offer~~ the rate coefficients for the  
24 reference compounds employed ( $k_R$ ) the value of the absolute rate coefficient for each methyl saturated alcohol  
25 ( $k_{MSA}$ ) has been determined.

26 Rate coefficients of reference compounds, for Cl atom reactions (in  $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  units) were: 2-  
27 methylpropene ( $3.40 \pm 0.28$ ), 1-butene ( $3.38 \pm 0.48$ ), (Ezzel et al., 2002) and propene ( $2.23 \pm 0.31$ ) (Ceacero-Vega  
28 et al., 2009); for OH radical reactions (in  $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  units): propene ( $2.66 \pm 0.40$ ), (Atkinson and  
29 Aschman, 1989), cyclohexene ( $6.77 \pm 1.69$ ) (Atkinson and Arey, 2003), isopropanol ( $0.51 \pm 0.008$ ) (IUPAC  
30 www.iupac-kinetic.ch.cam.ac.uk) and 2-methyl-2-butanol ( $0.36 \pm 0.06$ ) (Jiménez et al., 2005). And for NO<sub>3</sub>  
31 reactions (in  $10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  units): 1-butanol ( $3.14 \pm 0.97$ ) and 2-ethyl-1-hexanol ( $2.93 \pm 0.9246$ )  
32 (Gallego-Iniesta et al., 2010). The ratios of the rate coefficients,  $k_{MSA}/k_R$ , the absolute rate coefficients and the  
33 weighted average are shown in Table 1. The error of  $k_{MSA}/k_R$  are given by 2 times the statistical deviation calculated  
34 from the least-square fit of the plot of Eq. (1). The uncertainties for rate coefficients of MSA ( $\sigma_{k_{MSA}}$ ) were  
35 calculated from the uncertainty of slope of plots ( $\sigma_{\text{slope}}$ ) and the uncertainty of the reference ( $\sigma_{k_R}$ ) by using the  
36 propagation of uncertainties. The average value of the rate coefficient obtained with different reference compounds

1 ~~and its associated error were obtained by weighted average (See footnote Table 1). The experimental data are~~  
2 ~~shown in Table 1.~~ The rate coefficients obtained in this work are the first kinetic data reported for these MSA,  
3 therefore ~~the~~ results obtained ~~can not~~ cannot be compared with literature values.

4  
5 As it has been mentioned in introduction section, it is well established that the gas-phase reaction mechanism of  
6 saturated organic compounds (alkanes, alcohols, ethers, etc) with the atmospheric oxidants (Cl atoms, OH and  
7 NO<sub>3</sub> radicals) are initiated “via” hydrogen atom abstraction from the organic compound to form a stable molecule  
8 and an alkyl radical (Finlayson-Pitts and Pitts, 2000; Atkinson and Arey, 2003; Calvert et al., 2011; Ziemann and  
9 Atkinson, 2012). The presence of hydroxyl group in saturated alcohols implies two types of hydrogens that can be  
10 ~~abs~~abstracted, hydrogen bonded to ~~a~~ carbon (C-H) of ~~the~~ main chain or ~~of~~ an alkyl substituent and hydrogen  
11 bonded to oxygen of hydroxyl ~~group~~substituent (-OH). Two literature reviews about reactivity of saturated  
12 alcohols (Calvert et al., 2011; Mellouki et al., 2015) conclude that:

13 1- The reactions of aliphatic alcohols with atmospheric oxidants proceed mainly by H atom abstraction from  
14 various C-H groups in the alkyl chain being the H atom abstraction from the O-H negligible.

15 2- Rate coefficients for the reactions of Cl, OH and NO<sub>3</sub> are higher for alcohols than those of the corresponding  
16 alkanes due to the activating effect of the OH group. This effect is extended over about 4 carbon atoms (Nelson et  
17 al., 1990). As will be discussed ~~below~~later, the activating effect of the OH group ~~is~~ dependsing on the oxidant.

18 3- The attack percentage of ~~a~~ radical to the different sites of ~~the~~ alcohol ( $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$ ) depends on the oxidants,  
19 structure of saturated alcohol, type ~~and~~; numbers of substituents, and temperature. (Moreno et al., 2012, 2014;  
20 McGillen et al., 2013, 2016).

21 ~~In order to check Taking into account~~ these remarks, the reactivity of the Methyl Saturated Alcohols studied in  
22 this work ~~has been~~will be analyzed and discussed comparing ~~a) the rate coefficients~~ of ~~these~~ MSA obtained  
23 for the different oxidants, with: a) the different oxidants, b) the rate coefficients of the MSA and the rate  
24 coefficients of their homologous alkanes available in bibliography the same oxidant with different alcohols and c)  
25 the rate coefficients obtained in the reaction of the same oxidant but with different alcohols.~~with the rate~~  
26 ~~coefficients of their homologous alkanes.~~ The data used to compare are summarized in Table S1 in supplementary  
27 material.

28 From the analysis of all data, it can be observed that:

29 a) 1- The trend in the reactivity of MSA in relation to the different oxidants is the same that the observed for other  
30 saturated alcohols:  $k_{Cl}$  ( $k \sim 10^{-10}$ )  $>$   $k_{OH}$  ( $k \sim 10^{-11}$ )  $\gg$   $k_{NO_3}$  ( $k \sim 10^{-15}$ ), ( $k$  in  $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$  units). This behavior  
31 could be explained considering the geometry and the electronic density of each oxidant, together with the kinetic  
32 Collision Theory. As Cl atom has spherical distribution of its density, for the collision any orientation is adequate,  
33 in addition the Cl atoms presents less steric hindrance. Then, comparatively the Cl reaction is less selective and  
34 faster with values for the rate coefficients,  $k$ , in the collision limit. However, the OH radical presents an asymmetric  
35 electron density located mostly over its oxygen atom. Therefore, for the OH reaction the oxygen of OH radical,  
36 must be specific oriented to the hydrogen of the MSA that will be abstracted. The electronic density of nitrate  
37 radical is distributed around the three oxygens which implies several appropriate orientations. However, as the  
38 nitrate radical has a non-linear structure, the steric hindrance is much bigger than for the OH and it reduces the  
39 reactivity of NO<sub>3</sub> in relation to those of OH radical.

1 for the different size and electronic properties of each oxidant that make the Cl atom the most reactive (value of  $k$   
2 in the limit of collision) but also less selective than OH and NO<sub>3</sub> radicals.

3 b)2- The rate coefficient for the reaction of 4MCHexOH with Cl atoms is similar to the rate coefficient of its  
4 homologous alkane (E-1,4-dimethylcyclohexane):  $k_{4MCHexOH+Cl} = 37.04 \times 10^{-11} \cong k_{E-1,4-dimethylcyclohexane+Cl} = 36.3 \times$   
5  $10^{-11}$ . In the case of the reaction with OH radical, the rate coefficient of 4MCHexOH is 1.56 times higher than E-  
6 1,4-dimethylcyclohexane,  $k_{4MCHexOH+OH} = 18.7 \times 10^{-12} > k_{E-1,4-dimethylcyclohexane+OH} = 12.1 \times 10^{-12}$  (see data of Table  
7 S1). These results show that the activating effect of hydroxyl group (-OH) of the MSA group is less important for  
8 the Cl than OH reactions due to the high reactivity of Cl atoms. The activating effect of hydroxyl group of the  
9 alcohols was quantified by different authors (Kwok and Atkinson 1995; Kerdouci et al. 2010; Calvert et al. 2011)  
10 taking into account the available kinetic data reported in bibliography, obtaining the factor of reactivity for the  
11 hydroxyl group, F(-OH)). This factor of reactivity is different for each oxidant, 1.18 for Cl reaction, 2.35 for  
12 reaction with OH (Calvert et al. 2011) and 18 for NO<sub>3</sub> reaction (Kerdoueci et al., 2010). There are no data of rate  
13 coefficients for the reactions of the homologous alkanes of the MSA studied in this work with NO<sub>3</sub> radical, and  
14 therefore it is not possible to check out the effect of hydroxyl group in the reactivity of NO<sub>3</sub> reaction. However,  
15 according to the factor of reactivity obtained by Kerdouci et al. (2010) for the reactions of alcohols with NO<sub>3</sub>, this  
16 effect is higher than the corresponding to Cl and OH reactions. In the case of 3,3-dimethylbutanols, there is not  
17 data of rate coefficients of the homologous alkanes for comparison, but in general it is observed a large influence  
18 of the structure of the organic compound on the reactivity (SAR Method, Kwok and Atkinson, 1995). This effect  
19 has been quantified for each of the functional groups of an organic compound. So, in the case of alcohols the factor  
20 of hydroxyl group, is 1.18 for the reaction with Cl, 2.35 for the reactions with OH (Calvert et al., 2011) and 18 for  
21 the reactions of the nitrate radical (Kerdoueci et al., 2014).

22 c) 3- Rate coefficients obtained for these three MSA with the same oxidant are of the same order that the  
23 corresponding to other saturated alcohols (See data of Table S1). The activating effect of the length chain in the  
24 reactivity of alcohols is being more evident marked in the Cl reactions than in the case of OH and NO<sub>3</sub> reactions  
25 (See Table S1). Furthermore, if the rate coefficients of 3-methyl-1-butanol (3M1ButOH) and 3,3DM1ButOH with  
26 Cl and OH reactions are compared, it can be observed a slight increase of rate coefficient for Cl reaction  
27 ( $k_{3M1BuOH+Cl} = 25.0 \times 10^{-11}$ ;  $k_{3,3DM1BuOH+Cl} = 26.9 \times 10^{-11}$ ) and an important decrease of the rate coefficient for OH  
28 reactions ( $k_{3M1BuOH+OH} = 14 \times 10^{-12}$ ;  $k_{3,3DM1BuOH+OH} = 5.33 \times 10^{-12}$ ). ~~T~~ Again, this behavior could be explained by the  
29 different order of reactivity between the oxidants. For Cl atom, more reactive ( $k$  order of  $10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )  
30 but less selective, an increase of the length chain or in the number of methyl groups implies more hydrogens  
31 available to be ~~sub~~abstracted and therefore an increase of the rate coefficient. However, for the OH and NO<sub>3</sub>  
32 radicals, less reactive and more selective, the attack for H-abstraction to ~~subtract the hydrogen~~ will be carried out  
33 in a specific place, so an increase of the chain ~~has not a significant~~ doesn't affect to the reactivity significantly,  
34 even the presence of a second methyl group disfavor the reaction probably due to the steric hindrance near to the  
35 attack position.

36 In addition, as can be seen in Table S1, the position of hydroxyl group has a different effect depending on the  
37 oxidant. In the case of the Cl atom reactions, the rate coefficients for primary alcohols (1-propanol, 1-butanol, 1-  
38 pentanol, 3-methyl-1-butanol and 3,3-dimethyl-1-butanol) are higher than the ones of the secondary alcohols (2-  
39 propanol, 2-butanol, 2-pentanol, 3-methyl-2-butanol and 3,3-dimethyl-2-butanol) contrary to the OH and NO<sub>3</sub>

1 ~~radical reactions. This fact indicates that in the reaction of Cl atoms the formation of the most stable radical seems~~  
2 ~~to have less importance in the reactivity than the number of hydrogens in  $\alpha$  position available to be abstracted. In~~  
3 ~~the reactions of OH and NO<sub>3</sub> radicals, the presence of activating substituents or the formation of a more stable~~  
4 ~~radical after the H abstraction could have a major effect in the reactivity than in the case of Cl atom reaction. This~~  
5 ~~last assumption could also explain the minor rate coefficient observed for the Cl reaction with secondary alcohols~~  
6 ~~(2-propanol, 2-butanol, 2-pentanol, 3-methyl-2-butanol and 3,3-dimethyl-2-butanol) instead of primary alcohols~~  
7 ~~(1-propanol, 1-butanol, 1-pentanol, 3-methyl-1-butanol and 3,3-dimethyl-1-butanol) (see Table S1).~~

8 All ~~these observations (a, b and c) that~~ could imply a different mechanism in the hydrogen abstraction process for  
9 Cl atoms versus OH and NO<sub>3</sub> radicals. Nelson et al. (1990) and Smith and Ravishankara (2002) indicate the  
10 possible formation of an intermediate adduct between the OH radical and the oxygen of the hydroxyl group via  
11 hydrogen bond that will imply a specific orientation. Theoretical studies found in bibliography show this different  
12 hydrogen-abstraction process in the reaction of saturated alcohols with Cl atoms (Garzon et al., 2006) and OH  
13 ~~radical~~ (Moc and Simmie, 2010).

14 ~~These different mechanisms in the hydrogen abstraction process for each oxidant should will imply~~  
15 ~~different product distributions and molecular yields as it will be shown below, in the section of product and~~  
16 ~~mechanistic study, be observed in the analysis of the reaction products implying different yields and products~~  
17 ~~distributions.~~

### 19 3.1.1 Estimation of rate coefficients

20  
21 In order to estimate the rate coefficients of the reactions of organic compounds with the atmospheric oxidants,  
22 multitude of methods have been proposed (Vereecken et al. 2018). The most popular and used is the SAR method  
23 developed initially by Kwok and Atkinson (1995) to estimate the rate coefficients at room temperature for gas  
24 phase reactions ~~with~~ OH radical. This method has been updated for OH reactions (Jenkin et al., 2018) and  
25 extended to NO<sub>3</sub> (Kerdouci et al., 2010, 2014) and Cl (Calvert et al., 2011; Poutsma 2013) reactions. The EPA  
26 (United States Environmental Protection Agency) has developed the EPI Suite™-Estimation Program Interface  
27 that allows to estimate the rate coefficient for the reaction of OH radical and organic compounds using the  
28 AOPWIN v1.92 program. In ~~our~~ this work the rate coefficients of MSA with the three oxidants have been estimated  
29 using the SAR method (See S2 supplementary material). ~~The results and~~ are shown in Table 2.

30 The values of estimated rate coefficients agree with experimental data with ratios  $k_{exp}/k_{SAR}$  between 0.98 and 1.287,  
31 except for the case of 3,3DM1ButOH and NO<sub>3</sub> radical with a  $k_{exp}/k_{SAR}$  of 3.249. In general, the SAR method  
32 applied to alcohols predicts better rate coefficients for Cl atoms and OH radical than for NO<sub>3</sub> radical, especially  
33 for primary alcohols. It is important to note that the kinetic database for the -NO<sub>3</sub> reactions is more limited than  
34 for Cl and OH reactions, so the estimated rate coefficient for NO<sub>3</sub> radical should be treated with caution (Kerdouci  
35 ~~et al. 2010, 2014~~; Calver et al., 2011).

36 It is known that organic compounds which reacts in the same way with different atmospheric oxidants, present a  
37 correlation between their rate coefficients. In this sense, along the years, different correlations have been proposed

1 that allow to estimate the unknown rate coefficient when the other one is known (Wayne, 1991, 2000; Atkinson,  
2 1994; Calvert et al., 2011; Gallego-Iniesta et al., 2014). Correlations  $\log k_{\text{Cl}} - \log k_{\text{OH}}$  and  $\log k_{\text{NO}_3} - \log k_{\text{OH}}$  have been  
3 built for a set of alcohols, ethers and saturated alcohols by Calvert et al., (2011) obtaining the following  
4 relationships:

$$\log(k_{\text{Cl}}/\text{cm}^{-3}\text{molecule}^{-1}\text{s}^{-1}) = 0.634 \times \log(k_{\text{OH}}/\text{cm}^{-3}\text{molecule}^{-1}\text{s}^{-1}) - 2.71 \quad (r^2=0.72) \quad (2)$$

$$\log(k_{\text{NO}_3}/\text{cm}^{-3}\text{molecule}^{-1}\text{s}^{-1}) = 1.11 \times \log(k_{\text{OH}}/\text{cm}^{-3}\text{molecule}^{-1}\text{s}^{-1}) - 2.42 \quad (r^2=0.66) \quad (3)$$

7 These equations have been used to estimate the rate coefficients of the reactions of MSA with Cl and nitrate radical  
8 using the experimental rate coefficients measured in this work for OH reactions. The estimated rate coefficients,  
9  $k_{\text{log}}$ , according with Eq (2) and Eq (3), and the ratios ( $k_{\text{exp}}/k_{\text{log}}$ ), results obtained are also shown in Table 2. ( $k$  in  $\text{cm}^3$   
10  $\text{molecule}^{-1}\text{s}^{-1}$  units):  $k_{\text{Cl-3,3DM1ButOH}} = 14.3 \times 10^{-11}$ ;  $k_{\text{Cl-3,3DM2ButOH}} = 21.4 \times 10^{-11}$ ;  $k_{\text{Cl-4MCHexOH}} = 31.2 \times 10^{-11}$ ;  $k_{\text{NO}_3-}$   
11  $_{3,3DM1ButOH} = 1.22 \times 10^{-15}$ ;  $k_{\text{NO}_3-3,3DM2ButOH} = 2.48 \times 10^{-15}$  and  $k_{\text{NO}_3-4MCHexOH} = 4.81 \times 10^{-15}$ . This estimation method  
12 obtains slightly better rate coefficient for 3,3DM1ButOH + NO<sub>3</sub> reaction ( $k_{\text{exp}}/k_{\text{log}} = 1.53$ ) than SAR ( $k_{\text{exp}}/k_{\text{SAR}} =$   
13 3.24). However, for Cl reactions the ratios  $k_{\text{exp}}/k_{\text{log}}$  are in the range of 0.6-1.97, indicating that the Eq (2) predicts  
14 worse the rate coefficients than SAR method. results than SAR for NO<sub>3</sub> reactions. The better prediction for the  
15 NO<sub>3</sub> rate coefficients than for those of Cl could be due to the Again, this fact could be due to that the mechanism  
16 for Cl atom reactions is the different mechanism reaction in the H-abstraction process for Cl and than for OH  
17 radical reactions. Such as it has been indicated above Assumption that must be satisfied to apply these relationships  
18 both oxidants must react according to the same mechanism correlation. It is important to indicate that in the case  
19 of Cl reactions, other effects such as thermochemistry and the polar effect, must be considered to estimate the rate  
20 coefficients for hydrogen abstraction reactions (Poutsma, 2013).

21

### 22 3.2 Product and Mechanistic Study

23

24 A product study of 4MCHexOH, 3,3DM1ButOH and 3,3DM2ButOH with chlorine atoms in absence/presence of  
25 NO<sub>x</sub>, hydroxyl and nitrate radicals has been performed by employing the two experimental set-ups mentioned  
26 above (FTIR and SPME/GC-TOFMS). IR absorption bands of HCl, CO<sub>2</sub>, CO, HNO<sub>3</sub>, N<sub>2</sub>O, NO<sub>2</sub>, HCOOH,  
27 HCOH, ClNO, ClNO<sub>2</sub> and CH<sub>3</sub>NO<sub>3</sub> were observed in the FTIR experiments. These bBands that are due to the  
28 decomposition of the precursors employed (Cl<sub>2</sub>, CH<sub>3</sub>NO<sub>2</sub> and N<sub>2</sub>O<sub>5</sub>) and in some cases are due to heterogeneous  
29 reactions of these precursors with the walls of the Pyrex® reactor gas cell. The formation of O<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> have also  
30 been observed at large reaction times for the reactions of the MSA with and Cl atoms + in presence of NO, due to  
31 the high concentration of the NO<sub>2</sub> in the medium of reaction and in presence of radiation. Quantitative analysis  
32 was carried out by linear subtraction of a spectrum's absorption bands and peak areas of GC chromatograms with  
33 the use of calibrated spectra and reference chromatograms.

34 The experimental conditions and molecular yields of the main products formed in the reactions of MSA and  
35 analyzed by FTIR and SPME/GC-TOFMS techniques are given in Tables 3-6. Molecular yYields could be affected  
36 to large errors associated with the SPME sampling method and due to the presence of interfering IR absorption

bands absorptions, mainly associated with precursors of the OH and NO<sub>3</sub> radicals or by nitrated compounds formed.

### 3.2.1 - 4MCHexOH

E-4-methylcyclohexanone was identified in the reaction with Cl, Cl + NO, OH + NO and NO<sub>3</sub> + NO<sub>2</sub>. An example of the product spectra obtained in the FTIR system is shown in Fig. 2. Formation of the E-4-methylcyclohexanone was confirmed by introducing a sample of the commercial product (spectrum (e)). A set of experiments using the SPME/GC-TOFMS system were also carried out for the reaction of 4MCHexOH with Cl atoms and OH and NO<sub>3</sub> radicals. An example of the chromatogram obtained for the reaction of 4MCHexOH with chlorine atoms is shown in Fig. 3. In all the studied reactions, formation of a product peak at 10.35 min was observed. This peak (B) showed in Fig. 3 was assigned to E-4-methylcyclohexanone and confirmed by comparing with the retention time and MS spectrum of a commercial sample. In the reactions with chlorine atoms (absence/presence of NO<sub>x</sub>) and OH radical two additional peaks at 19.80 min (C) and 20.25 min (D) were observed.

The time-concentration profiles of 4MCHexOH and E-4-methylcyclohexanone obtained by FTIR for the reaction with chlorine atoms in the presence of NO<sub>x</sub> is shown on Fig. S24. The concentrations of E-4-methylcyclohexanone, corrected according to Eq (S1), (S2) and (S3), were plotted versus the amounts of 4MCHexOH consumed in order to obtain the yield of 4-methylcyclohexanone from the slope. An example of the obtained plots is shown in Fig. 4. Molecular yields, Y (%), of E-4-methylcyclohexanone obtained in all experiments are listed in Table 3. Based on the average molecular yield of E-4-methylcyclohexanone, the carbon balance is below to 50 % for reactions with Cl and OH radical and ~ 60 % for NO<sub>3</sub>.

Residual spectra after subtraction of the E-4-methylcyclohexanone show IR absorption bands compatible with the presence of hydroxy carbonyl compounds (~1750, 1720, 1060 cm<sup>-1</sup>) and nitrated organic compounds (RONO<sub>2</sub> ~ 16260, 1264 and 862 cm<sup>-1</sup>, and/or ROONO<sub>2</sub> ~ 1720, 1300 and 760 cm<sup>-1</sup>) (See residual spectra, Fig. S32 in supplementary material). The amount of nitrated compounds was estimated using the average integrated absorption coefficient of  $1.2 \times 10^{-17}$  cm molecule<sup>-1</sup> of similar compounds corresponding to the IR rangeband 1260-1305 cm<sup>-1</sup> (Tuazon and Atkinson,1990). The calculated yields of RONO<sub>2</sub> were 20 % and 60 % for Cl + NO and NO<sub>3</sub> reactions respectively. A yield of 10 % of nitrated compounds was estimated for the reaction with OH radical. This lower yield could be due to fact that the NO<sub>x</sub>, presents in the reaction medium, reacts faster with the CH<sub>3</sub>O\* (formed in the reaction of CH<sub>3</sub>ONO with NO) than others alcoxyradicals. Table 6 shows a summary of the average yields of reaction products quantified for 4MCHexOH reactions.

Considering the products detected here and the detected in the study of Bradley et al., (2001) relative to cyclohexanol with OH radical reactions, a degradation mechanism for 4MCHexOH with the atmospheric oxidants has been proposed. Figure 5A shows the paths to explain the formation of carbonyl or hydroxy carbonyl compounds and Figure 5B shows an example of a path to explain the formation of nitrated organic compounds (ROONO<sub>2</sub> and RONO<sub>2</sub>). Similar nitrated compounds could be formed by routes II-IV. The abstraction of hydrogen atoms in  $\alpha$ -position with respect to alcohols group (routechannel I) followed by the addition of oxygen,

1 formation of a peroxy radical and fast decomposition of this radical explains the formation of E-4-  
2 methylcyclohexanone. Based on the molecular yield obtained for E-4-methylcyclohexanone for each oxidant (See  
3 Table 6), this routechannel represents ~ 25-30 %, ~ 40 % and ~ 60 % of the reaction mechanism of 4M~~C~~eHexOH  
4 with Cl and Cl + NO, OH and NO<sub>3</sub>-reaction, respectively. Percentages are two times higher than SAR method  
5 prediction in the case of Cl atoms reactions and 1.3 and 1.5 times lowerhigher for OH and NO<sub>3</sub> reactions  
6 respectively. ~~It should be noted that T~~these data should be taken with caution, since they could imply many sources  
7 of error.

8 Apart from E-4-methylcyclohexanone, other carbonyl and hydroxy carbonyl compounds could be formed by  
9 routes II, III, and IV. The presence of this kind of compounds have been observed in the reactions with Cl and OH.  
10 According to the Electron Ionization Mass S-spectra (EI MS) (Fig. S43, supplementary material) of peaks (C) and  
11 (D) shown in Fig. 3, an assignation to 2-hydroxy-5-methyl-cyclohexanone, ~~and~~ 5-hydroxy-2-methyl-  
12 cyclohexanone and/or 3-methyl-1,6-hexanedial-respectively has been proposed. However, according to the  
13 atmospheric reactivity (Finlayson and Pitts, 2000; Calvert et al., 2011; Ziemann and Atkinson, 2012) and the study  
14 of Bradley et al., (2001), the compound that would be expected is the 3-methyl-1,6-hexanedial, which comes from  
15 the decomposition of the alkoxy radical formed in route II. However, confirmation was not possible since these  
16 compounds wereare not commercially available. The detection of HCOH about 9 % in the reaction with Cl atoms  
17 indicates that the elimination of the methyl group in route IV is minority.

18 In the case of nitrate radical only E-4-methylcyclohexanone was detected as carbonyl compound, suggesting that  
19 the route I may be the dominant pathway for this radical. The large difference between the yields of E-4-  
20 methylcyclohexanone obtained using the SPME/GC-TOFMS system (~ 75 %) or the FTIR (35 %) could be due  
21 to the different way to add the precursor in both reactors (small aliquots of N<sub>2</sub>O<sub>5</sub> in the Teflon® reactor versus one  
22 large addition in the Pyrex® reactor). This procedure causes a lower initial concentration of nitrated inorganic  
23 species (NO<sub>3</sub>, NO<sub>2</sub>, HNO<sub>3</sub>) in reactor of 150 L than in reactor of 50 L, favoring the formation of carbonyl  
24 compounds instead of nitrated organic compounds. the influence of the volume of reactor (150 or 500 liters in the  
25 SPME/GC-TOFMS compared to 50 L of the FTIR), which favors the formation of carbonyl compounds instead  
26 of nitrates in the case of using a large volume reactor. This fact is more pronounced in the case of reactions with  
27 nitrate radical since, due to the precursor used, the reaction occurs in the presence of high concentrations of NO<sub>2</sub>  
28 favoring the addition of NO<sub>2</sub> to peroxy or alkoxy radicals (See Figure 5B). Taking into account, the yields of E-4-  
29 methylcyclohexanone and the nitrated compounds for the NO<sub>3</sub> reaction using FTIR, a total carbon balance of 100%  
30 is obtained (See Table 6).

### 32 3.2.2 -3,3DM1ButOH

34 Following the same procedure as above, 3,3-dimethylbutanal was identified as the main reaction product in the  
35 reaction of 3,3DM1ButOH with the three atmospheric oxidants. Figure S54A shows the FTIR spectra obtained for  
36 the reactions of 3,3DM1ButOH with Cl, Cl + NO, OH and NO<sub>3</sub> after subtraction.

1 Residual FTIR spectra after subtraction of 3,3-dimethylbutanal (Fig. S54B), the SPME/GC-TOFMS  
2 chromatograms (Fig. S65) and EI MS spectra (Fig. S76), show that other reaction products as carbonyl, hydroxy  
3 carbonyl and nitrated compounds are formed. These ~~reaction products compounds~~ could be ~~formaldehyde HCOH~~,  
4 2,2-dimethylpropanal, glycolaldehyde, acetone, peroxy-3,3-dimethyl-buteryl nitrate (P33DMBN)  
5  $(\text{CH}_3)_3\text{CCH}_2\text{C}(\text{O})\text{OONO}_2$ . These compounds can be formed as primary products (~~see Fig. 6 below~~) or secondary  
6 products from degradation of 3,3-dimethylbutanal (See Fig. S87). The SPME/GC-TOFMS chromatograms show  
7 common peaks for the three oxidants, but the number of peaks and ~~their~~ distribution are very different, especially  
8 for OH reactions. In the case of SPME/GC-TOFMS system a set of experiment using Field Ionization was carried  
9 out in order to help us to establish the identification of reaction products.

10 Time-concentration profiles of 3,3DM1ButOH, 3,3-dimethylbutanal and those reaction products positively  
11 identified by FTIR analysis were made in order to establish if the profiles correspond with a primary or secondary  
12 reaction products. An example of the reactions with chlorine atoms in the absence and presence of NO<sub>x</sub> is shown  
13 ~~in~~ Fig. 6, observing that in the absence of NO the profiles of acetone and formaldehyde show a typical profile of  
14 secondary reactions. This ~~profile behaviour~~ is ~~only~~ clearly observed ~~for in the profile of~~ nitrated compounds in the  
15 reaction of Cl atoms in ~~the~~ presence of NO (Fig. 6B).

16 Commercial sample of 3,3-dimethylbutanal was used to estimate ~~the molecular~~ yields in both experimental  
17 systems. These ~~molecular~~ yields are shown in the Table 4. The yields of acetone and ~~formaldehyde HCOH~~ were  
18 calculated using a FTIR reference spectrum of commercial sample and FTIR reference spectra from Eurochamp  
19 database (<https://data.eurochamp.org/data-access/spectra/>), respectively. A FTIR reference spectrum of 2-  
20 methylpropanal (from this same database) has been used to estimate the ~~molecular~~ yield of 2,2-dimethylpropanal.  
21 The amounts of 3,3-dimethylbutanal formed were corrected by ~~their~~ reactions with Cl atoms, and OH and NO<sub>3</sub>  
22 radicals as is described previously using the rate coefficients available in bibliography or for reactions of  
23 structurally ~~similar~~ compounds ~~similar~~ (see footnote Table 4). Estimated yields of formaldehyde, acetone, 2,2-  
24 dimethylpropanal and nitrated compounds are summarized in Table 6 ~~along together~~ with an average yield of 3,3-  
25 dimethylbutanal. The higher yield of nitrated compounds in the reaction of 3,3DM1ButOH with nitrate radical  
26 could indicate secondary products (See Fig. S87). A total of carbon yield (nitrated compounds have not been  
27 accounted) of ~~~6070~~ %, ~~~815~~ % and ~~36-40~~ % have been justified for Cl (absence and presence of NO), OH and  
28 NO<sub>3</sub> reaction respectively, but must be noted that there are reaction products that could not ~~possibly~~ be quantified  
29 as carbonyl or hydroxy carbonyl compounds in the Cl atoms reactions and primary nitrated compounds in the Cl  
30 + NO and NO<sub>3</sub> radical reactions.

31 This work is the first study of reaction products of 3,3DM1ButOH with the atmospheric oxidants, so there is ~~not~~  
32 any study to compare. Figure 7 shows the reaction mechanism proposed based on the literature studies about  
33 saturated alcohols reactions with Cl atoms and OH radical (Cavalli et al., 2002; Hurley et al., 2009; -McGillen et  
34 al., 2013; Welz et al., 2013) and considering the reaction products identified in this work. Table S2, in  
35 supplementary material, shows a summary of the reaction products proposed in this mechanism observed or  
36 tentatively identified in the reactions of 3,3DM1ButOH with the atmospheric oxidants.

37 Estimated ~~molecular~~ yields of 3,3-dimethylbutanal (formed by H-Abstraction in  $\alpha$  position of 3,3DM1BuOH) for  
38 Cl and OH reaction ( $\sim(40-43)$  %, ~~~6057~~ %) are very similar to the one predicted by the SAR method (40 % and  
39 66 % respectively). In the case of NO<sub>3</sub> radical a large difference between both yields are observed (~~363~~ % estimated



1 in this work, 86.5 % predicted by SAR method). This discrepancy could be explained by the fact that the SAR  
2 method (Kerdouci et al., 2010, 2014) underestimates the attack of NO<sub>3</sub> in β-position, ~~since because~~ it does not  
3 consider the possible effect of the ~~hydroxylalcohol~~ group jointed to -CH<sub>2</sub>- (F(-CH<sub>2</sub>OH)). ~~That is, the SAR method~~  
4 ~~considers the effect of -CH<sub>2</sub> and perhaps must also consider the factor of -CH<sub>2</sub>OH.~~ This could also explain the  
5 large difference observed between the estimated and measured rate coefficient as was shown in Table 2. On the  
6 other hand, On the other hand, as it has been discussed above, the volume of the reactor ~~could an~~ also have influence  
7 ~~to on~~ formation of 3,3-dimethylbutanal.

8 According ~~to with~~ the molecular yields of the products quantified and/or observed in the SPME/GC-TOFMS  
9 chromatograms, it can be concluded that for OH radical reaction, the route I (attack in α position) seems to be the  
10 main reaction route. For Cl atoms the three routes can occur with a high percentage although the I and III (attack  
11 in δ position, especially evident in presence of NO) seem to be the major routes. The major molecular yield of  
12 formaldehydeHCOH and -acetone (route III) and 2,2-dimethylpropanal in the reactions of Cl atoms in presence  
13 of NO versus Cl atoms reactions in absence of NO could indicate that in absence of NO the self peroxy radical  
14 reaction “via” molecular channel (~~formation of carbonyl and dihydroxy organic compounds~~) is more favored than  
15 “via” radical channel, ~~with formation of two alkoxy radicals.~~ For NO<sub>3</sub> radical, routes I and II (attack in β position)  
16 with formation of nitrated compounds ~~apart from 3,3-dimethylbutanal~~ seem to be the unique routes.

### 17 3.2.3 -3,3DM2ButOH

18 The analysis of FTIR spectra obtained for the reactions of 3,3DM2ButOH with Cl atoms, in presence and absence  
19 of NO, OH radical and NO<sub>3</sub> radical shows the formation of 3,3-dimethyl-2-butanone as a main product (see Fig.  
20 S98). Others compounds such as formaldehydeHCOH, acetone, 2,2-dimethylpropanal and Peroxy Acetyl Nitrate  
21 (PAN), have also been observed. The residual FTIR spectra after subtraction of all known IR bands, again shows  
22 the presence of carbonyl compounds (IR bands absorption in the range of 1820-1700 cm<sup>-1</sup>); hydroxy compounds  
23 (1060-1040 cm<sup>-1</sup>) in the reaction of Cl atoms in absence of NO and also nitrated compounds (RONO<sub>2</sub>; 1650, 1305-  
24 1260, 890 cm<sup>-1</sup>) in the reaction of Cl + NO and NO<sub>3</sub> radical (Fig. S98C). The presence in the residual FTIR spectra  
25 of a IR absorption band around 1800 cm<sup>-1</sup> ~~for in~~ the reaction of Cl atoms at large reaction times could be due to the  
26 formation of chlorine compounds by reaction of 3,3-dimethyl-2-butanone with Cl<sub>2</sub> (Ren et al., 2018) or the  
27 formation of cyclic compounds as hydrofurans. The SPME/GC-TOFMS chromatograms and MS spectra (Fig.  
28 S109 and S110) confirm other reaction products apart from 3,3-dimethyl-2-butanone in the case of Cl, Cl + NO  
29 and NO<sub>3</sub> reactions. Only one significant peak is observed in chromatograms obtained for the OH reactions.

30 Acetone, formaldehydeHCOH, 2,2-dimethylpropanal, nitrated compounds and acetaldehyde have also been  
31 quantified. Plots of concentration versus time show, typical profiles of secondary reactions for  
32 formaldehydeHCOH, acetone (Fig. S12A) and nitrated compounds in the reactions of Cl with NO (See-Fig.  
33 S12B+). These compounds could also be formed by degradation of 3,3-dimethyl-2-butanone (See-Fig. S132). The  
34 estimated molecular yields of 3,3-dimethyl-2-butanone for all individual experiments are given in Table 5, where  
35 the measured concentrations have ~~again~~ been corrected again for secondary reactions. Table 6 summarizes the  
36 molecular yields of all quantified products.

37 A total carbon yields of ~60 %, 100±2 %, 90.5 % and 60.58 % have been accounted for Cl (absence and presence  
38 of NO), OH and NO<sub>3</sub> reaction, respectively (See-Table 6). It is important to note that in the case of the reaction of

1 Cl atoms without NO where the total carbon yield is lower than 100 % there are many reaction products that could  
2 not be quantified, as carbonyl and/or hydroxy carbonyl compounds. In the reaction of NO<sub>3</sub> radical, due to our  
3 experimental conditions, an important amount of primary nitrated compounds is expected to be formed (See-Fig.  
4 S98C).

5 A mechanism of hydrogen abstraction in different positions of the carbon chain has been proposed for the reaction  
6 of 3,3DM2ButOH with Cl, OH and NO<sub>3</sub> reactions. The mechanism is shown in Figure 8. Table S3, in  
7 supplementary material, shows a summary of the reaction products proposed in this mechanism observed or  
8 tentatively identified in the reactions of 3,3DM2ButOH with the atmospheric oxidants.

9 Molecular yields of 3,3-dimethyl-2-butanone obtained in this work imply a percentage of attack of the oxidant  
10 in  $\alpha\beta$  position (~~route II of mechanism~~) of: 43 % and 44 %, in the case of chlorine atom; 81 % for OH radical  
11 and 58 % for NO<sub>3</sub> radical. Percentages are very similar to that predicted by SAR method except for NO<sub>3</sub> radical.  
12 High NO<sub>2</sub> concentration present in the reaction would highly favor the formation of nitrated compounds versus  
13 3,3-dimethyl-2-butanone. The main reaction products observed in the reaction of Cl atoms in presence of NO (3,3-  
14 dimethyl-2-butanone, formaldehydeHCOH, 2,2-dimethylpropanal, acetone, acetaldehyde) confirm that the Cl  
15 atoms could attack in other sites (apart of  $\alpha$  position) with an important percentage. Based on the estimated  
16 molecular yield of acetone, the attack in  $\delta$  position with abstraction of hydrogen of methyl groups (~~route III~~)  
17 could be ~58 %, and based on the estimated molecular yield for 2,2-dimethylpropanal, the attack in  $\beta$  position  
18 (~~route I~~) could account with a 10 %. These data agree with the SAR predictions for Cl atom reactions. On  
19 the other hand, the major molecular yields of acetone, formaldehydeHCOH, 2,2-dimethylpropanal and  
20 acetaldehyde (route III) in the reaction of Cl atoms in presence of NO than in absence of NO could indicate that  
21 in presence of NO the peroxy self-reactions (RO<sub>2</sub>) “via” molecular channel is negligible. The lower yield (17 %)   
22 estimated by acetaldehyde versus 58% of its coproduct (acetone) is due to its fast degradation by Cl atoms reaction  
23 with formation of Peroxy acetyl nitrates as it has been observed in the FTIR experiments (See Fig. S98B).  
24 Moreover, the molecular yield of acetone could be overestimated due to secondary reactions as can be seen in  
25 FigS12 and FigS13.

#### 26 4. Atmospheric Implications

27 The pollutants in the atmosphere, could create serious environmental problems such a photochemical smog, acid  
28 rain and degradation of the ozone layer (Finlayson-Pitts and Pitts, 2000). So, it is important to evaluate the  
29 parameters that help us to know the impact of the presence of these compounds in the atmosphere. These  
30 parameters are, the time that such compounds remains in the atmosphere, the Global Warming ~~Potencial~~Potential  
31 (GWP) and their degradation mechanisms in order to estimate the atmospheric effect impact of products formed.  
32 The first important parameter of the environmental impact of an Oxygenated Volatile Organic Compounds in the  
33 atmosphere, is the global lifetime,  $\tau_{global}$ , which considers all the degradation processes which could suffer these  
34 compounds in the Troposphere. This parameter can be obtained from the sum of the individual sink processes such  
35 as reactions initiated by OH and NO<sub>3</sub> radicals, Cl atoms, and O<sub>3</sub> molecules; photolysis and dry and wet deposition,  
36 Eq (4):

$$37 \tau_{global} = \left[ \frac{1}{\tau_{OH}} + \frac{1}{\tau_{Cl}} + \frac{1}{\tau_{NO_3}} + \frac{1}{\tau_{O_3}} + \frac{1}{\tau_{photolysis}} + \frac{1}{\tau_{other\ processes}} \right]^{-1} \quad (4)$$

1 Tropospheric lifetime ( $\tau$ ) of 4MCHexOH, 3,3DM1ButOH and 3,3DM2ButOH for each process have been  
2 estimated considering Eq (4) and (5).

$$3 \quad \tau = \frac{1}{k_{Ox}[Ox]} \quad (5)$$

4 where  $k_{Ox}$  and  $[Ox]$  are the rate coefficient obtained in this work for each oxidant and typical atmospheric  
5 concentration of the oxidants Cl, OH and  $NO_3$ , respectively. Concentrations employed were as follows: for 24  
6 hours average:  $1 \times 10^3$  atoms  $cm^{-3}$  (Platt and Janssen, 1995) for chlorine atoms, 12-hours average day-time  
7 concentration of  $1 \times 10^6$  radicals  $cm^{-3}$  for OH (Prinn et al., 2001) and  $5 \times 10^8$  radicals  $cm^{-3}$  for  $NO_3$  radicals  
8 (Atkinson, 2000), and a peak concentration of chlorine atoms of  $1.3 \times 10^5$  atoms  $cm^{-3}$  in the coastal marine  
9 boundary layer at dawn (Spicer et al., 1998). Reactions with  $O_3$  and photolysis are negligible loss processes for  
10 this kind of compounds (Mellouki et al., 2015). Other processes are referred to dry or wet deposition. For estimating  
11 the lifetime associated with wet deposition, Eq (6) proposed by (Chen et al. 2003) has been used:

$$12 \quad \tau_{wet} = \frac{H_{atm}}{v_{pm}RTk_H} \quad (6)$$

13 Where  $k_H$  is the Henry's law constant,  $H_{atm}$  is the height in the troposphere taking a value of 630 m,  $v_{pm}$  is the  
14 average precipitation rate for Ciudad Real (Spain) (402 mm/year) (www.aemet.es),  $R$  is the gases constant and  $T$   
15 is the temperature considered as constant and equal to 298 K. In bibliography there is only data of the constant of  
16 Henry for 3,3DM2ButOH ( $5.6 \times 10^{-1}$  mol  $m^{-3}$  Pa $^{-1}$ ) (Sander, 2015). Comparing the available data for similar  
17 compounds it has been used an approximated value of  $K_H$  of 3 mol  $m^{-3}$  Pa $^{-1}$  and 0.4 mol  $m^{-3}$  Pa $^{-1}$  for 4MCHexOH  
18 and 3,3DM1ButOH respectively.

19 Lifetime calculated of the three studied alcohols in this work are shown in the Table 7. It can be seen that the  
20 dominant tropospheric loss process for the three alcohols is clearly their reaction with OH radicals followed by  
21 their reaction with  $NO_3$  radicals at night. However, in places where there is a peak concentration of chlorine atoms  
22 (coastal areas) the reaction of these alcohols with chlorine atoms may compete with OH radicals becoming their  
23 main degradation process.

24 The global lifetime of the three alcohols is of the order of ~ 1-2 days, indicating that these compounds will probably  
25 be degraded near their sources. -These global lifetimes also indicate that MSA do not have ~~not~~ a significant  
26 contribution to radiative forcing of climate change (Mellouki et al., 2015), which is supported through the  
27 estimation of their GWP values. For time-horizon of 20 years, the values estimated have been:  $8.33 \times 10^{-4}$ ,  $1.78 \times$   
28  $10^{-2}$  and  $5.80 \times 10^{-3}$  for 4MCHexOH, 3,3DM1ButOH and 3,3DM2ButOH respectively, which are very low. So,  
29 these compounds will only have an important impact in the troposphere at local or regional level.

30 Their degradation products (mostly carbonyl-containing compounds and nitro-compounds in polluted areas) must  
31 be considered. Thus, the nitrated compounds generated can act as  $NO_x$  reservoir species especially during the  
32 night (Altshuller, 1993) and could have influence at global scale. Moreover, since 4MCHexOH, 3,3DM1ButOH  
33 and 3,3DM2ButOH react quickly with chlorine atoms and OH radicals, their contribution to the formation of  
34 photochemical smog might be important. -For that reason, the contribution of these three alcohols to the formation  
35 of smog was estimated by obtaining the average ozone production during 99 % of their reactions with OH radical,  
36 using the equation indicated by Dash and Rajakumar (2013). The values obtained were 3.24, 0.90 and 1.69 ppm  
37 for 4MCHexOH, 3,3DM1ButOH and 3,3DM2ButOH, respectively. These values suggest that these compounds

1 may be a potential generators of tropospheric ozone and could contribute significantly to the formation of  
2 photochemical smog (depending on their ~~environmental~~ concentrations in the atmosphere).

### 3 **5. Conclusions**

4 The main conclusions that have been obtained with the present study, are the following:

5 -The kinetic and product study ~~supporte~~onfirms that: ~~-1 -T~~the atmospheric degradation mechanism for MSA~~methyl~~  
6 ~~saturated alcohols~~, and possibly for the rest of unstudied saturated alcohols, proceeds mainly by abstraction of the  
7 hydrogen atom bonded to a carbon instead of hydrogen atoms bonded to the oxygen atom of the alcohol group. 2

8 -The reaction mechanism in the H-abstraction process depends on the oxidant.

9 -Chlorine atoms ~~abs~~subtract any type of alkyl hydrogen from saturated alcohols with a high percentage, compared  
10 to the hydroxyl radical and the nitrate radical. OH and NO<sub>3</sub> radicals ~~su~~abtract mainly the hydrogen in the α  
11 position, if the saturated alcohols are secondary. For primary alcohols, the abstraction of a hydrogen in β~~ε~~ position  
12 could be is also important in the reaction with ~~subtracted almost exclusively for the OH radical and α and β position~~  
13 to 50 % in the case of the NO<sub>3</sub> radical, ~~extending the inductive effect to α and β position~~. Therefore, more kinetic  
14 studies for NO<sub>3</sub> radical with primary alcohols are for the reaction of NO<sub>3</sub> radical, it is necessary to update the SAR  
15 method developed by Kerducci et al., ~~(2010, 2014)~~ and to quantify to take into account the effect of the OH  
16 group in β position, ~~(-CH<sub>2</sub>OH)~~ and not only the effect in α position (-OH).

17 -Theoretical ab-initio studies of the reactions of MSA with atmospheric oxidants should be done in order to obtain  
18 more information about their reaction mechanisms in the H-abstraction process. ~~how the type of radical determine~~  
19 ~~the distribution of reaction products specially in reactions that occurs by an initial hydrogen abstraction, that is the~~  
20 ~~case of primary methyl saturated alcohols.~~

21 -The atmospheric conditions determine the reaction mechanism and therefore the reaction products obtained in the  
22 degradation of methyl saturated alcohols. So, in polluted environments with high concentrations of NO<sub>x</sub>, the  
23 peroxyradicals (RO<sub>2</sub>·) reacts mainly with NO to form the alkoxy radical instead of molecular compounds. ~~ether~~  
24 ~~peroxyradical~~. In these conditions, nitrated organic compounds (RONO<sub>2</sub>) are formed apart from polyfunctional  
25 organic compounds. Also, when the concentration of NO<sub>2</sub> is higher than NO concentration, ozone is formed. In  
26 clean atmosphere, as in the case of the experiments of Cl atoms in absence of NO, the reaction products are  
27 different because of peroxyradicals (RO<sub>2</sub>·) could react mainly “via” self-reaction molecular channel instead to  
28 “via” self-reaction radical channel.

29 -The uncounted polyfunctional organic compounds could explain the low carbon balance obtained in Cl or NO<sub>3</sub>  
30 reaction. ~~T~~However, the carbon balance must be taken with caution since the calculated molecular yields have a  
31 high degree of uncertainty.

32 -Calculated lifetimes for methyl saturated alcohols (the order of ~1 day) imply that these compounds are pollutants  
33 at local-regional scale, but it is also important to indicate that MSA are sources of stable nitrated compounds  
34 (ROONO<sub>2</sub>), depending on environment conditions, that can travel to large distances s from their sources contributing  
35 to form ozone in clean areas, for example in forest or rural areas.

36 -The main products coming from the degradation of the MSA~~methyl saturated alcohols~~, aldehydes and ketones,  
37 develop a very important secondary chemistry with formation of products of special relevance such as the PAN  
38 observed in the degradation of 3,3-dimethyl-2-butanol. M~~Also, more~~ experiments should be done using other

1 detection techniques, in order to evaluate the formation of SOA because it is well known that polyfunctional  
2 organic compounds are important SOA precursors.

3 -From the environmental point of view, this work shows that the degradation of MSA methyl saturated alcohols is  
4 an important source of pollutants in the atmosphere with greater or lesser impact depending on the environmental  
5 conditions and the quantities of thesaturated alcohols present in the atmosphere. Therefore, the use of  
6 MSAsaturated alcohols as additives in the production of biofuels should be controlled, avoiding that a bad handling  
7 involves high concentrations of these alcohols in the atmosphere.

8 -Rate coefficients and reaction products measured in this work are the first available data, so this work contributes  
9 to a better understanding of atmospheric chemistry of oxygenated compounds, expanding the kinetic and  
10 mechanistic data-base, and additionally, it contributes to develop or to improve prediction models whichthat help  
11 us to avoid or mitigate the effects of climate change or air quality. -However, kinetic experiments in the  
12 tropospheric temperature range are necessary to obtain more information about the reaction mechanism and to  
13 extrapolate the data of rate coefficients to other typical atmospheric conditions and thus be able to better establish  
14 the atmospheric impact of the alcohols

## 15 6. Supplementary material.

16 -Attached in a separated file.

## 17 7. Author contribution

18 Salgado S. and Martín P. designed the experiments. Cabañas B. is the leader of the group and the responsible to  
19 control the research and got the financial support for the project leading to this publication. Colmenar I. carried  
20 out the experiments of 4MCHexOH. Tapia A. carried out the kinetic experiments of 3,3DM1ButOH and  
21 3,3DM2ButOH and Aranda I. carried out the product experiments of 3,3DM1ButOH and 3,3DM2ButOH. Martín  
22 P. supervised all analysis of data and prepared the manuscript with contributions from all co-authors.

## 23 8. Competing interests

24 The authors declare that they have no conflict of interest. \_\_\_\_\_

## 25 9. Acknowledgment

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1 **Table 1.** Rate coefficient ratios, absolute rate coefficients and average rate coefficients for the reactions of a series  
 2 of MSA with Cl atoms and OH and NO<sub>3</sub> radicals at 298 K and 720 ± 20 Torr of pressure. Rate coefficients, k, in  
 3 cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

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

4 <sup>a</sup>The uncertainties for rate coefficients of MSA (σ<sub>KMSA</sub>) were calculated from the uncertainty of slope of plots (σ<sub>slope</sub>) and  
 5 the uncertainty of the reference (σ<sub>KR</sub>) by using the propagation of uncertainties. <sup>b</sup>Weighted average according to the  
 6 equation (w<sub>1</sub>k<sub>1</sub>+ w<sub>2</sub>k<sub>2</sub>+...)/(w<sub>1</sub>+ w<sub>2</sub>+...); (w<sub>i</sub>=1/σ<sub>i</sub><sup>2</sup>). The uncertainty of weighted average (σ) was given by (1/w<sub>1</sub>+1/w<sub>2</sub>+...)<sup>0.5</sup>.  
 7 <sup>0.5</sup>Table 1. Rate coefficients for the reactions of a series of MSA with Cl atoms and OH and NO<sub>3</sub> radicals at 298 K and ~ 720  
 8 Torr of pressure. Rate coefficients, k, in cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

Reaction	Reference	$(k_{Cl} \pm 2\sigma)/10^{-10}$	$k_{Cl} \pm 2\sigma/10^{-10}$	$\bar{k}_{Cl} \pm 2\sigma/10^{-10}$
3,3DM1ButOH + Cl	1-butene	2.89 ± 0.45	2.72 ± 0.44	2.70 ± 0.55
		2.68 ± 0.43		
		2.58 ± 0.43		
3,3DM2ButOH + Cl	Propene	2.63 ± 0.34	2.68 ± 0.35	1.21 ± 0.37
		2.70 ± 0.35		
		2.71 ± 0.35		
3,3DM2ButOH + Cl	1-butene	1.42 ± 0.31	1.32 ± 0.30	1.21 ± 0.37
		1.17 ± 0.29		
		1.38 ± 0.31		
4MCHexOH + Cl	2-methylpropene	1.08 ± 0.22	1.15 ± 0.23	3.71 ± 0.53
		1.12 ± 0.22		
		1.26 ± 0.24		
4MCHexOH + Cl	1-butene	3.69 ± 0.31	3.66 ± 0.31	3.71 ± 0.53
		3.95 ± 0.31		
		3.35 ± 0.32		
4MCHexOH + Cl	1-butene	3.86 ± 0.52	3.84 ± 0.52	3.71 ± 0.53
		3.78 ± 0.52		
		3.90 ± 0.53		
Reaction	Reference	$(k_{OH} \pm 2\sigma)/10^{-12}$	$k_{OH} \pm 2\sigma/10^{-12}$	$\bar{k}_{OH} \pm 2\sigma/10^{-12}$
3,3DM1BuOH + OH	Isopropanol	5.09 ± 0.21	5.53 ± 0.36	5.57 ± 0.66
		5.78 ± 0.47		
		5.72 ± 0.40		
3,3DM1BuOH + OH	2-methyl 2-butanol	5.85 ± 0.82	5.80 ± 0.82	5.57 ± 0.66
		5.71 ± 0.81		
		5.86 ± 0.83		
3,3DM2BuOH + OH	Isopropanol	11.90 ± 0.46	10.77 ± 0.44	10.51 ± 0.81
		10.46 ± 0.44		
		9.95 ± 0.42		
3,3DM2BuOH + OH	2-methyl 2-butanol	8.70 ± 0.98	9.18 ± 1.00	10.51 ± 0.81
		10.64 ± 1.08		
		8.21 ± 0.95		
4MCHexOH + OH	Propene	17.1 ± 3.2	—	19.1 ± 6.5
		20.2 ± 3.6	19.2 ± 3.5	
		20.4 ± 3.5	—	
4MCHexOH + OH	Cyclohexene	18.2 ± 8.8	18.2 ± 8.8	19.1 ± 6.5
		18.4 ± 8.8		
		18.0 ± 8.8		
Reaction	Reference	$(k_{NO_3} \pm 2\sigma)/10^{-15}$	$k_{NO_3} \pm 2\sigma/10^{-15}$	$\bar{k}_{NO_3} \pm 2\sigma/10^{-15}$
4MCHexOH + NO <sub>3</sub>	1-butanol	3.39 ± 1.11	3.86 ± 1.25	2.92 ± 1.38
		5.70 ± 1.82		
		2.51 ± 0.81		
4MCHexOH + NO <sub>3</sub>	2-ethyl 1-hexanol	2.08 ± 0.72	2.51 ± 0.83	2.92 ± 1.38
		2.93 ± 0.96		
		2.51 ± 0.82		

1 The uncertainties for rate coefficients of MSA were calculated from the uncertainty of slope of plots and the  
2 uncertainty of the reference by using the propagation of uncertainties. The average value of the rate coefficient

1 ~~obtained with different reference compounds and its associated error were obtained by weighted average.  $2\sigma$~~   
2 ~~statistical errors were obtained from the regression analysis ( $\sigma_{\text{slope}}$ ) and the quoted error in the value of the rate~~  
3 ~~coefficient for the reference compound ( $\sigma_{kR}$ ).~~

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1 **Table 2.** Estimated and experimental rate coefficients ( $k_{SAR}$ ,  $k_{log}$  and  $k_{exp}$ ) for the reaction of MSA with atmospheric  
 2 oxidants and ratio of rate coefficients ( $k_{exp}/k_{SAR}$  and  $k_{exp}/k_{log}$ ),  $k_{Cl}/10^{-11}$ ,  $k_{OH}/10^{-12}$  and  $k_{NO_3}/10^{-15}$  in  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$   
 3 units.

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	<b>4MCHexOH</b>			<b>3,3DM1ButOH</b>			<b>3,3DM2ButOH</b>		
	$k_{Cl}$	$k_{OH}$	$k_{NO_3}$	$k_{Cl}$	$k_{OH}$	$k_{NO_3}$	$k_{Cl}$	$k_{OH}$	$k_{NO_3}$
$k_{exp}$	37.0 <sup>a</sup>	18.7 <sup>a</sup>	2.69 <sup>a</sup>	26.9 <sup>a</sup>	5.33 <sup>a</sup>	1.78 <sup>b</sup>	12.1 <sup>a</sup>	10.5 <sup>a</sup>	3.4 <sup>b</sup>
$k_{SAR}$	34.2 <sup>c</sup>	19.2 <sup>c</sup>	2.27 <sup>c</sup>	21.0 <sup>c</sup>	6.08 <sup>c</sup>	0.55 <sup>c</sup>	15.2 <sup>c</sup>	9.16 <sup>c</sup>	3.86 <sup>c</sup>
$k_{exp}/k_{SAR}$	1.08	0.97	1.18	1.28	0.88	3.24	0.80	1.15	0.88
$k_{log}$	30.7 <sup>d</sup>	-	4.69 <sup>d</sup>	13.9 <sup>d</sup>	-	1.16 <sup>d</sup>	21.4 <sup>d</sup>	-	3.19 <sup>d</sup>
$k_{exp}/k_{log}$	1.21	-	0.57	1.94	-	1.53	0.57	-	1.07

5 <sup>a</sup>Data obtained in this work

6 <sup>b</sup>Data obtained by Moreno et al., 2014

7 <sup>c</sup>See S2 supplementary material

8 <sup>d</sup>Estimated using the correlations  $\log_{Cl}-\log_{OH}$  (Eq. (2)) and  $\log_{NO_3}-\log_{OH}$  (Eq. (3)) described by Calvert et al., 2011.

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10 **Table 2.** Estimated and experimental rate coefficients ( $k_{SAR}$  and  $k_{exp}$ ) for the reaction of MSA with atmospheric  
 11 oxidants and ratio of rate coefficients ( $k_{exp}/k_{SAR}$ ),  $k$  in  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  unit.

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	<b>Cl atoms</b>			<b>OH radical</b>			<b>NO<sub>3</sub> radical</b>		
	$k/10^{-11}$		ratio	$k/10^{-12}$		ratio	$k/10^{-15}$		Ratio
	$k_{SAR}$	$k_{exp}$	$k_{exp}/k_{SAR}$	$k_{SAR}$	$k_{exp}$	$k_{exp}/k_{SAR}$	$k_{SAR}$	$k_{exp}$	$k_{exp}/k_{SAR}$
<b>4MCHexOH</b>	34.2 <sup>a</sup>	37.1 <sup>b</sup>	1.08	19.2 <sup>e</sup>	19.1 <sup>b</sup>	0.99	2.28 <sup>d</sup>	2.91 <sup>b</sup>	1.27
<b>3,3DM1ButOH</b>	20.1 <sup>a</sup>	27.0 <sup>b</sup>	1.34	6.75 <sup>e</sup>	5.57 <sup>b</sup>	0.82	0.54 <sup>d</sup>	1.78 <sup>e</sup>	3.29
<b>3,3DM2ButOH</b>	15.2 <sup>a</sup>	12.1 <sup>b</sup>	0.79	9.03 <sup>e</sup>	10.5 <sup>b</sup>	1.16	3.86 <sup>d</sup>	3.4 <sup>e</sup>	0.88

13 <sup>a</sup>Estimated using method described by Calvert et al., 2011

14 <sup>b</sup>Data obtained in this work

15 <sup>c</sup>Estimated using AOPWIN v1.92

16 <sup>d</sup>Estimated using method described by Kerducci et al., 2010, 2014

17 <sup>e</sup>Data obtained by Moreno et al., 2014

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1 **Table 3.** Experimental conditions and molecular yields of E-4-methylcyclohexanone for the reaction  
 2 of 4MCHexOH with atmospheric oxidants.

MSA	Oxidants	Exp	[MSA] (ppm)	[Precursor] (ppm)	[NO] (ppm)	Carbonyl compound <sup>d</sup> Yield (%)	Technique	Average <sup>f</sup> (%)	SAR Yield (%)
4MCHexOH	Cl <sup>a</sup>	1	3	21	-	24.8±0.9	FTIR	25.2±1.9	14
		2	8	22	-	23.8±0.6	FTIR		
		3	13	16	-	27.5±0.2	SPME/GC- TOFMS <sup>e</sup>		
	Cl <sup>a</sup> + NO	1	11	23	30	30.4±0.9	FTIR	29.5±0.7	
		2	5	25	19	30.0±0.6	FTIR		
		3	7	13	12	31.6±1.3	SPME/GC- TOFMS <sup>e</sup>		
	OH <sup>b</sup>	1	7	36	23	35.1±1.3	FTIR	40.2±5.4	53
		2	13	31	29	38.2±1.5	FTIR		
		3	11	28	28.5	47.8±0.4	FTIR		
		4	6	19	12	39.8±0.9	SPME/GC- TOFMS <sup>e</sup>		
	NO <sub>3</sub> <sup>c</sup>	1	3	6	-	56.8±11.4	SPME/GC- TOFMS <sup>e</sup>	58.0±23.5	<u>8675</u>
		2	6	34	-	88.3±7.0	SPME/GC- TOFMS <sup>e</sup>		
		3	4	30	-	77.1±4.6	SPME/GC- TOFMS <sup>e</sup>		
		4	4	21	-	34.6±0.5	FTIR		
		5	7	10	-	33.4±0.6	FTIR		

3 <sup>a</sup> Rate coefficient k (in cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> unit) used to correct the concentration of E-4-methylcyclohexanone by  
 4 loss with the reaction of Cl atoms ~~=was of~~ 11.2 × 10<sup>-11</sup> (data of 2-methylcyclohexanone and Cl atoms (Herath et  
 5 al., 2018)). Photolysis rate ~~coefficient constant~~ estimated for E-4-methylcyclohexanone under our experimental  
 6 conditions. ~~k<sub>p</sub>~~ = 5 × 10<sup>-5</sup> s<sup>-1</sup>

7 <sup>b</sup> Rate coefficient k (in cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> unit) used to correct the concentration of E-4-methylcyclohexanone by  
 8 loss with the reaction of OH radical ~~=was of~~ 13.7 × 10<sup>-12</sup> (estimated using AOPWIN, v1.92). Photolysis rate  
 9 ~~coefficient constant~~ estimated for E-4-methylcyclohexanone under our experimental conditions. ~~k<sub>p</sub>~~ = 5 × 10<sup>-5</sup> s<sup>-1</sup>

10 <sup>c</sup> Rate coefficient k (in cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> unit) used to correct the concentration of E-4-methylcyclohexanone by  
 11 loss with the reaction of NO<sub>3</sub> radical ~~=was of~~ 2.28 × 10<sup>-16</sup> (estimated using SAR method, Kerducci et al., 2014)

12 <sup>d</sup> Indicated errors are the associated error to the slope of plots obtained in the least square analysis

13 <sup>e</sup> Experiment using a Teflon gas Bag of 150 ~~or~~ 500-L

14 <sup>f</sup> Standard deviations 1σ

15

1 **Table 4.** Experimental conditions and molecular yields of 3,3-dimethylbutanal for the reaction of  
 2 3,3DM1ButOH with atmospheric oxidants.

MSA	Oxidant	Exp	[MSA] (ppm)	[Precursor] (ppm)	[NO] (ppm)	Carbonyl compound Yield (%)	Technique	Average <sup>g</sup> (%)	SAR Yield (%)	
3,3DM1ButOH	Cl <sup>a</sup>	1	11	24	-	40.3±0.2 41.8±4.6	FTIR SPME/GC- TOFMS <sup>d</sup>	39.4±15.0	40	
		2	2.6	8	-	19.6±0.5	SPME/GC- TOFMS <sup>e</sup>			
	Cl <sup>a</sup> + NO	3	6	25	-	55.9±1.7	FTIR	43.3±17.7		
		1	10	21	21	61.6±3.4 34.7±4.4	FTIR SPME/GC- TOFMS <sup>d</sup>			
	OH <sup>b</sup>	2	4	9	8	23.0±4.2	SPME/GC- TOFMS <sup>e</sup>	62.2±15.0		66
		3	10	25	25	48.8±0.6	FTIR			
		1	10	60	36	82.1±4.2 40.8±2.7	FTIR SPME/GC- TOFMS <sup>d</sup>			
		2	7	35	57	67.4±1.4	FTIR			
		3	11	28	55	61.9±0.9	FTIR			
		4	11	29	30	59.1±3.8	FTIR			
		1	11	36	-	29.2±0.5 53.9 <sup>h</sup>	FTIR SPME/GC- TOFMS <sup>d</sup>			
	2	11	32	-	26.5±1.6	FTIR				

3 <sup>a</sup> Rate coefficient k (in cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> unit) used to correct the concentration of 3,3-dimethylbutanal by loss  
 4 with the reaction of Cl atoms ~~= was of~~  $1.7 \times 10^{-10}$  (data of iso-Butyraldehyde and Cl atoms (Thevenet et al., 2000)).  
 5 Photolysis rate coefficient~~stant~~ estimated for 3,3-dimethylbutanal under our experimental conditions. ~~k<sub>p</sub> =~~  $1 \times$   
 6  $10^{-4}$  s<sup>-1</sup>

7 <sup>b</sup> Rate coefficient k (in cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> unit) used to correct the concentration of 3,3-dimethylbutanal by loss  
 8 with the reaction of OH radical ~~= was of~~  $2.73 \times 10^{-11}$  (Aschmann et al., 2010). Photolysis rate coefficient~~stant~~  
 9 estimated for 3,3-dimethylbutanal under our experimental conditions. ~~k<sub>p</sub> =~~  $1 \times 10^{-4}$  s<sup>-1</sup>

10 <sup>c</sup> Rate coefficient k (in cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> unit) used to correct the concentration of 3,3-dimethylbutanal by loss  
 11 with the reaction of NO<sub>3</sub> radical ~~= was of~~  $1.27 \times 10^{-14}$  (D'Anna, 2001).

12 <sup>d</sup> Experiment using a FTIR Gas Cell of 50 L

13 <sup>e</sup> Experiment using a Teflon gas Bag of 150 ~~or~~ 500 L

14 <sup>f</sup> Indicated errors are the associated error to the slope of plots obtained in the least square analysis

15 <sup>g</sup> Standard deviations 1σ

16 <sup>h</sup> Yield estimated using only one data

17

1 **Table 5.** Experimental conditions and molecular yields of 3,3-dimethyl-2-butanone for the reaction  
 2 of 3,3DM2ButOH with atmospheric oxidants

MSA	Oxidant	Exp	[MSA] (ppm)	[Precursor] (ppm)	[NO] (ppm)	Carbonyl compound <sup>f</sup> Yield (%)	Technique	Average <sup>gk</sup> (%)	SAR Yield (%)	
3,3DM2ButOH	Cl <sup>a</sup>	1	14	31	-	42.8±0.7 45.2±1.1	FTIR SPME/GC- TOFMS <sup>d</sup>	43.2±1.8		
		2	2.3	8	-	41.7±3.2	SPME/GC- TOFMS <sup>e</sup>			
	Cl <sup>a</sup> + NO	1	14	28	20	36.7±5.0 49.6±4.5	FTIR SPME/GC- TOFMS <sup>d</sup>	44.2±7.4	40	
		2	3	7	6	39.0±6.1	SPME/GC- TOFMS <sup>e</sup>			
	OH <sup>b</sup>	3	8	28	27	51.5±3.9	FTIR	80.7±6.5	91	
		1	8	55	42	82.8±3.1 71.2±2.6	FTIR SPME/GC- TOFMS <sup>d</sup>			
	NO <sub>3</sub> <sup>c</sup>		2	5	66	36	85.4±5.8	FTIR	58.0±10.9	99
			3	11	28	29	83.6±3.0	FTIR		
		1	12	30	-	66.7±2.05 45.9±1.6	FTIR SPME/GC- TOFMS <sup>d</sup>			
		2	9	30	-	61.5±1.4	FTIR			

3 <sup>a</sup> Rate coefficient k (in cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> unit) used to correct the concentration of 3,3-dimethyl-2-butanone by  
 4 loss with the reaction of Cl atoms ~~=was of~~  $4.8 \times 10^{-11}$  (Farrugia et al., 2015)). Photolysis rate ~~coefficient~~  
 5 estimated for 3,3-dimethyl-2-butanone under our experimental conditions: ~~k<sub>p</sub> = 7 × 10<sup>-5</sup> s<sup>-1</sup>~~

6 <sup>b</sup> Rate coefficient k (in cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> unit) used to correct the concentration of 3,3-dimethyl-2-butanone by  
 7 loss with the reaction of OH radical ~~= was of~~  $1.21 \times 10^{-12}$  (Wallington and Kurylo., 1987). Photolysis rate  
 8 ~~coefficient~~ estimated for 3,3-dimethyl-2-butanone under our experimental conditions: ~~k<sub>p</sub> = 7 × 10<sup>-5</sup> s<sup>-1</sup>~~

9 <sup>c</sup> No corrected

10 <sup>d</sup> Experiment using a FTIR Gas Cell of 50 L

11 <sup>e</sup> Experiment using a Teflon gas Bag of 150 ~~or~~ 500 L

12 ~~<sup>f</sup> Standard deviations 1σ~~

13 <sup>f</sup> Indicated errors are the associated error to the slope of plots obtained in the least square analysis

14 ~~<sup>g</sup> Standard deviations 1σ~~

15

16

1 **Table 6:** Summary of molecular yields (%) of reaction products identified in the reaction of MSA  
 2 with atmospheric oxidants and the total carbon balance (%).

Product	MSA			
	4MCHexOH			
	Cl	Cl + NO	OH	NO <sub>3</sub>
E-4-methylcyclohexanone <sup>1</sup>	25.2 ± 1.9	29.5 ± 0.7	40.2 ± 5.4	58.0 ± 23.5
HCOH <sup>2</sup>	9	-	-	-
Nitrated compounds	-	20	10	60
Total Carbon	<del>26</del> <sup>34</sup>	50	50	~100
	3,3DM1ButOH			
	Cl	Cl + NO	OH	NO <sub>3</sub>
3,3-dimethylbutanal <sup>1</sup>	39.4 ± 15.0	43.3 ± 17.7	62.2 ± 15.0	36.2 ± 14.6
HCOH <sup>2</sup>	10	22	-	-
2,2-dimethylpropanal <sup>2</sup>	22	8	23	-
Acetone <sup>2</sup>	5	17	-	-
Nitrated compounds	-	40 <sup>54</sup>	35 <sup>65</sup>	200 <sup>76</sup>
Total Carbon <sup>3,4</sup>	<del>61</del> <sup>7</sup>	<del>62</del> <sup>8</sup>	<del>81</del> <sup>5</sup>	36
	3,3DM2ButOH			
	Cl	Cl + NO	OH	NO <sub>3</sub>
3,3-dimethyl-2-butanone <sup>1</sup>	43.2 ± 1.8	44.2 ± 7.4	80.7 ± 6.5	58.0 ± 10.9
HCOH <sup>2</sup>	10	64	-	-
2,2-dimethylpropanal <sup>2</sup>	14	10	14	-
Acetone <sup>2</sup>	3	58	-	-
Acetaldehyde <sup>2</sup>	-	17	-	-
Nitrated compounds	-	30	20	120
Total Carbon <sup>3,4</sup>	~60	<del>98</del> <sup>12</sup>	<del>93</del> <sup>4</sup>	58

3 <sup>1</sup>Average Tables 3-5; <sup>2</sup>Molecular yield obtained in earlier step of reaction.;

4 
$$^{33}\text{Total Carbon (\%)} = \sum_1^i \left( \frac{n^{\circ} \text{ of carbon of product}_i}{n^{\circ} \text{ of carbon of MSA}} \times \text{molar yield}_i(\%) \right)$$

5 <sup>4</sup>Without accounting nitrated compounds; <sup>54</sup>From analysis of the experiment number 3 for the reaction of Cl +  
 6 NO; <sup>65</sup>From average of experiments number 2, 3 and 4 for the reaction with OH; <sup>76</sup>From analysis of the  
 7 experiments number 1 and 2 for reaction with NO<sub>3</sub>.

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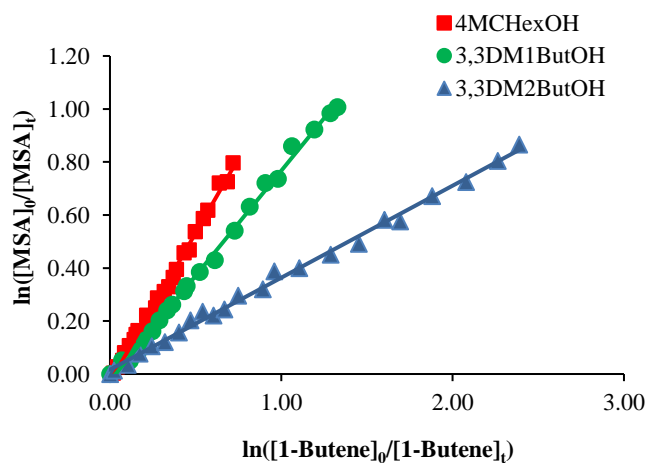
**Table 7.** Lifetimes of 4MCHexOH, 3,3DM1ButOH and 3,3DM2ButOH.

	$\tau_{OH}$ (days)	$\tau_{Cl}^a$ (days)	$\tau_{Cl}^b$ (days)	$\tau_{NO_3}$ (days)	$\tau_{wet}$ (years)	$\tau_{global}^a$ (days)
<b>4MCHexOH</b>	0.624	31.280	0.24	8.617-93	~2.1	0.585
<b>3,3DM1ButOH</b>	2.1708	432.0387	0.33	13 <sup>c</sup>	~15.8	1.782
<b>3,3DM2ButOH</b>	1.10	95.65	0.74	6.73 <sup>c</sup>	11.3	0.94

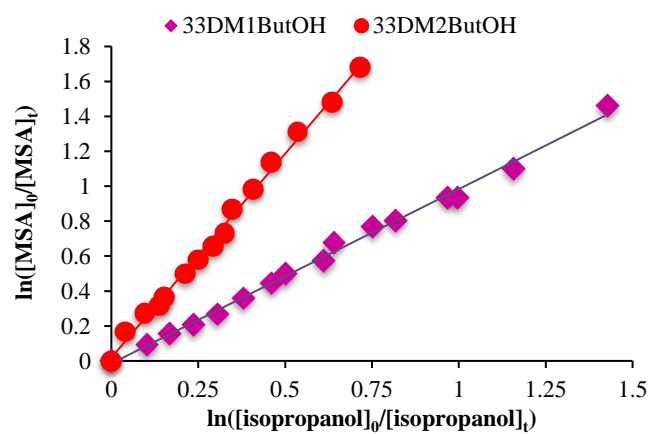
6 <sup>a</sup>Determined with the 24 hours average of chlorine atoms.  
7 <sup>b</sup>Determined with the peak concentration of chlorine atoms.  
8 <sup>c</sup>Determined using the rate coefficient obtained by Moreno A. et al., 2014.

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1 A)

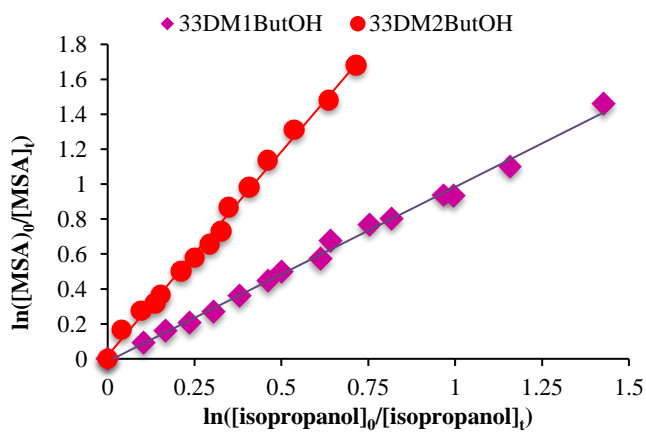


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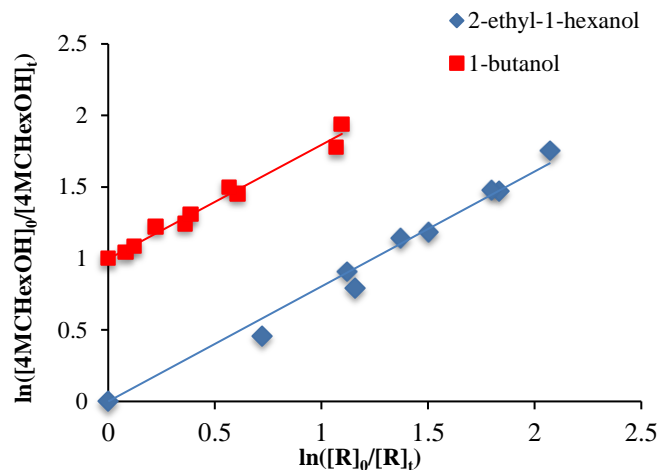
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B)



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5 C)

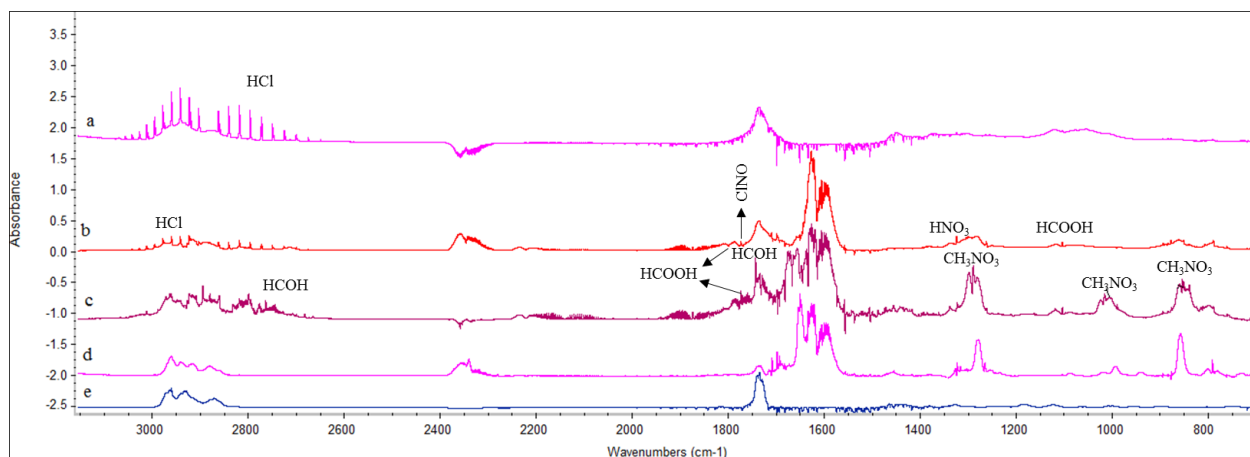


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2 Fig.1: Relative rate plots for the reaction of (A) MSA with chlorine atoms employing 1-butene as a reference  
 3 compound (B) 3,3-Dimethylbutanols and OH radical with isopropanol as a reference compound and (C)  
 4 4MCHexOH and NO<sub>3</sub> with two reference compounds. Data for 1-butanol have been vertically displaced for clarity.

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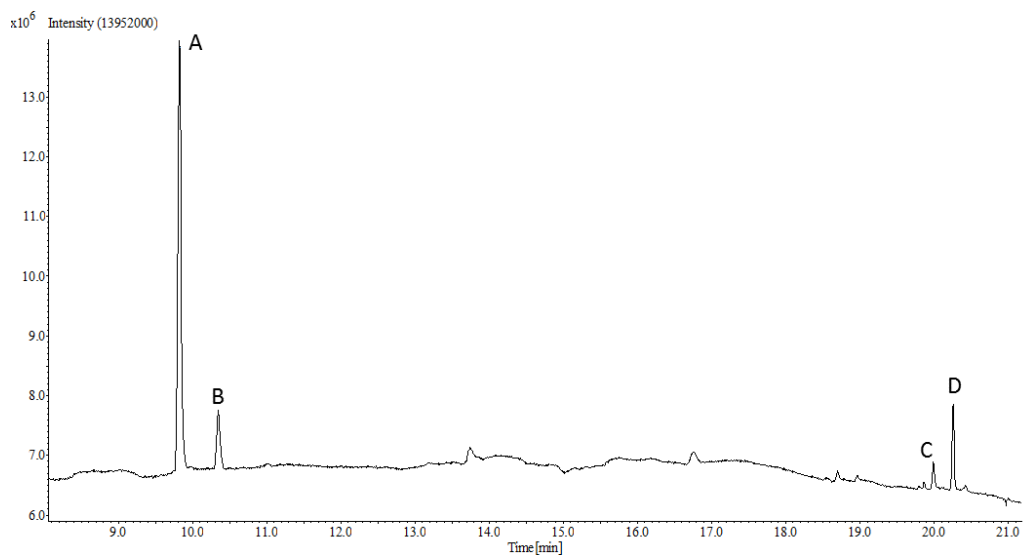
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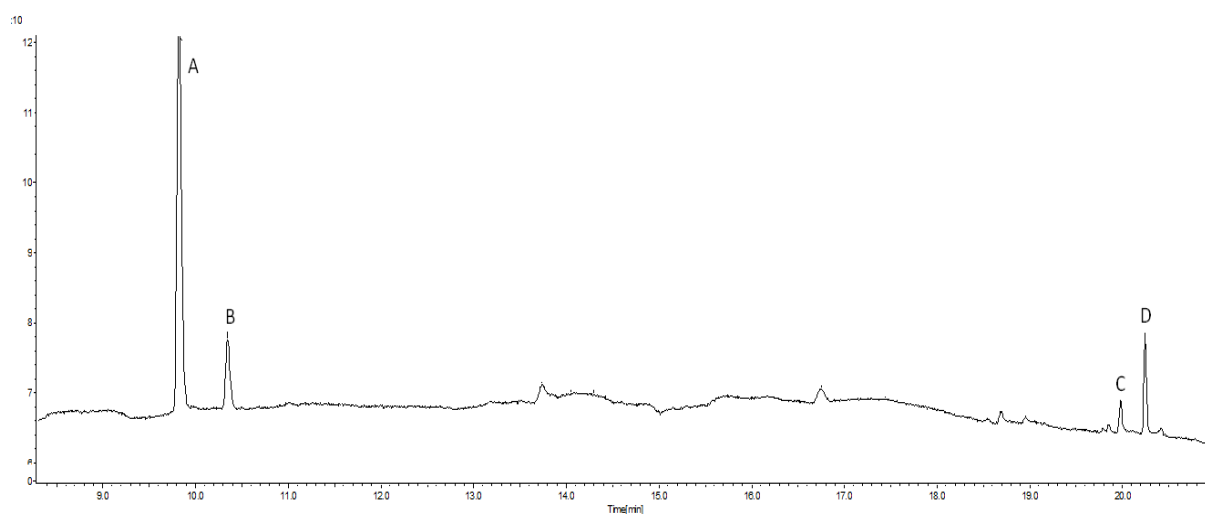
9 Fig. 2: Product spectra for reaction of 4MCHexOH with: (a) chlorine atoms at 10 min (x 2 to clarify), (b) ~~Chlorine~~  
 10 atoms and NO<sub>x</sub> at 7 min. (c) OH radical at 40 min and (d) NO<sub>3</sub> radical at 32 min. (e) Spectrum of 4-  
 11 methylcyclohexanone a commercial sample.

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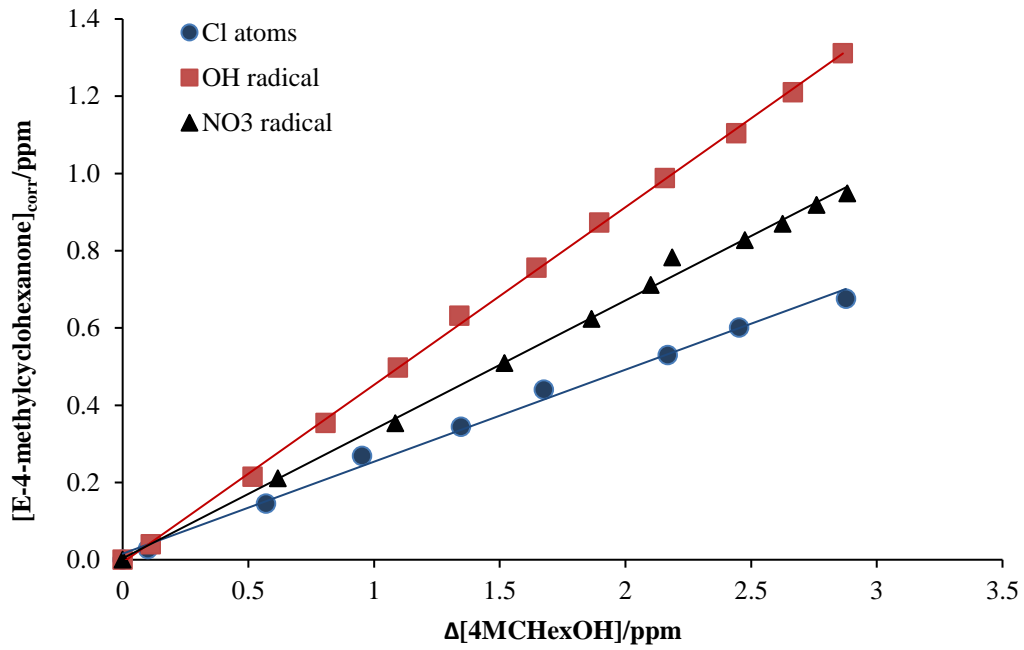
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Fig. 3: SPME/GC-TOFMS chromatogram for the reaction of 4MCHexOH with Chlorine atoms after 15 minutes of reaction. Peak (A) 4MCHexOH. Peak (B) E-4-methylcyclohexanone. Peaks (C) and (D) reaction products.

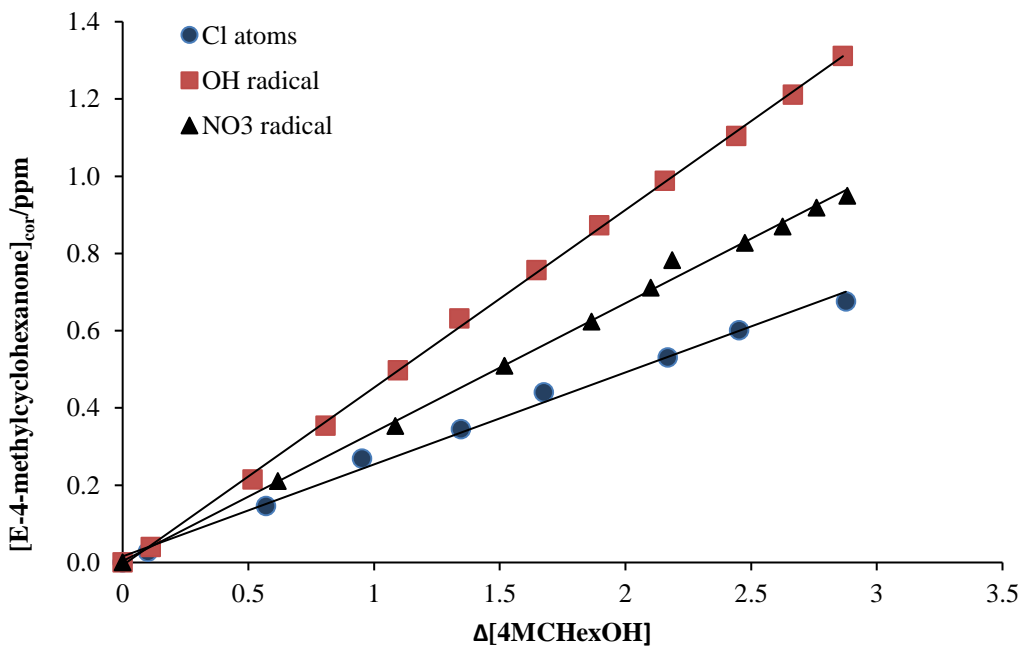
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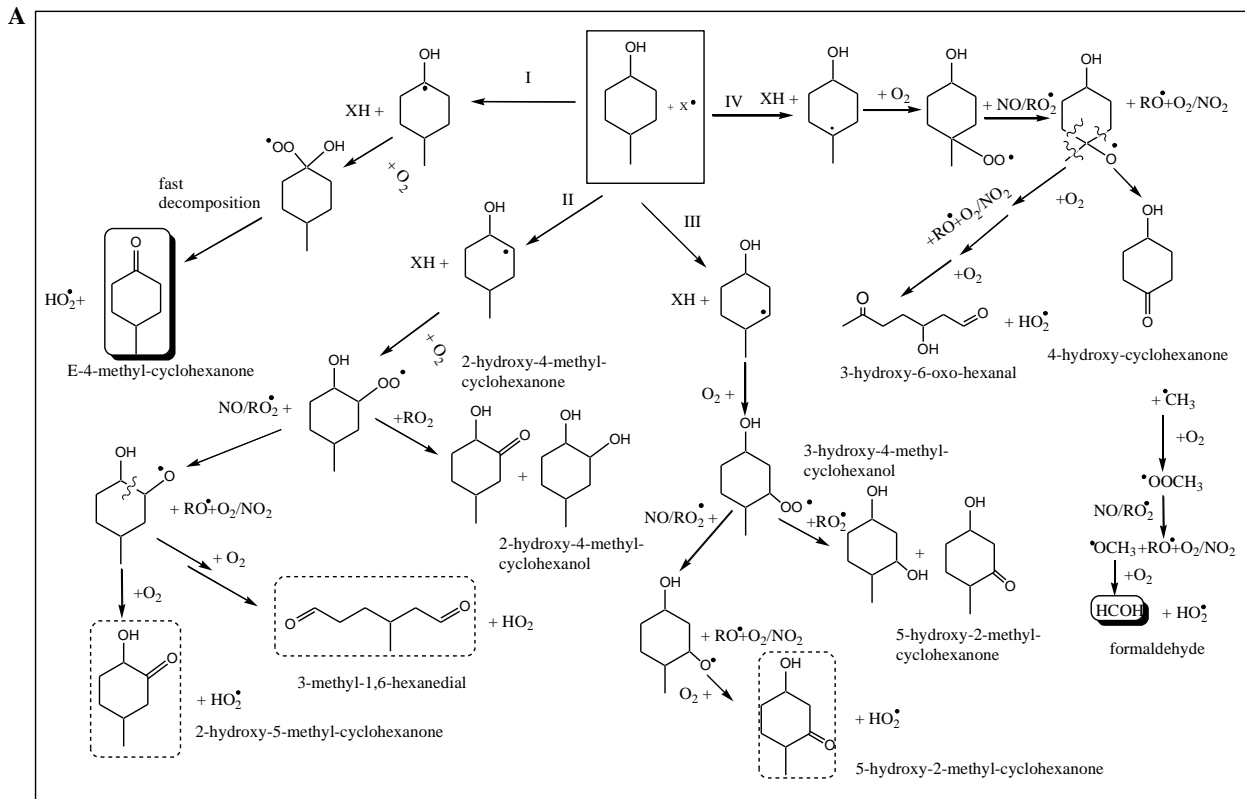


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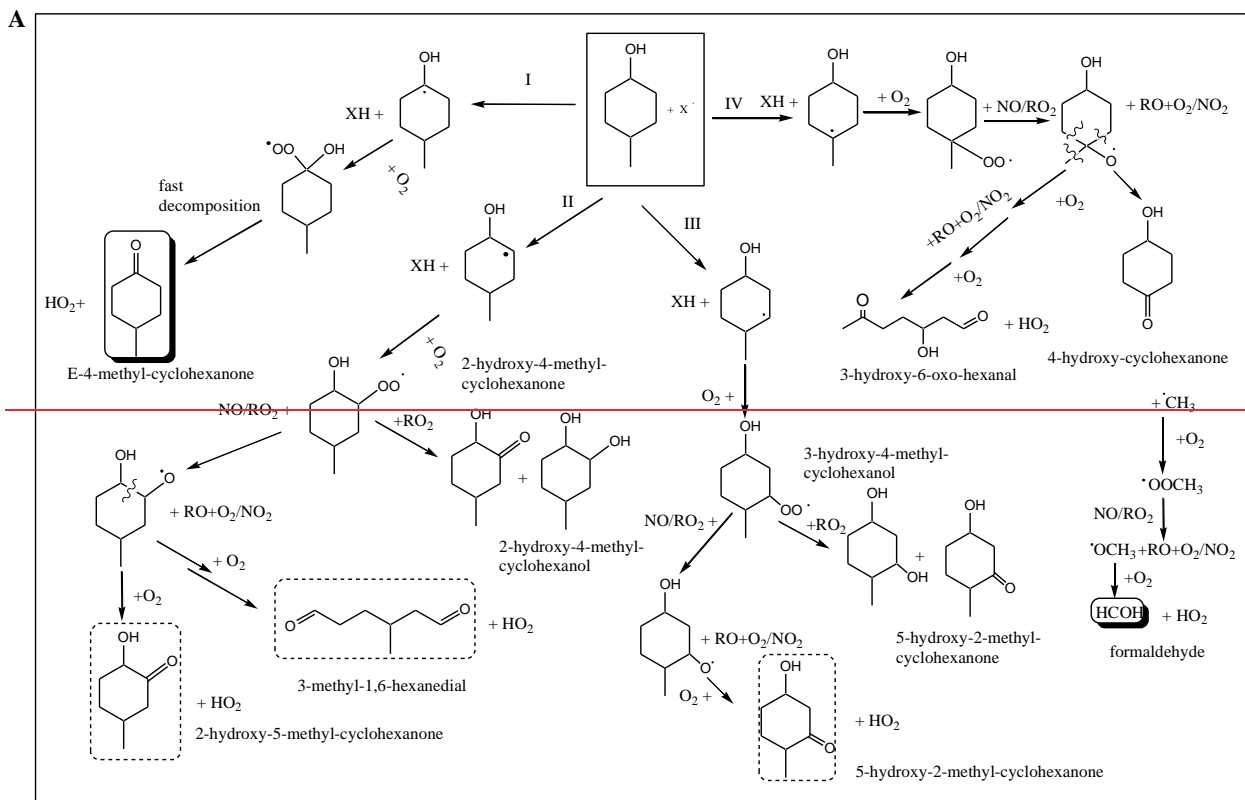


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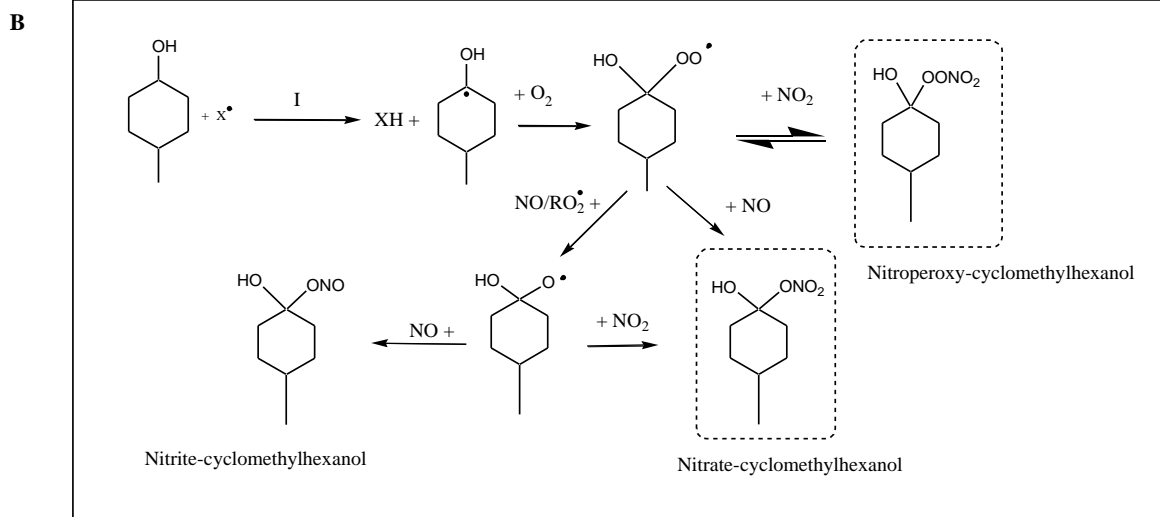
Fig. 4: Plots of corrected concentration of concentrations of E-4-methylcyclohexanone ([E-4-methylcyclohexanone]<sub>corr</sub>) against 4MCHexOH consumed ( $\Delta[4MCHexOH]$ ) for Cl atoms (in absence of NO<sub>x</sub>) and OH and NO<sub>3</sub> radical reactions.



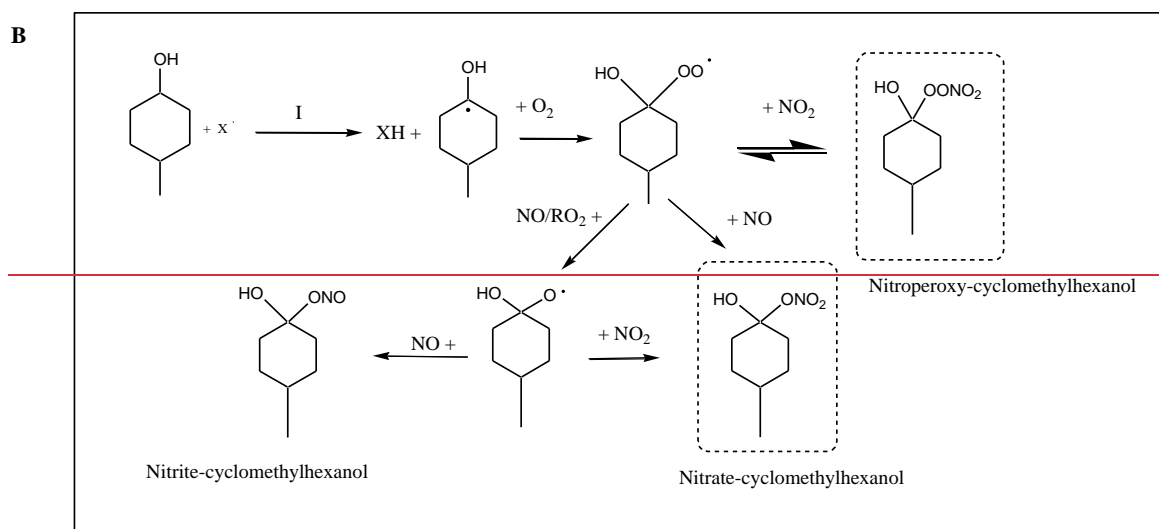
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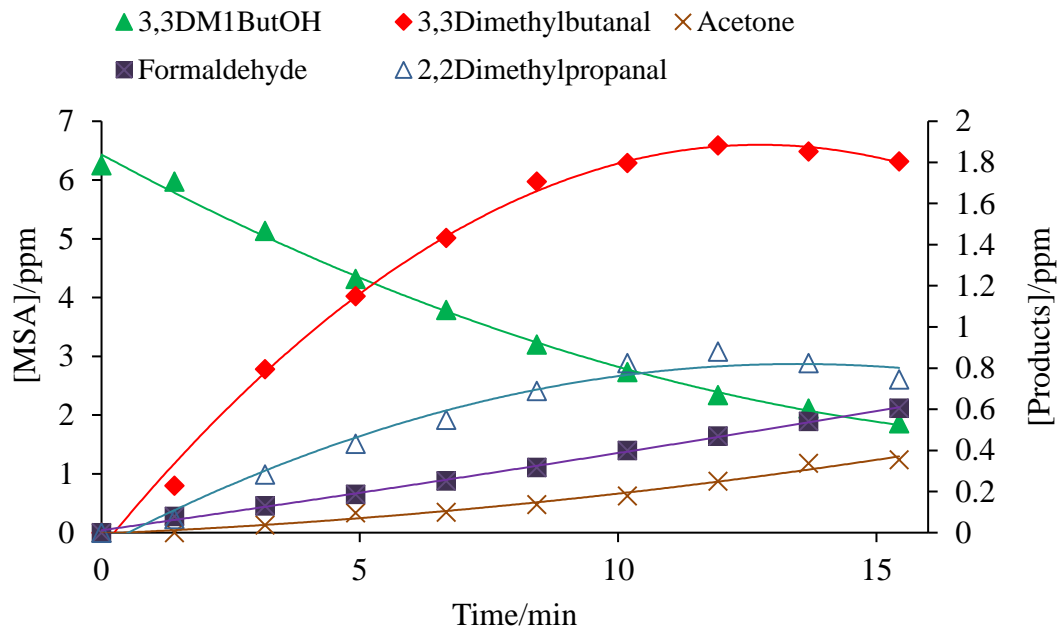
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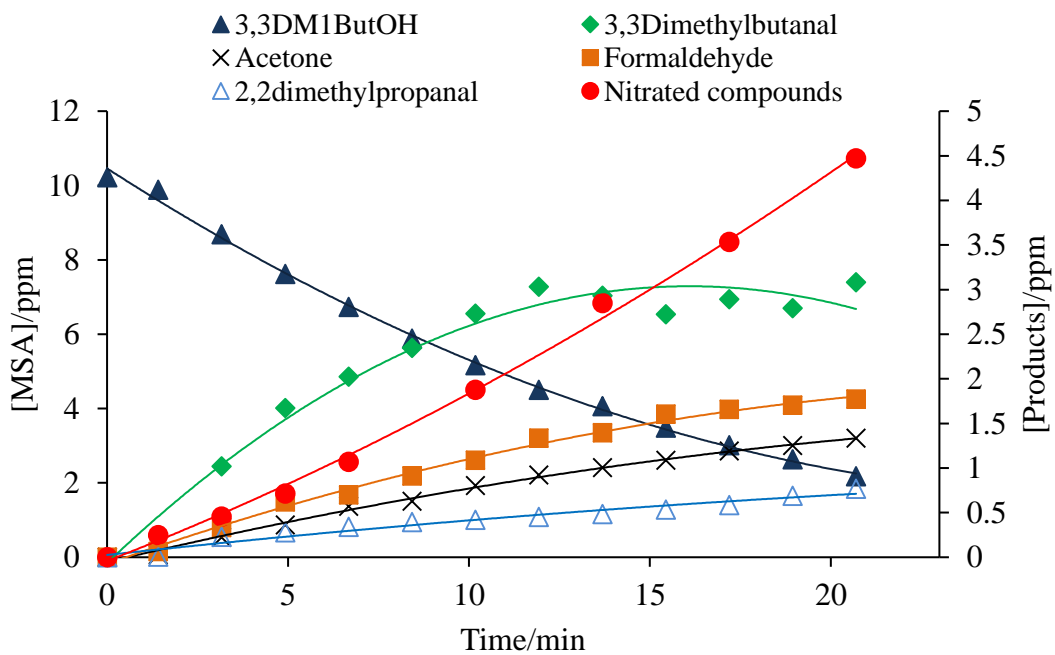
3 Fig. 5: Reaction mechanism for the degradation of 4MCHexOH with X (Cl atom, OH and NO<sub>3</sub> radicals). (A)  
 4 Mechanism for the formation of carbonyl compounds, (B) Mechanism for the formation of nitrated compounds.  
 5 Compounds marked with solid line are positively identified. Compounds marked with shaded lines are not  
 6 positively identified.

1 A)



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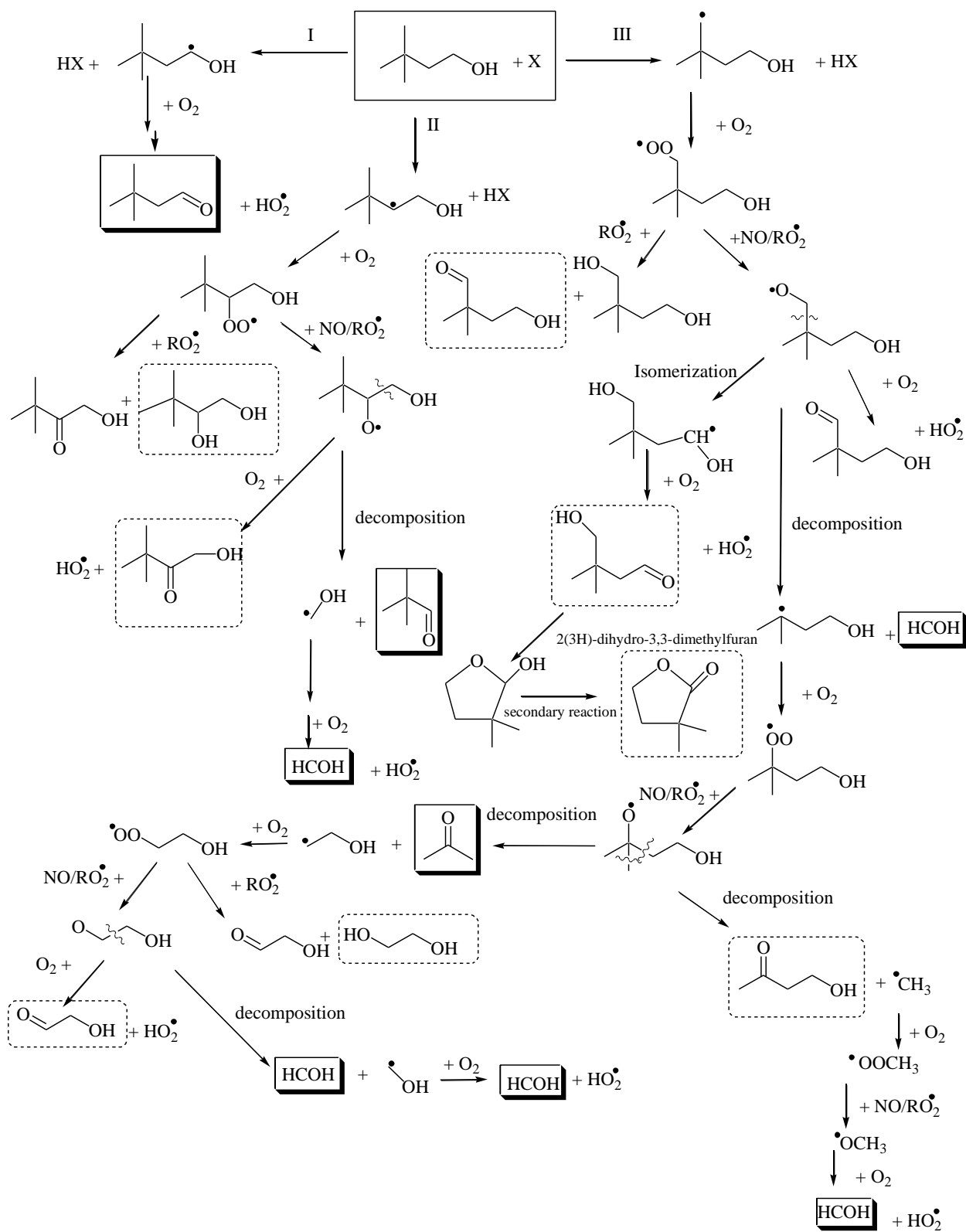
3 B)

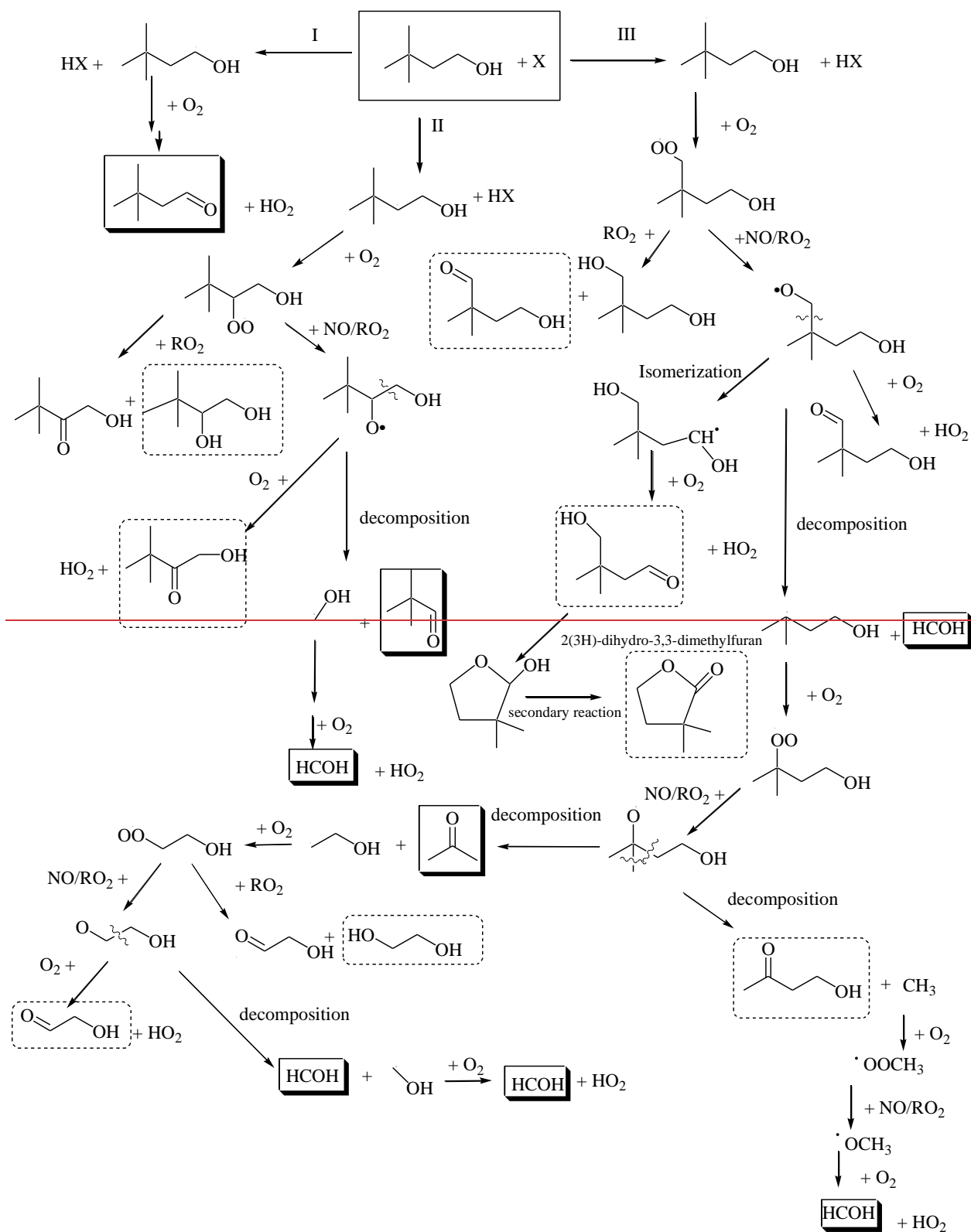


4

5 Fig. 6: Concentration-time profiles of MSA (3,3DM1ButOH) and reaction products formed in the reaction of  
6 3,3DM1ButOH with Cl atoms in absence (A) and presence of NO (B).

7



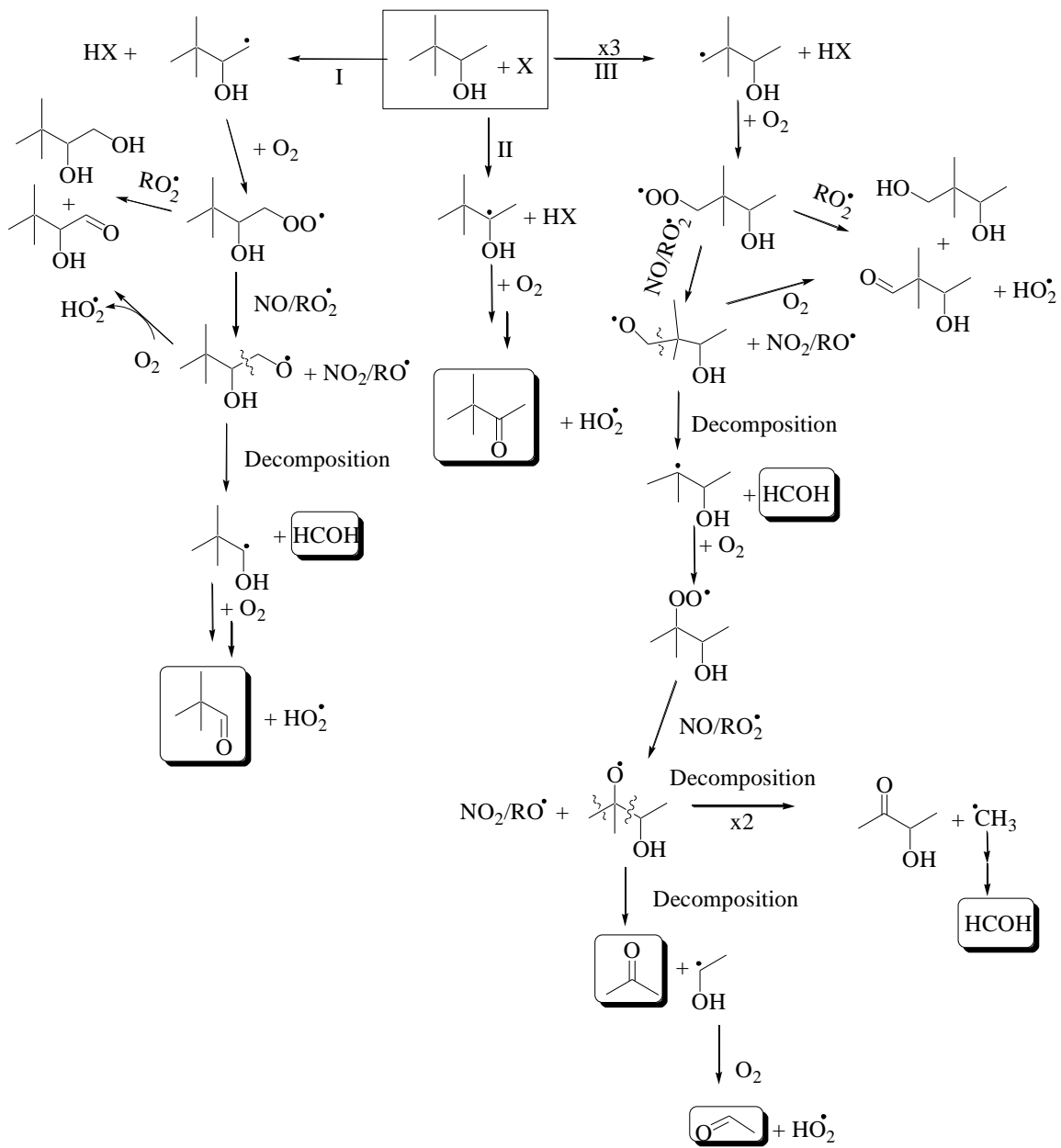


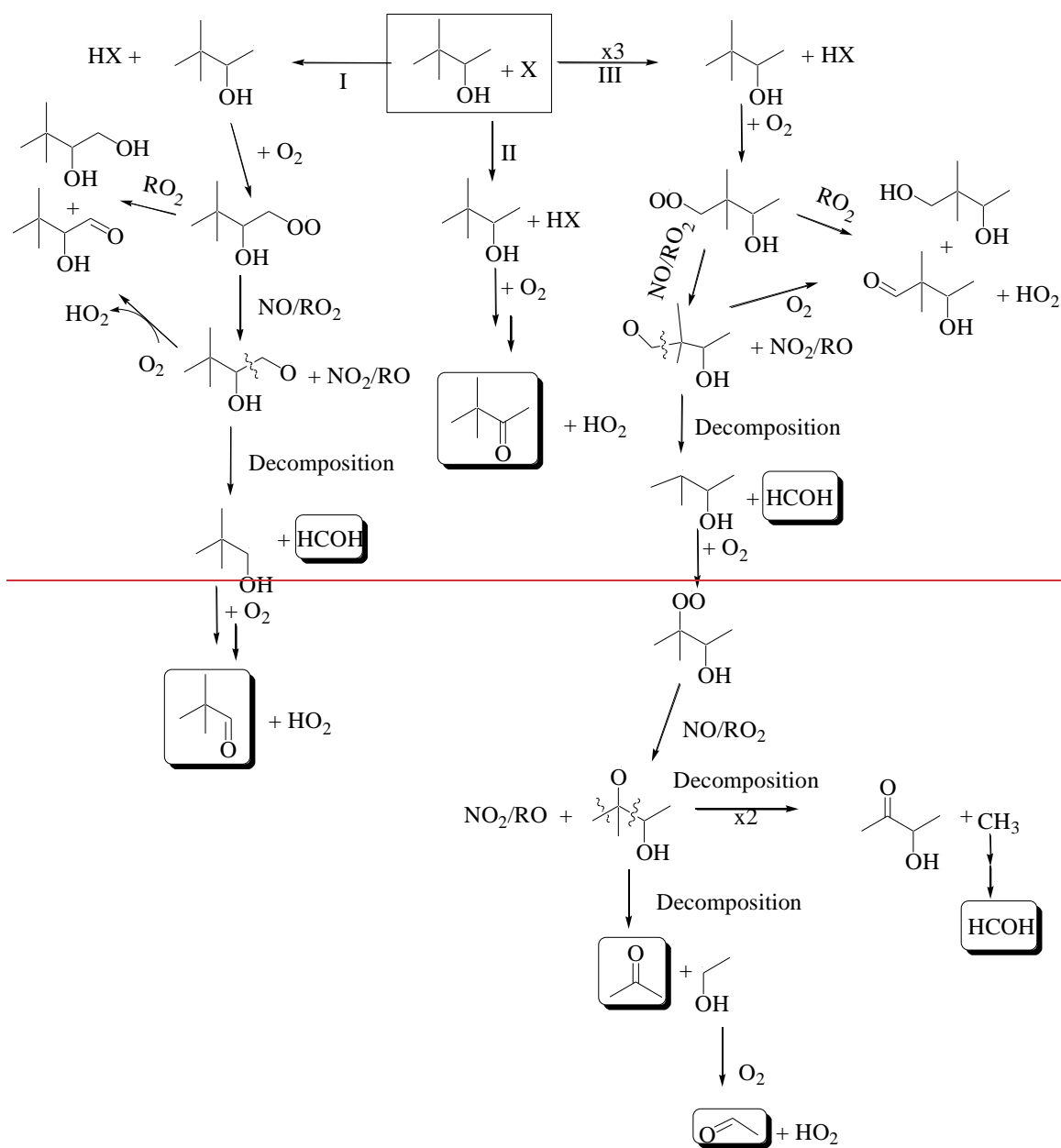
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2 Fig. 7: Reaction mechanism for the degradation of 3,3DM1ButOH with X (Cl atom, OH and NO<sub>3</sub> radical).  
 3 Mechanism for the formation of carbonyl compounds. Compounds marked with solid line are positively identified.  
 4 Compounds marked with shaded lines are not positively identified.

5

6





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2 Fig. 8: Reaction mechanism for the degradation of 3,3DM2ButOH with X (Cl atom, OH and NO<sub>3</sub> radical).  
 3 Mechanism to form carbonyl compounds. Compounds marked with solid line are positively identified. Compounds  
 4 marked with shaded lines are not positively identified.

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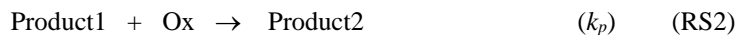
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## Supplementary material

### S1. Tuazon formalism

Formulism of Tuazon et al. (1986). This procedure is described in A1 supplementary information.



Where Y is the yield of the primary product (product1) from the oxidation of the methyl saturated alcohols.

If we assume that the concentration of oxidant was constant during the irradiation period, then:

$$[\text{MSA}]_{t_2} = [\text{MSA}]_{t_1} \cdot e^{-(k_s \cdot [\text{Ox}])(t_2 - t_1)} \quad (\text{S1})$$

From Eq (S1) it is possible to calculate the concentration of oxidant in the system.

Using the relationship obtained by Tuazon et al. (1986) the corrected concentration of the reaction products can be calculated as follows:

$$[\text{product1}]_{t_2} = [\text{product1}]_{t_1} \cdot e^{-(k_p \cdot [\text{Ox}] + k_1)(t_2 - t_1)} + \frac{Y_{t_1-t_2} \cdot [\text{MSA}]_{t_1} \cdot k_s [\text{Ox}]}{\{(k_p - k_s) \cdot [\text{Ox}] + k_1\}} \cdot [e^{-(k_s \cdot [\text{Ox}])(t_2 - t_1)} - e^{-(k_p \cdot [\text{Ox}] + k_1)(t_2 - t_1)}] \quad (\text{S2})$$

Where  $[\text{MSA}]_{t_1}$ ,  $[\text{product1}]_{t_1}$  and  $[\text{MSA}]_{t_2}$ ,  $[\text{product1}]_{t_2}$  are the observed concentrations of the methyl saturated alcohol and the products at times  $t_1$  and  $t_2$  respectively, and  $Y_{t_1-t_2}$  is the yield of formation of the individual products on the period of time  $(t_1 - t_2)$ .

By means of equations (S1) and (S2),  $Y_{t_1-t_2}$  can be calculated. The concentration of the reaction products, corrected for the reaction with radical and other processes of loss is given by:

$$[\text{product1}]_{t_2}^{\text{corr}} = [\text{product1}]_{t_1}^{\text{corr}} + Y_{t_1-t_2} \cdot ([\text{MSA}]_{t_1} - [\text{MSA}]_{t_2}) \quad (\text{S3})$$

Where  $[\text{product1}]_{t_1}^{\text{corr}}$  and  $[\text{product1}]_{t_2}^{\text{corr}}$  are the concentrations of the product1 corrected at times  $t_1$  and  $t_2$  respectively:

The value of  $k_s$  has been obtained in this work. The value of  $k_p$  is taken from the bibliography or estimates with SAR method and  $k_1$  is obtained from experiments carried out in the laboratory, taken from bibliography or estimated with the best fit of experimental data.

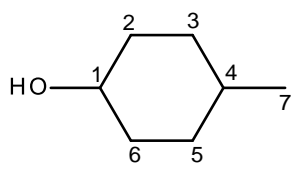
## S2. Structure-Activity Relationship (SAR) method

SAR method allows to estimate a rate coefficient of an organic compound from its structure. The only possibility of the reaction of the studied compounds in this work with the atmospheric oxidants is the abstraction of an hydrogen atom. Consequently, the estimated rate coefficients of MSA are obtained from the sum of the rate coefficients for the H-atom abstraction from the primary ( $k_{\text{prim}}$  ( $\text{CH}_3\text{-}$ )), secondary ( $k_{\text{sec}}$  ( $-\text{CH}_2\text{-}$ )) and tertiary ( $k_{\text{tert}}$  ( $-\text{CH}<$ )) groups and from the alcohol ( $k_{\text{OH}}$  ( $-\text{OH}$ )) group, taking into account the influence of the substituents attached to these groups, through substituent factors  $F(X)$ ,  $F(Y)$  and  $F(Z)$  (Equation S4).

$$k_{\text{abs}} = \sum k_{\text{prim}}F(X) + \sum k_{\text{sec}}F(X)F(Y) + \sum k_{\text{tert}}F(X)F(Y)F(Z) + \sum k_{\text{OH}} \quad (\text{S4})$$

At 298K rate coefficients for H-atom abstraction (in units of  $\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ ) and the reactivity factor for the reaction with OH are  $k_{\text{prim}} = 1.36 \times 10^{-13}$ ;  $k_{\text{sec}} = 9.34 \times 10^{-13}$ ;  $k_{\text{tert}} = 1.94 \times 10^{-12}$  and  $k_{\text{OH}} = 1.4 \times 10^{-13}$ ;  $F(\text{CH}_3) = 1$ ;  $F(-\text{CH}_2\text{-}) = F(-\text{CH}<) = F(>\text{C}<) = 1.23$  and  $F(-\text{OH}) = 3.5$  from AOPWIN. The parameters for the reaction with Cl atoms are  $k_{\text{prim}} = 2.84 \times 10^{-11}$ ;  $k_{\text{sec}} = 8.95 \times 10^{-11}$ ;  $k_{\text{tert}} = 6.48 \times 10^{-11}$  (in units of  $\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ );  $F(\text{CH}_3) = 1$ ;  $F(-\text{CH}_2\text{-}) = F(-\text{CH}<) = 0.8$  and  $F(-\text{OH}) = 1.18$  from Calvert et al. 2011. By last, the parameters used for the reaction with  $\text{NO}_3$  radicals are  $k_{\text{prim}} = 1 \times 10^{-18}$ ;  $k_{\text{sec}} = 2.56 \times 10^{-17}$ ;  $k_{\text{tert}} = 1.05 \times 10^{-16}$  and  $k_{\text{OH}} = 2 \times 10^{-17}$  (in units of  $\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ );  $F(\text{CH}_3) = 1$ ;  $F(-\text{CH}_2\text{-}) = 1.02$ ;  $F(-\text{CH}<) = 1.61$ ;  $F(>\text{C}<) = 2.03$  and  $F(-\text{OH})=18$  from Kerdouci et al. 2010, 2014.

The calculations for 4-methyl-cyclohexanol are the following:



$$k_1 = k_{\text{tert}} \times F(-\text{OH}) \times F(-\text{CH}_2\text{-}) \times F(-\text{CH}_2\text{-})$$

$$k_2 = k_3 = k_5 = k_6 = k_{\text{sec}} \times F(-\text{CH}<) \times F(-\text{CH}_2\text{-})$$

$$k_4 = k_{\text{tert}} \times F(-\text{CH}_3) \times F(-\text{CH}_2\text{-}) \times F(-\text{CH}_2\text{-})$$

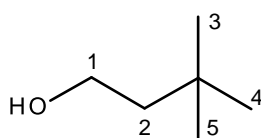
$$k_7 = k_{\text{prim}} \times F(-\text{CH}<)$$

$$k_{4\text{MCHexOH+Cl}} = 3.42 \times 10^{-10} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$$

$$k_{4\text{MCHexOH+OH}} = 1.92 \times 10^{-11} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$$

$$k_{4\text{MCHexOH+NO}_3} = 2.27 \times 10^{-15} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$$

The calculations for 3,3-dimethyl-1-butanol are the following:



$$k_1 = k_{\text{sec}} \times F(-\text{OH}) \times F(-\text{CH}_2\text{-})$$

$$k_2 = k_{\text{sec}} \times F(>\text{C}<) \times F(-\text{CH}_2\text{-})$$

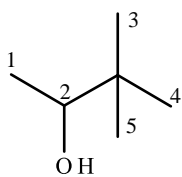
$$k_3 = k_4 = k_5 = k_{\text{prim}} \times F(>\text{C}<)$$

$$k_{3,3\text{DM1ButOH+Cl}} = 2.10 \times 10^{-10} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$$

$$k_{3,3\text{DM1ButOH+OH}} = 6.08 \times 10^{-12} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$$

$$k_{3,3\text{DM1ButOH+NO}_3} = 0.55 \times 10^{-15} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$$

The calculations for 3,3-dimethyl-2-butanol are the following:



$$k_1 = k_{\text{prim}} \times F(-\text{CH} <)$$

$$k_2 = k_{\text{tert}} \times F(>\text{C} <) \times F(-\text{CH}_3) \times F(-\text{OH})$$

$$k_3 = k_4 = k_5 = k_{\text{prim}} \times F(>\text{C} <)$$

$$\underline{k_{3,3\text{DM}2\text{ButOH}+\text{Cl}} = 1.52 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}}$$

$$\underline{k_{3,3\text{DM}2\text{ButOH OH}} = 9.16 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}}$$

$$\underline{k_{3,3\text{DM}2\text{ButOH}+\text{NO}_3} = 3.86 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}}$$

## Tables

**Table S1:** Rate coefficients at 298 K for Cl, OH and NO<sub>3</sub> reactions with alkanes, saturated alcohols and saturated compounds with a similar structure of MSA. k in cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> unit.

Compound	k <sub>Cl</sub> ×10 <sup>11</sup>	k <sub>OH</sub> ×10 <sup>12</sup>	k <sub>NO<sub>3</sub></sub> ×10 <sup>15</sup>
<b>Alkanes</b>			
Methane	0.01	0.0064	<0.001 <sup>f</sup>
Ethane	5.70 <sup>a</sup>	0.24 <sup>f</sup>	<0.01 <sup>f</sup>
Propane	12.7 <sup>a</sup>	1.09 <sup>f</sup>	<0.07 <sup>f</sup>
Butane	19.4 <sup>a</sup>	2.36 <sup>f</sup>	0.046 <sup>f</sup>
Pentane	25.0 <sup>a</sup>	3.80 <sup>f</sup>	0.087 <sup>f</sup>
Hexane	30.5 <sup>a</sup>	5.20 <sup>f</sup>	0.110 <sup>f</sup>
Heptane	36.5 <sup>a</sup>	6.76 <sup>f</sup>	0.150 <sup>f</sup>
Octane	40.9 <sup>a</sup>	8.11 <sup>kf</sup>	0.190 <sup>f</sup>
Nonane	46 <sup>b</sup>		0.220 <sup>b</sup>
Decane	52.7 <sup>b</sup>		0.260 <sup>b</sup>
2-Methylpropane	13.0 <sup>a</sup>	2.12 <sup>f</sup>	0.106 <sup>f</sup>
2-Methylbutane	19.6 <sup>a</sup>	3.60 <sup>f</sup>	0.162 <sup>f</sup>
2-Methylpentane	25.8 <sup>a</sup>	5.2 <sup>f</sup>	0.180 <sup>f</sup>
3-Methylpentane	26.9 <sup>b</sup>	5.2 <sup>f</sup>	0.220 <sup>f</sup>
2-Methylhexane	31.2 <sup>a</sup>	6.72 <sup>e</sup>	-
2,3-Dimethylbutane	20 <sup>a</sup>	5.78 <sup>f</sup>	0.44 <sup>f</sup>
2,2-Dimethylbutane	-	22.3 <sup>f</sup>	-
2,2,4-trimethylpentane	22.5 <sup>a</sup>	3.34 <sup>f</sup>	0.09 <sup>f</sup>
Cyclopentane	32.6 <sup>c</sup>	4.97 <sup>f</sup>	-
Cyclohexane	33 <sup>d</sup>	6.97 <sup>f</sup>	0.14 <sup>f</sup>
Methylcyclohexane	35.1 <sup>e</sup>	9.5 <sup>e</sup>	-
Trans-1,4-dimethylcyclohexane	36.3 <sup>e</sup>	12.1 <sup>e</sup>	-
Ethylcyclohexane	38.8 <sup>e</sup>	11.8 <sup>e</sup>	-
<b>Saturated Alcohols</b>			
Methanol	5.5	0.9	0.13
Ethanol	10	3.2	<2
1-propanol	16	5.8	<2.1
2-propanol	8.7	5.1	1.4
1-butanol	22	8.5	1.87 <sup>g</sup>
2-butanol	12 <sup>h</sup>	8.7	2.51 <sup>q</sup>
1-pentanol	24 <sup>i</sup>	11 <sup>i</sup>	-
2-pentanol	22 <sup>i</sup>	11.8 <sup>i</sup>	-
3-pentanol	20 <sup>i</sup>	13 <sup>i</sup>	-
1-hexanol	31 <sup>i</sup>	13 <sup>i</sup>	-
2-hexanol	-	12 <sup>i</sup>	-

1-heptanol	37 <sup>i</sup>	13 <sup>i</sup>	-
4-heptanol	-	-	<6.2
1-octanol	42 <sup>i</sup>	13 <sup>i</sup>	-
2-methyl-1-propanol	20.6 <sup>j</sup>	11.4 <sup>j</sup>	-
2-methyl-2-propanol	3.26 <sup>k</sup>	1.07 <sup>k</sup>	-
2-ethyl-1-hexanol	18.8 <sup>l</sup>	11.3 <sup>l</sup>	-
2-methyl-1-butanol	-	-	2.32 <sup>g</sup>
2-methyl-2-butanol	7 <sup>h</sup>	3.64 <sup>n</sup>	1.57 <sup>q</sup>
3-methyl-1-butanol	25 <sup>i</sup>	14 <sup>i</sup>	2.09 <sup>g</sup>
3-methyl-2-butanol	11.7 <sup>h</sup>	12.5 <sup>o</sup>	3.06 <sup>q</sup>
2-methyl-2-pentanol	-	7.1 <sup>i</sup>	-
4-methyl-2-pentanol	-	17 <sup>i</sup>	-
2,2-dimethyl-1-propanol	-	5.5 <sup>i</sup>	-
<b>3,3-dimethyl-1-butanol</b>	<b><del>26.97</del>0</b>	<b><del>5.33</del>57</b>	1.78 <sup>g</sup>
<b>3,3-dimethyl-2-butanol</b>	<b>12.1</b>	<b><del>10.50</del>1</b>	3.44 <sup>g</sup>
2,3-dimethyl-2-butanol	10.3 <sup>h</sup>	9.1 <sup>n</sup>	3.64 <sup>q</sup>
2,4-dimethyl-2-pentanol	-	11 <sup>i</sup>	-
3,5-dimethyl-3-hexanol	-	13 <sup>i</sup>	-
cyclopentanol	-	10.7 <sup>k</sup>	-
cyclohexanol	32.1 <sup>m</sup>	19.0 <sup>p</sup>	-
<b>4MCHexOH</b>	<b><del>37.01</del></b>	<b><del>18.79</del>1</b>	<b><del>2.69</del>2</b>

Data obtained from IUPAC Subcommittee on Gas Kinetics Data Evaluation and the following references:

<sup>a</sup>Hooshiyar and Niki, 1995; <sup>b</sup>Calvert et al., 2015; <sup>c</sup>Wallington et al., 1989; <sup>d</sup>Calvert et al., 2008; <sup>e</sup>Began et al., 2018; <sup>f</sup>Atkinson, 2003; <sup>g</sup>Moreno et al., 2014; <sup>h</sup>Ballesteros et al., 2007; <sup>i</sup>Calvert et al., 2011; <sup>j</sup>Andersen et al., 2010; <sup>k</sup>Wallington et al., 1988; <sup>l</sup>Gallego-Iniesta et al., 2010; <sup>m</sup>Ceacero-Vega et al., 2012; <sup>n</sup>Jiménez et al., 2005; <sup>o</sup>Mellouki et al., 2004; <sup>p</sup>Bradley et al., 2001; <sup>q</sup>Moreno 2012.

**Table S2.** A summary of the reaction products observed or tentative identified in the reactions of 3,3DM1ButOH with the atmospheric oxidants.

Reaction Product of reaction mechanism	FTIR				GC-MS				t <sub>R</sub> /min
	Cl	Cl + NO	OH	NO <sub>3</sub>	Cl	Cl + NO	OH	NO <sub>3</sub>	
<b>Route I</b>									
3,3-dimethylbutanal	X	X	X	X	X	X	X	X	6.00
<b>Route II</b>									
1-hidroxy-3,3-dimethyl-2-butanone	-	-	-	-	-	-	-	-	-
3,3-dimetil-1,2-butanodiol	-	-	-	-	-	-	-	-	-
2,2-dimethylpropanal	X	X	X	-	/	-	-	-	8.61?
Formaldehyde	X	X	X*	-	-	-	-	-	-
<b>Route III</b>									
4-hidroxy-2,2-dimethylbutanal	-	-	-	-	-	-	-	-	-
2,2-dimethyl-1,4-butanodiol	-	-	-	-	-	-	-	-	-
4-hidroxy-3,3-dimethylbutanal	-	-	-	-	-	-	-	-	-
Cyclic alcohols	-	-	-	-	-	-	-	-	-
Cyclic carbonyls (2(3H)dihydro,3,3-dimethylfuran)	-	-	-	-	/	/	/	/	13.17
4-hidroxy-2-butanone	-	-	-	-	-	-	-	-	-
Acetone	X	X	-	-	-	/	-	-	2.14
Glycolaldehyde	-	/	-	-	-	/	/	/	5.05
1,2-etanodiol	-	-	-	-	-	-	-	-	-
Formaldehyde	X	X	X*	-	-	-	-	-	-

The compounds with X have been positively identified with reference FTIR or MS spectrum. Those that have / have been probably identified through the analysis of the IR bands of the residual spectra and Mass Spectra using as a source of ionization Electron ~~ie~~ Ionization impact (EI) and Field Ionization (FI) source that allows us to know the molecular ion. X\* Formaldehyde in the reaction of OH, is formed by decomposition of the precursor, so it is observed in the reaction, but it cannot know how much come from the reaction of 3,3DM1ButOH and OH

**Table S3.** A summary of the reaction products observed or tentative identified in the reactions of 3,3DM2ButOH with the atmospheric oxidants.

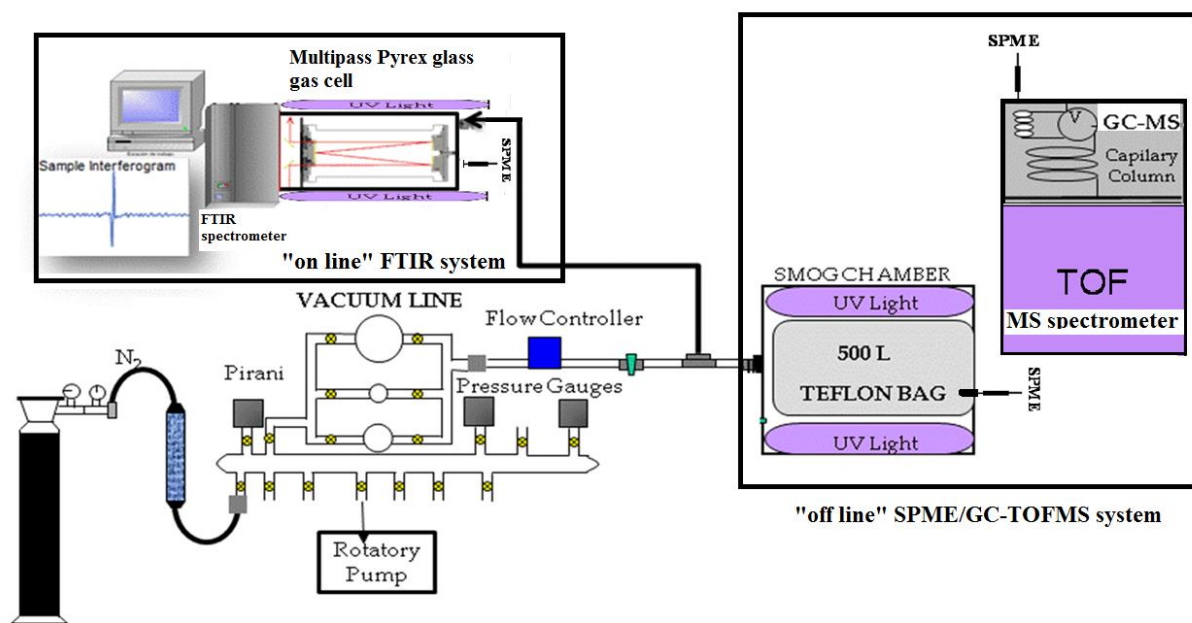
Product propose in the <u>mechanism</u>	FTIR						GC-MS		Retention time (min)
	Cl	Cl + NO	O H	NO <sub>3</sub>	Cl	Cl + NO	OH	NO <sub>3</sub>	
<b>Route I</b>									
3,3-dimethyl-1,2- butanediol	-	-	-	-	-	-	-	-	-
3,3-dimethyl-2- hydroxybutanal	-	-	-	-	-	-	-	-	-
Formaldehyde	X	X	X*	-	-	-	-	-	-
2,2- dimethylpropanal	X	X	X	-	-	-	/	/	5.39
<b>Route II</b>									
3,3-dimethyl-2- butanone	X	X	X	X	X	X	X	X	6.04
<b>Route III</b>									
2,2-dimethyl-1,3- butanediol	-	-	-	-	/	-	-	-	13.46
2,2-dimethyl-3- hydroxybutanal	-	-	-	-	-	-	-	-	-
Formaldehyde	X	X	X*	-	-	-	-	-	-
3-hydroxybutanone (Acetoin)	-	-	-	-	-	-	-	-	-
Acetone	X	X	-	-	/	/	-	-	2.16
Acetaldehyde	-	X	-	-	-	-	-	-	-

The compounds with X have been positively identified in denoted equipment. Those that have / have been probably identified through the analysis of the IR bands of the residual spectra and the analysis of the mass spectra using as a source of ionization by electron ~~ionization~~ ionization ~~mpact~~ and field ionization source that allows us to know the molecular ion.

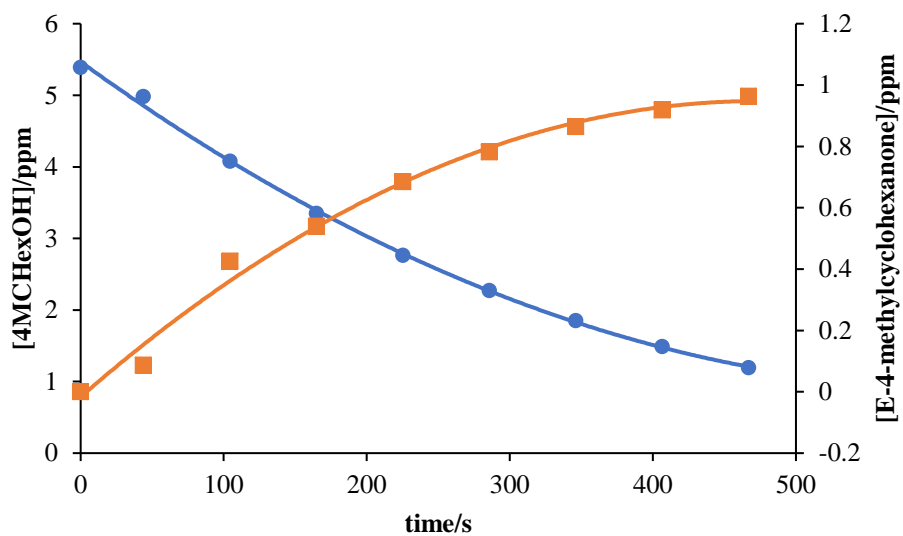
X\* Formaldehyde is a product, but it is also formed by decomposition of the precursor in the reaction with OH radical, and it is not possible to differentiate which comes from the reaction or from the decomposition process.

|

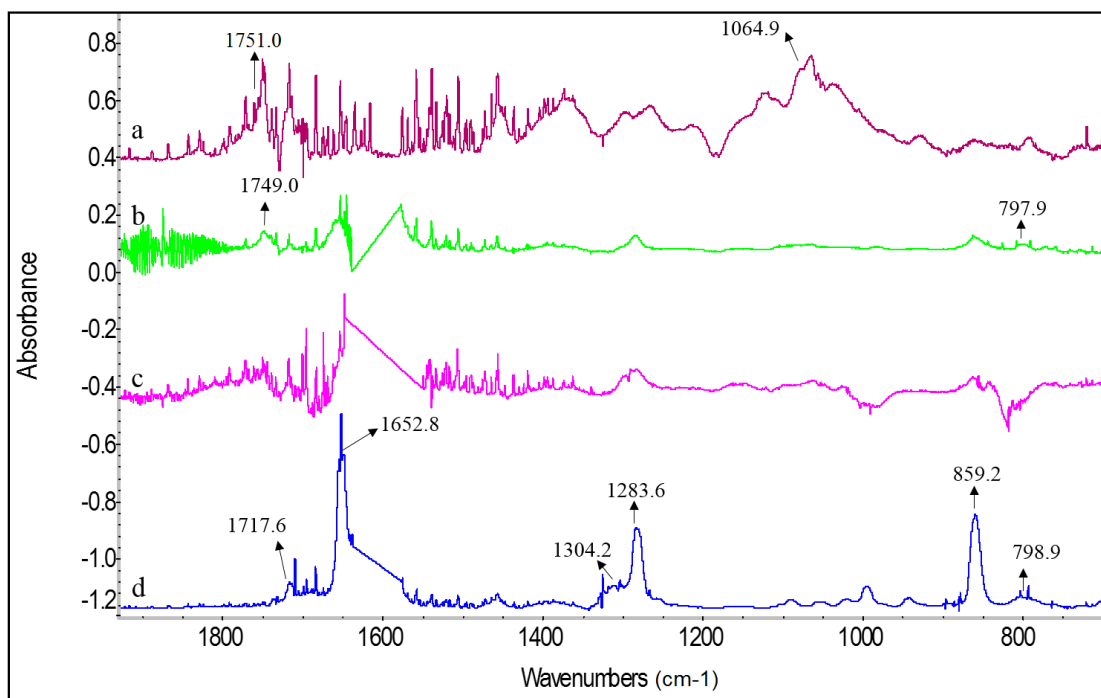


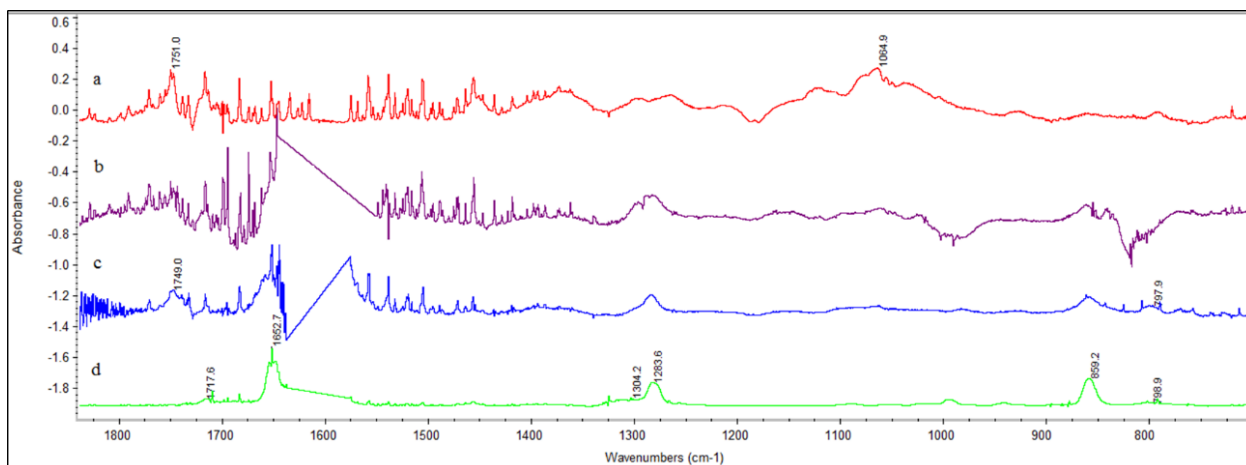


**Fig.S1** Schematic diagram of experimental system: FTIR and SPME/GC-TOFMS.

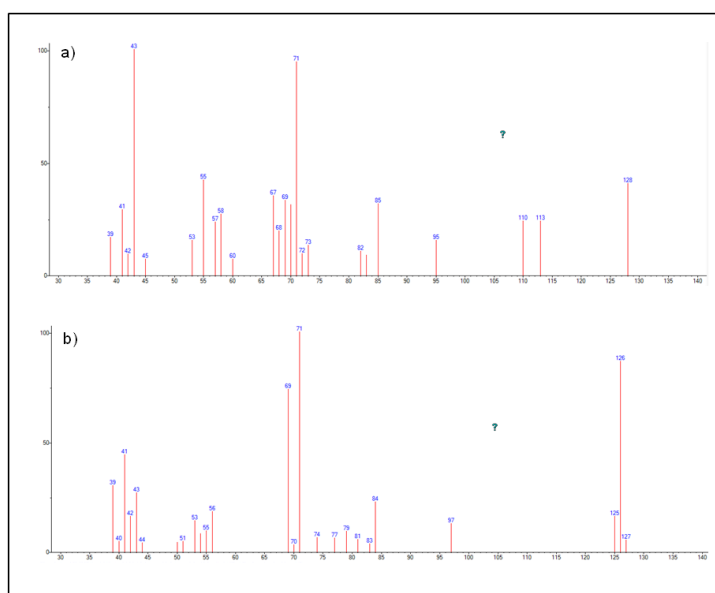


**Fig. S24.** Time-concentration profiles of 4MCHexOH ● and 4-methylcyclohexanone ■, for the reaction of 4MCHexOH with chlorine atoms in the presence of NO<sub>x</sub> obtained by FTIR.

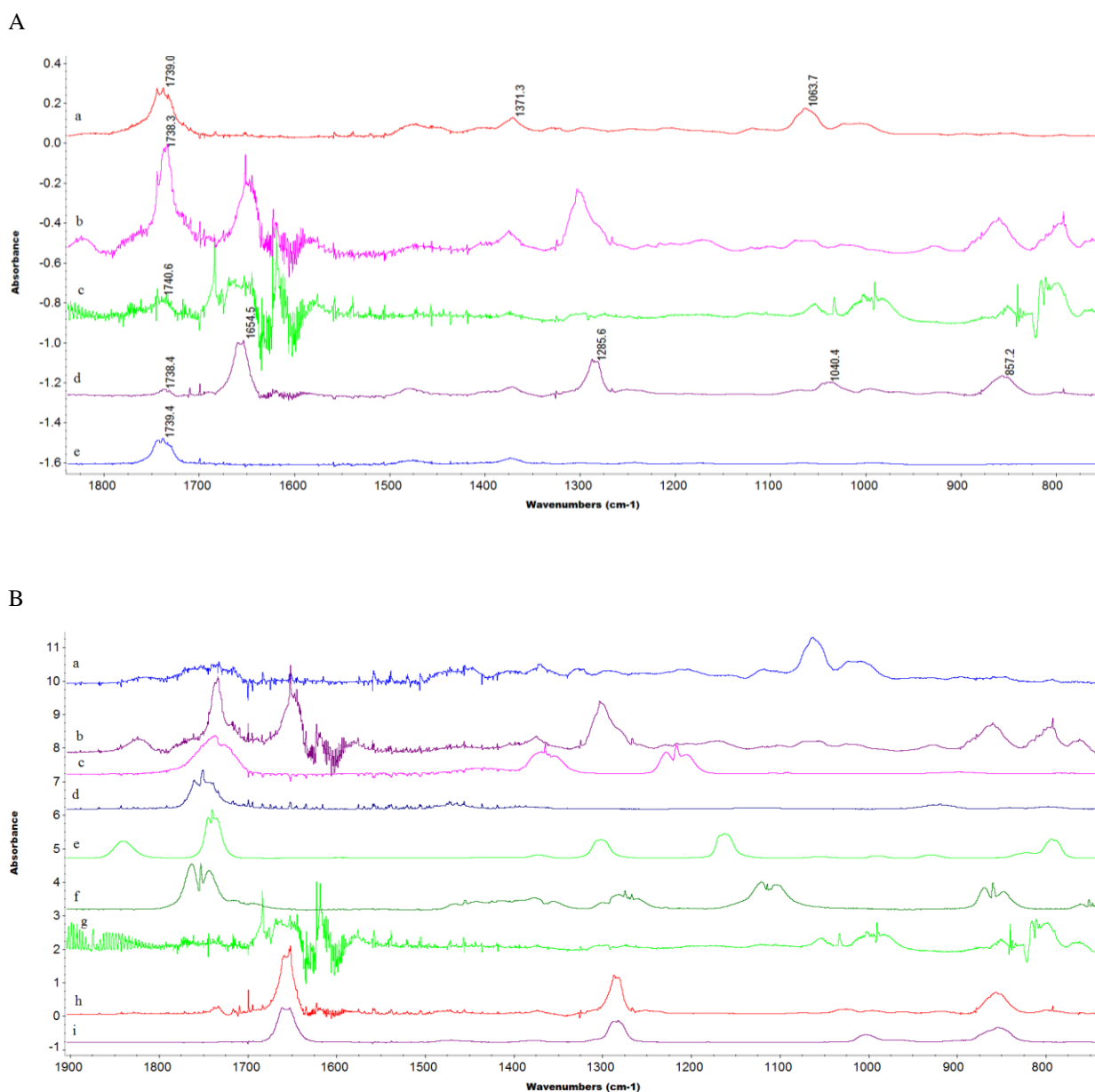




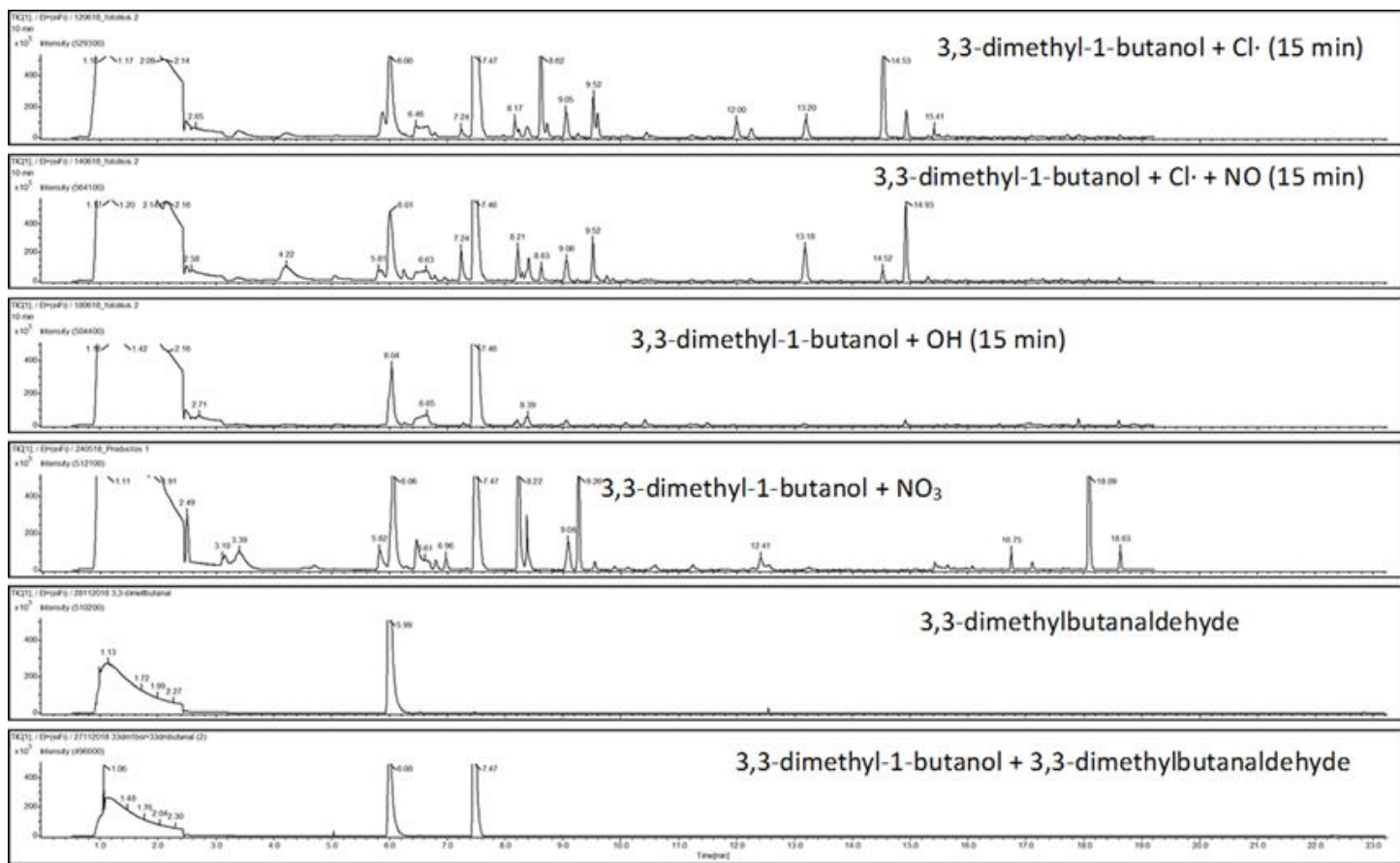
**Fig. S32.** Residual FTIR spectra obtained in the reaction of 4MCHexOH with Cl (a), Cl + NO (c), HO (b) and NO<sub>3</sub> (d). The gap in the range of 1650-1590 cm<sup>-1</sup> corresponds to NO<sub>2</sub> absorption.



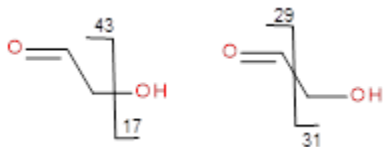
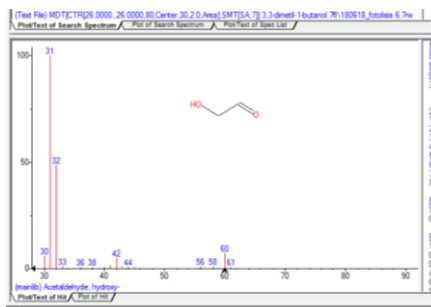
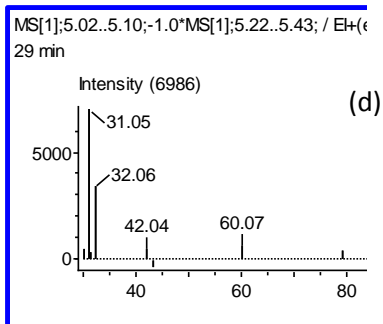
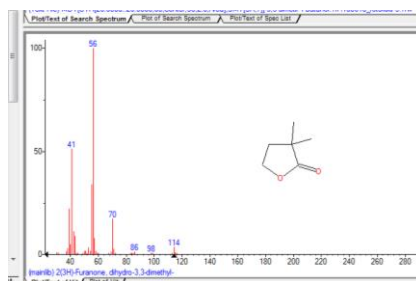
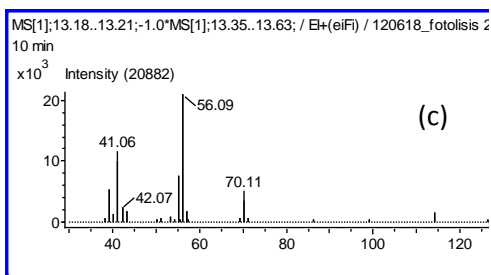
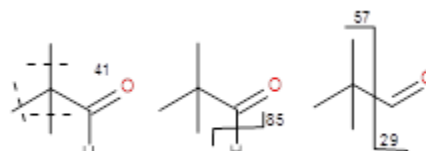
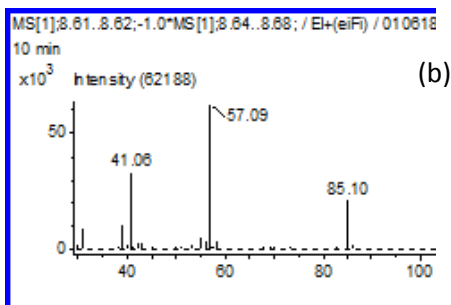
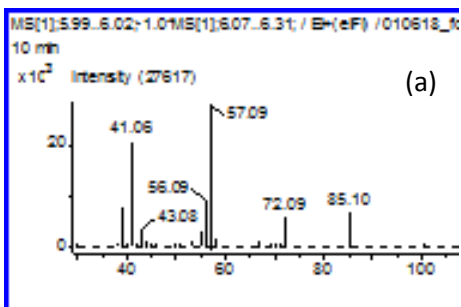
**Fig. S43.** EI MS spectra of peak C (a) and D (b) observed at 20 and 23 min of retention time in the reaction of 4MCHexOH-methyleyclohexanol with Clchlorine atoms. Tentatively assigned to 2-hydroxy-5-methyl cyclohexanone, 5-hydroxy-2-methyl-cyclohexanone and or 3-methyl-1,6-hexanedial.



**Fig. S54. A)** Residual FTIR spectra obtained in the reaction of 3,3DM1ButOH with Cl (a), Cl + NO (b), OH (c) NO<sub>3</sub> (d). The IR absorption bands subtracted were: 3,3DM1ButOH, HCl, ClNO<sub>2</sub>, ClNO, HCOH, HCOOH, HONO, NO<sub>2</sub>, NO, N<sub>2</sub>O and peroxy nitric acid (for Cl and Cl + NO reactions); N<sub>2</sub>O<sub>5</sub>, HNO<sub>3</sub>, NO<sub>2</sub> (for NO<sub>3</sub> reactions) and HCOH, HCOOH, HNO, NO<sub>2</sub>, CH<sub>3</sub>ONOmethyl nitrite and CH<sub>3</sub>ONO<sub>2</sub>-methyl nitrate (for OH reactions). (e) FTIR reference spectrum of 3,3-dimethylbutanal. **B)** Residual FTIR spectra: -Cl (a), Cl + NO (b), HO (g) and NO<sub>3</sub> (h) without 3,3-dimethylbutanal. Reference spectra of acetone (c) from a commercial sample; 2-methylpropanal (d); PAN (e); Glycolaldehyde (f); and isobutyl nitrate (i) from Eurochamp 2020 database.

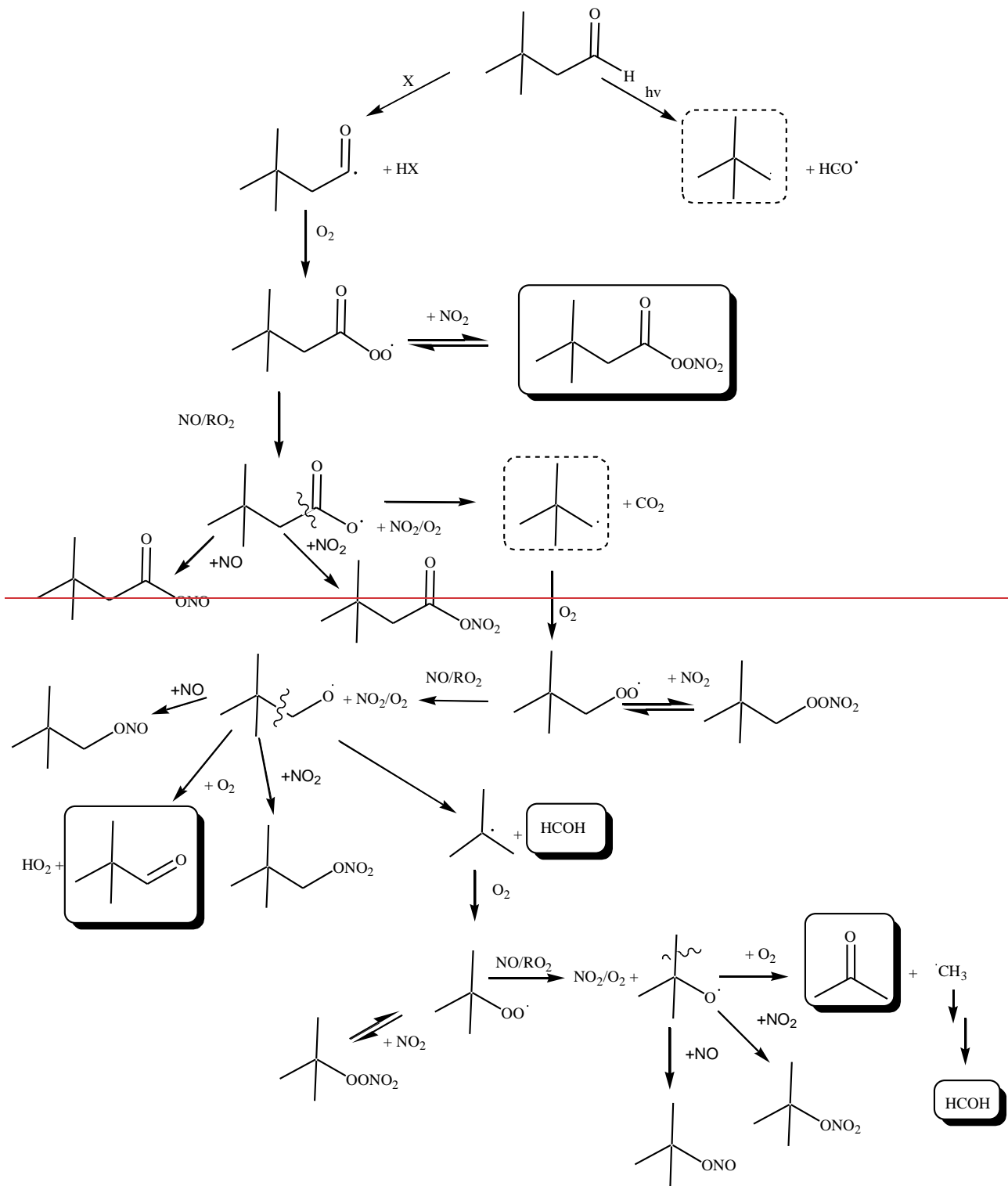


**Fig. S65.** SPME/GC-TOFMS chromatograms obtained for the reaction of 3,3-dimethyl-1-butanol with Cl, Cl + NO, HO and NO<sub>3</sub> (30 min) and reference chromatograms of 3,3-dimethyl-1-butanol and 3,3-dimethylbutanaldehyde.



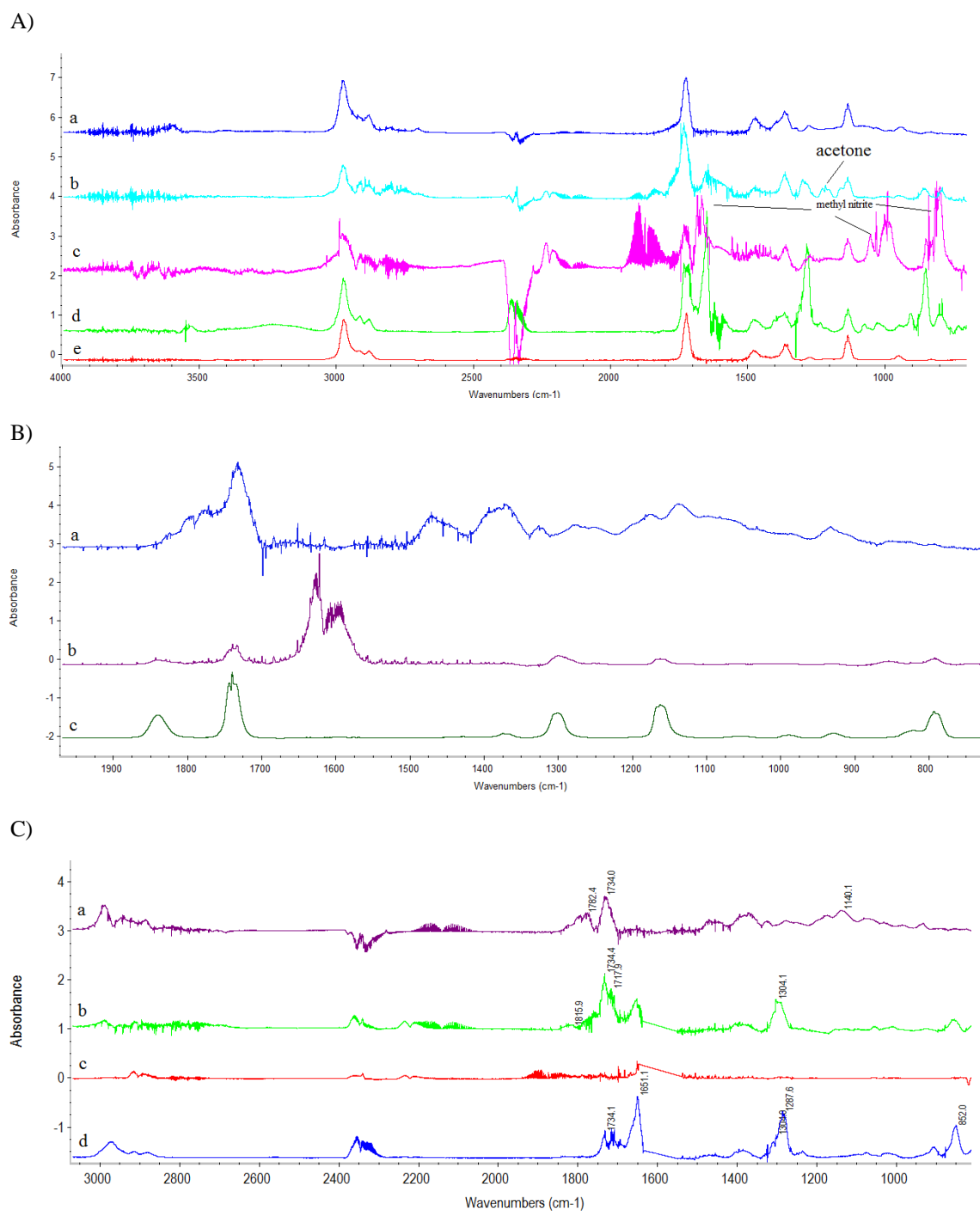
**Fig. S76.** EI MS spectra of the peaks of chromatograms shown in Fig. S6 obtained for the reaction of of 3,3DM1ButOH ~~3,3-dimethyl-1-butanol~~ with Cl, Cl + NO, HO and NO<sub>3</sub>. (a) t<sub>R</sub>= 6.00 min; (b) t<sub>R</sub>= 8.61 min; (c) t<sub>R</sub>= 13.17 min; (d) t<sub>R</sub>= 5.05 min).



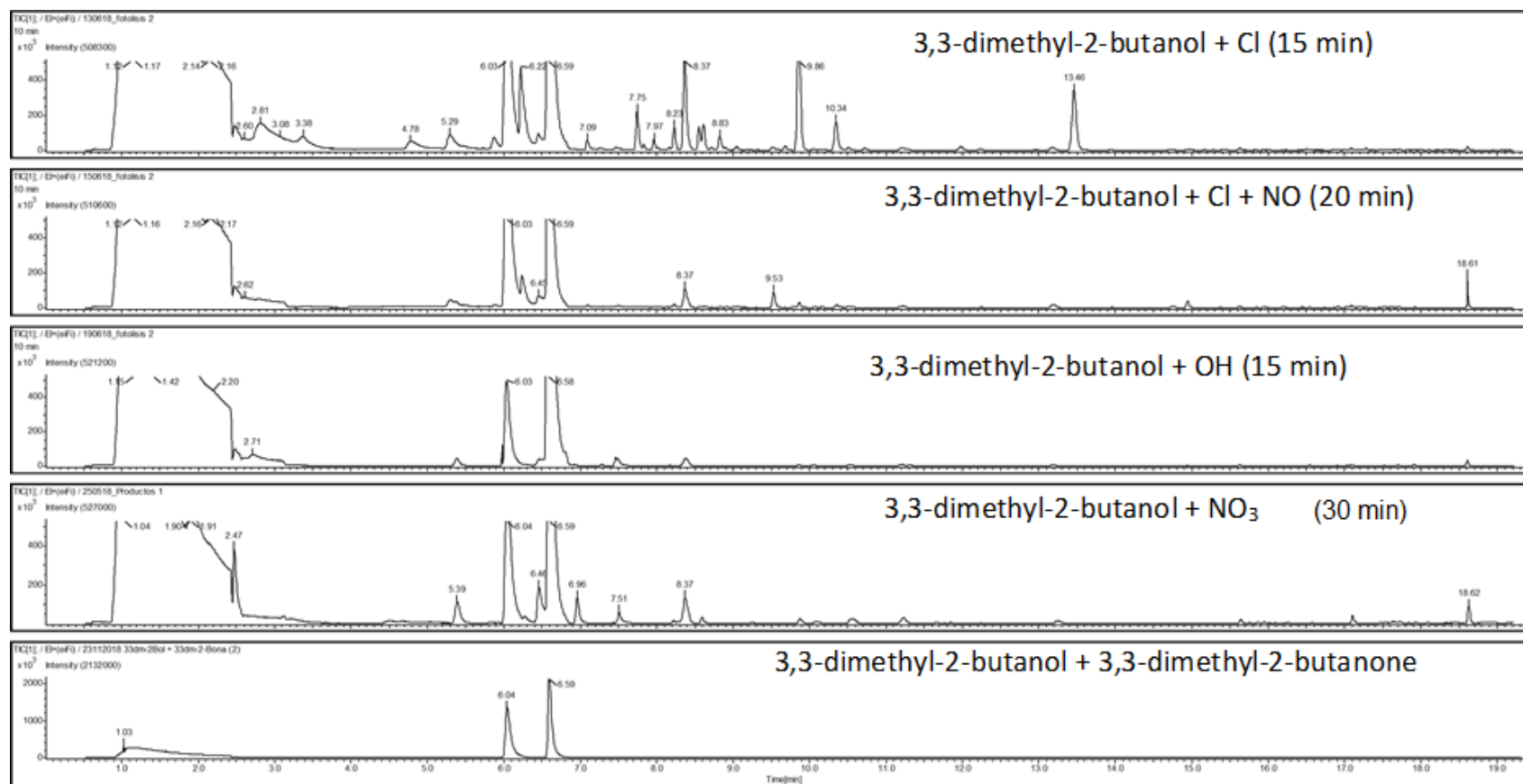








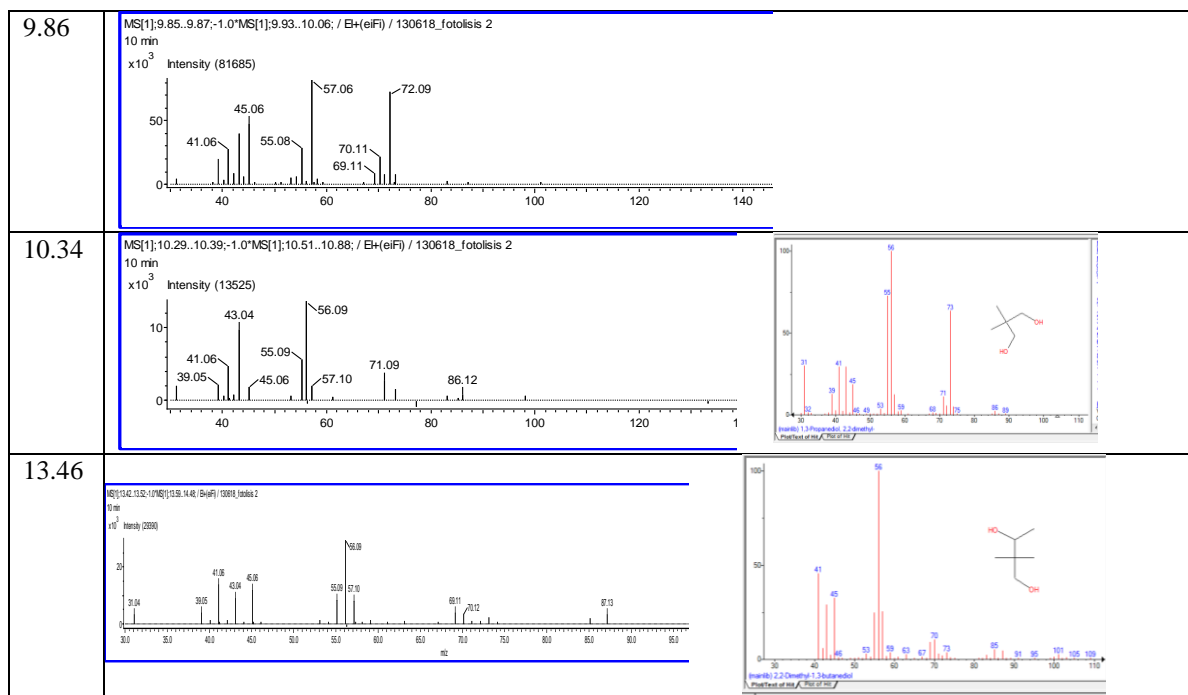
**Fig. S98.** A) FTIR spectra obtained in the reaction of 3,3DM2ButOH with Cl (a), Cl + NO (b), OH (c) NO<sub>3</sub> (d) at 5 minutes of reactions. (e) FTIR reference spectrum of 3,3-dimethyl-2-butanone. B) -FTIR spectra obtained in the reaction of 3,3-dimethyl-2-butanol with Cl (a), Cl + NO (b), 25 minutes and 35 minutes of reactions respectively. (c) IR PAN spectrum. -C) Residual FTIR spectra after subtraction of all known bands. Cl (a), Cl + NO (b), HO (c) and NO<sub>3</sub> (d).



**Fig. S109.** SPME/GC-TOFMS chromatograms obtained for the reaction of of 3,3DM2ButOH ~~3,3-dimethyl-2-butanol~~ with Cl, Cl + NO, HO and NO<sub>3</sub>, and reference chromatograms of 3,3DM2ButOH and 3,3-dimethyl-2-butanone.

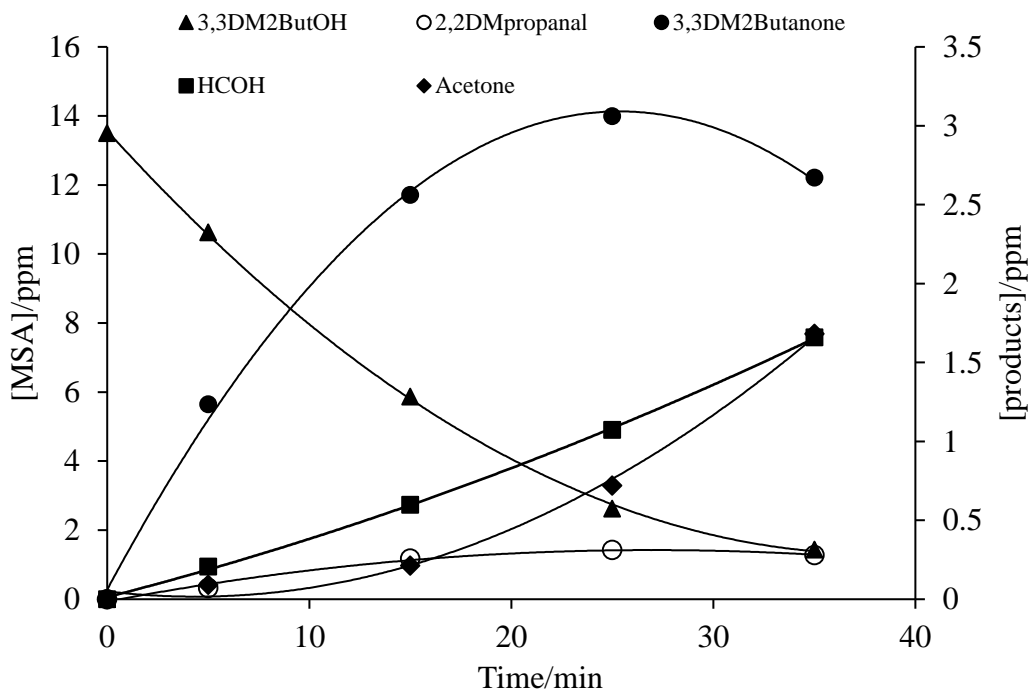
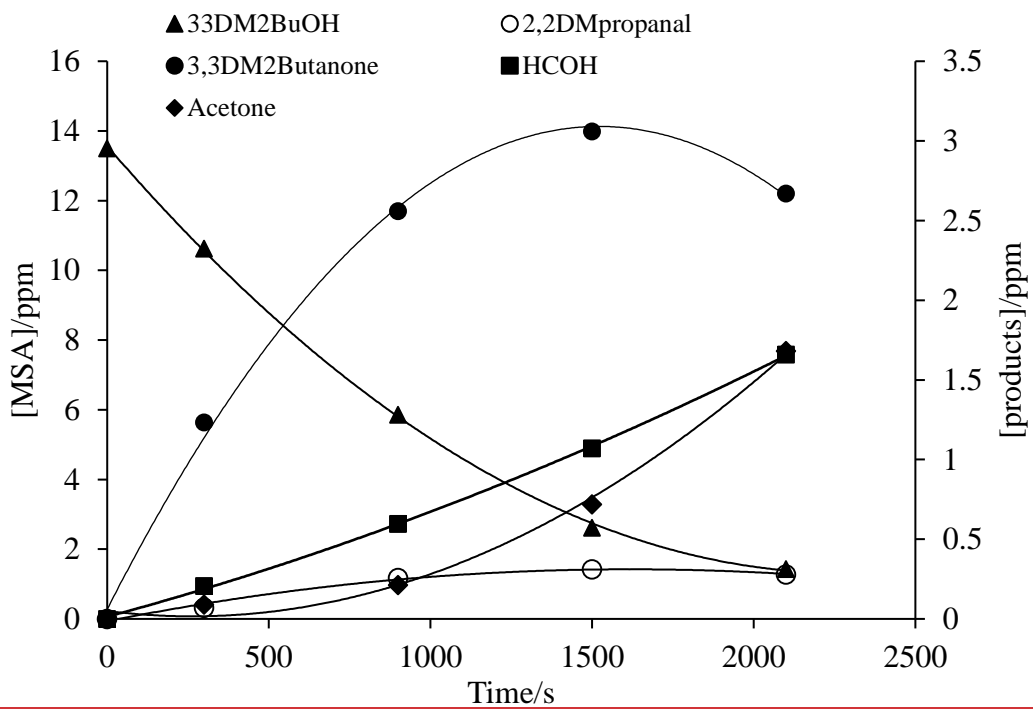


$t_R$ (min)	EI MS
2.16	<p>MS[1]:2.10..2.22;-1.0*MS[1]:2.43..2.93; / E+(eIF) / 130618_fotolis 2</p> <p>10 min</p> <p>Intensity (37940)</p> <p>Acetone</p> <p>30.0 35.0 40.0 45.0 50.0 55.0 60.0 65.0 70.0</p> <p>m/z</p>
5.39 ?	<p>MS[5]:5.44;-1.0*MS[5]:6.15; / E+(eIF) / 250518_Products 1</p> <p>Intensity (1722)</p> <p>2,2-dimethylpropanal</p> <p>30.0 35.0 40.0 45.0 50.0 55.0 60.0 65.0 70.0 75.0 80.0 85.0 90.0</p> <p>m/z</p> <p>Propanal, 2,2-dimethyl- MASS SPECTRUM</p> <p>100</p> <p>80</p> <p>60</p> <p>40</p> <p>20</p> <p>0.0</p> <p>0.0 20.0 40.0 60.0 80.0 100.0</p> <p>m/z</p> <p>NIST Chemistry WebBook (<a href="https://webbook.nist.gov/chemistry/">https://webbook.nist.gov/chemistry/</a>)</p>
6.03	<p>MS[1]:6.01..6.08;-1.0*MS[1]:6.14..6.58; / E+(eIF) / 150618_fotolis 2</p> <p>10 min</p> <p>Intensity (183851)</p> <p>3,3-dimethyl-2-butanone</p> <p>40 60 80 100 120</p> <p>m/z</p>
6.22	<p>MS[1]:6.20..6.24;-1.0*MS[1]:6.29..6.58; / E-</p> <p>10 min</p> <p>Intensity (45037)</p> <p>Acetic Acid (SI 80%)</p> <p>40 60 80</p> <p>m/z</p>
6.46	SPME
6.96	<p>MS[1]:6.94..6.98;-1.0*MS[1]:7.04..7.33; / E+(eIF) / 250518_Products 1</p> <p>Intensity (17807)</p> <p>40 60 80 100 120</p> <p>m/z</p> <p>Nitrated compound</p>
7.75	<p>MS[1]:7.73..7.76;-1.0*MS[1]:7.79..7.92; / E+(eIF) / 130618_fotolis 2</p> <p>10 min</p> <p>Intensity (28900)</p> <p>40 60 80 100</p> <p>m/z</p>
8.37	<p>MS[1]:8.38;-1.0*MS[1]:8.38..8.45; / E+(eIF) / 130618_fotolis 2</p> <p>10 min</p> <p>Intensity (69080)</p> <p>40 60 80 100 120</p> <p>m/z</p>

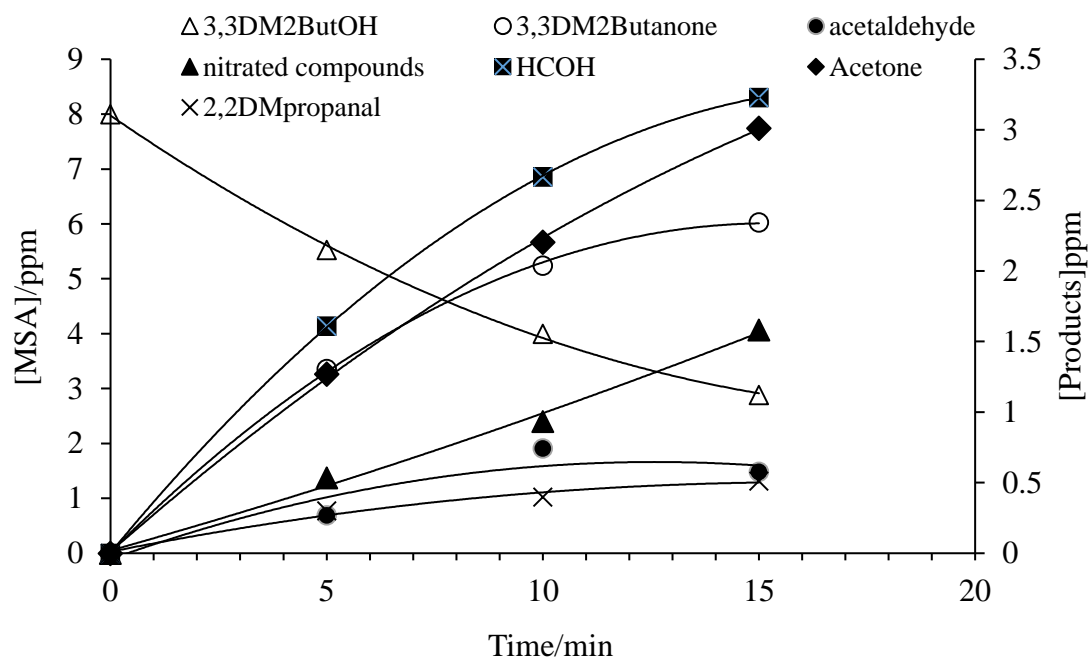


**Fig. S110.** EI MS spectra of the peaks of chromatograms shown in Fig. S10 obtained for the reaction of 3,3DM2ButOH with Cl, Cl + NO, HO and NO<sub>3</sub>.

A)



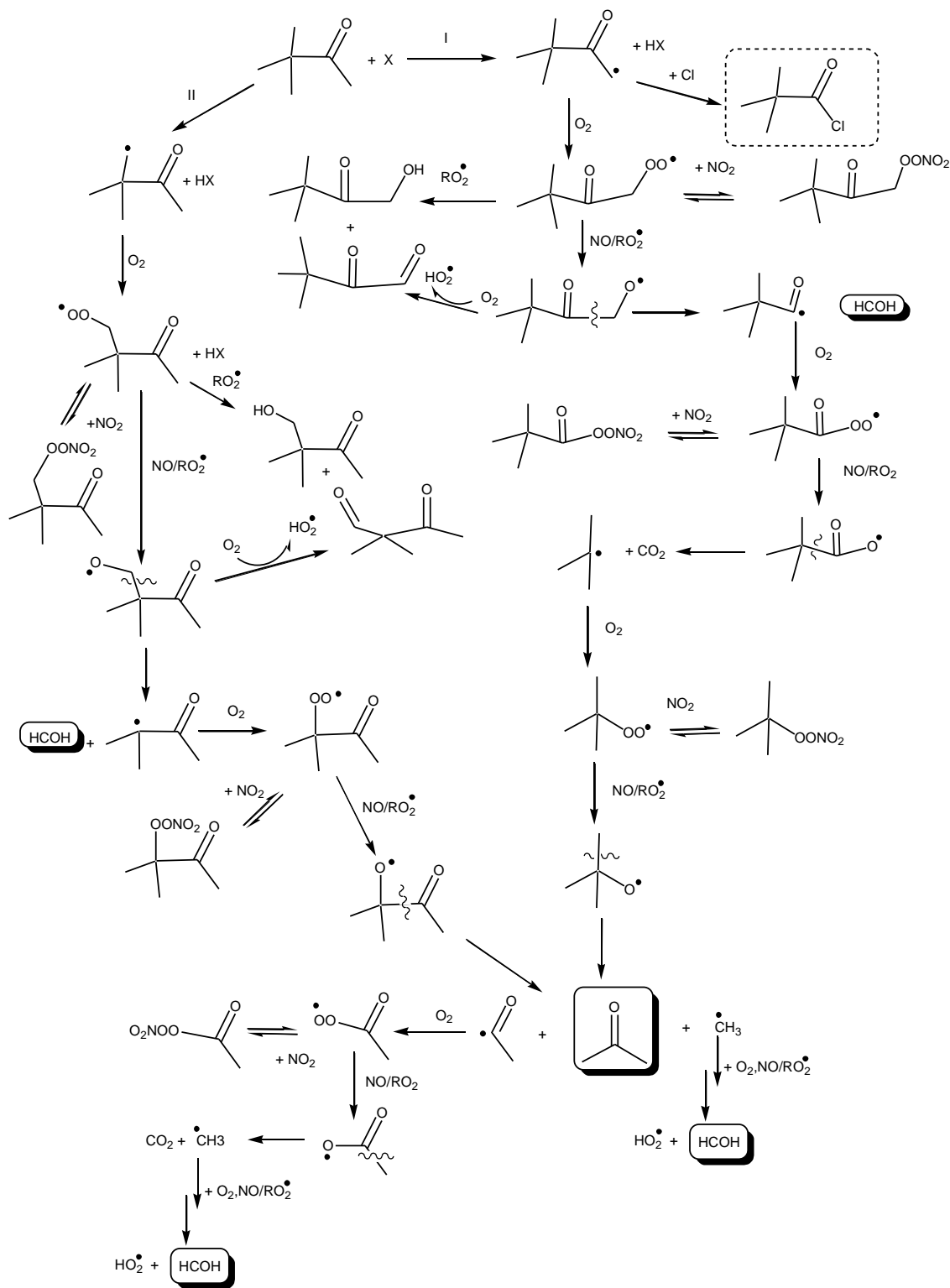
(B)



**Fig. S121.** Concentration-time profiles of 3,3DM2ButOH and reaction products formed obtained for the reaction of 3,3DM2ButOH with Cl atoms in absence (A) and presence of NO (B).







**Fig. S132.** Reaction mechanism for degradation of 3,3-dimethyl-2-butanone with the atmospheric oxidants in presence of NO<sub>x</sub>.

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