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

Editor comments:

However, the presentation of the work falls below normal publication standards. The overall quality and clarity of the presentation greatly hinders the communication of the scientific results.

On the basis of the reviewer comments and my review, I am requesting that the authors make major revisions to their manuscript to improve the communication, clarity, logic, (remove) unnecessary repetition ("As mentioned above" type text), (remove) meaningless general statements, English, and grammar. In addition, the presentation of the scientific results for the molecules under study could be made more concise and earlier to follow for the reader. The tables and figures seem fine.

AC: We thank the editor for the interest shown on our work and the comments and suggestions.

The manuscript has been revised and unnecessary repetitions have been removed. We expect that with the english revision the meaningless statements have been eliminated.

The authors have tried to make a presentation of the scientific results more concise but we consider that this is a work with many experiments and results, and it is difficult for us to reduce the work without loss of scientific rigor. We know that in the kinetic discussion section there are information relative to general topics of reactivity of alcohols that could be omitted (page 6 lines 28-38 and page 7, lines 1-3 of new manuscript.pdf) because this information is well established and known. The authors consider that given the scope and dissemination of the ACP, more details would help to anyone who was not an expert in the subject to understand better the work. Indeed, at the suggestions of both referees, more information and explications had to be included. However, if you consider that this information is not necessary to understand better the discussion of the kinetic results, we can eliminate it.

The authors would appreciate if you could tell us which parts should be reduced or otherwise should be discussed further. In our opinion we consider that this version is fine, although it is possible that there are still some grammatical errors, that would be eliminated in the final review before publication.

I highly recommend that the authors have a native English-speaking colleague critically (line-by-line) review the manuscript prior to re-submission. This is simply too large a task for a reviewer or editor.

AC: The text of manuscript has been sent to " Proof-Reading-Services.com" for american english revision in order to make a rigorous of /vocabulary/grammar/scientific expressions. In order to do not pay a lot of for the revision, abstract, references, tables, figures and Supplementary material have not been sent to english revision.

EC: A few general theme comments:

***Only one of the compounds included in this study (3,3DM2ButOH) is actually methyl saturated. Therefore, the title and text are in error. This correction would lead to the removal of the misleading MSA acronym.**

AC: All studied alcohols are saturated compounds (they do not have double or triple bonds) and all of them have at least one methyl group, so we considered methyl saturated alcohols to be a good acronym for the studied compounds, that is usual for compounds without multiple bonds. To avoid confusion, the authors have decided to use saturated alcohols generically (SAs)

EC: * The abstract mentions "tentative estimation of molecular yields" and quotes very large ranges of yields, which are not meaningful. The authors need to be more specific regarding the actual yield values and for what initiation reaction they are obtained from. I believe this information is actually available within the manuscript tables, although hard to follow in the text. Or, is this a problem with not having good standards?

AC: The individual molar yield of reaction product obtained for each reaction had not been included in the abstract in order to avoid making it very extensive. The phrase "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." has been removed to avoid confusion, and some new sentences have been included.

"The main products detected in the reaction of SAs with Cl atoms (absence/presence of NOx), OH and NO_3 radicals were: E-4-methylcyclohexanone for the reactions of E-4-methyl-cyclohexanol, 3,3-dimethylbutanal for the reactions of 3,3-dimethyl-1-butanol and 3,3-dimethyl-2-butanone for the reactions of 3,3-dimethyl-2-butanol"

"In addition, the molar yields of the reaction products were estimated".

The molar yields of the products are shown in Tables 3-6. In some cases, as 2,2-dimethylpropanal the molar yields could have large uncertainty because the reference spectra used was an FTIR spectra of a similar compound (2-methylpropanal).

EC * There is a long discussion of reactivity observations that have been well-established through the development of structure activity relationships (SARs) by Atkinson and co-workers. The small data set from this work is probably not sufficient to revise our thinking of SARs. The present work needs to be placed in the proper perspective.

AC: In the analysis made of the kinetic results obtained in our work, it is observed that the OH group exerts an activating effect that makes the reactivity of the alcohols greater than that of its alkane homologue, but it is also observed that this activating effect is different according to the oxidant. Indeed, these observations are well established through the development of structure activity relationships (SARs) by Atkinson and co-workers.

The authors do not have the intention of reviewing or changing results of the SARs method. On the contrary, what we want to highlight is that our results are in good agreement with those established by the SARs method in the case of reactions of saturated alcohols with Cl atoms and OH radical and in the case of NO_3 radical with secondary alcohols.

In order to avoid more confusion, the paragraph of page. 7, lines 31-37 (clean manuscript date 26/10/2019) has been replaced by.

"..These results show that the activating effect of the OH group of the SA is less important for the Cl than with the OH, behavior that agrees with that established by the Structure Activity Relationship (SARs) methods (Kwok and Atkinson 1995; Calvert et al. 2011).."

On the other hand, in the case of the nitrate radical our study shows that in addition to the activating effect of the OH group there is also an activating effect of the $-CH_2OH$ group and that it is necessary to perform more kinetic studies of reactions of primary alcohols with the nitrate radical, in order to establish this factor, since there are currently very few data available in bibliography. This last is indicated in the manuscript as a conclusion.

“..For primary alcohols, the abstraction of a hydrogen atom in β–position could also be important in the reaction with NO_3 radical. Therefore, more kinetic studies for NO_3 radical with primary alcohols are necessary to quantify the effect of the OH group in β–position, (-CH2OH) and to update the SAR method developed by Kerdouci et al.”

EC:* The introduction contains a great deal of seemingly unnecessary material and background information. Even with that said, it is not made clear why these particular compounds were chosen for study (biofuels?).

AC: The introduction has been reorganized in order to show better the relevance of compounds studied.

So, in the first paragraph the necessity of using biodiesel as alternative to conventional diesel is remarked. In this same paragraph, it is also shown that alcohol-diesel blends are a good alternative. Initially the alcohols used were alcohols of short chain (methanol, ethanol) but some problems were found due to their low cetane number, high latent heat of vaporization and high resistance to auto-ignition. In order to avoid these problems, high alcohols as propanol, n-butanol, isobutanol, n-pentanol and therefore the alcohols studied in this work, could be a good alternative as additives in the diesel blends. A new reference has been included to support this last.

“ Li, F., Yi, B., Song, L., Fu, W., Liu, T., Hu, H., & Lin, Q. Macroscopic spray characteristics of long-chain alcohol-biodiesel fuels in a constant volume chamber. Proceedings of the Institution of Mechanical Engineers, Part A: JPE, 232(2), 195–207. https://doi.org/10.1177/0957650917721336, 2017.”

In the second paragraph of introduction, a revision of sources of alcohols and data about concentrations found in the atmosphere is shown. The use of alcohols of long chain as additives for biodiesel fuel could imply an important source of these alcohols in the atmosphere. So, it is necessary to evaluate their atmospheric reactivity and to establish the atmospheric impact of these compounds.

In the next paragraph, a revision of the atmospheric reactivity of short and long alcohols is made, it does remark the absence of kinetic data or about reaction products of the alcohols studied in this work. The last paragraph explains the study that has been carried out and why it has been done.

We expect that this reorganization and correction of the introduction section, allows a better compression and better justification of the developed research.

LIST OF THE MAIN CHANGES MADE IN THE MANUSCRIPT.

Apart of the modification due to the English revision, the next modifications have been made at suggestion of the editor in order to more clarity. Pages and lines indicated are related to the manuscript.pdf with date sent of 26_10_2019.

1-Page 1. Lines 1 and 2. The title has been modified. The acronym MSA has been removed, and "methyl saturated alcohols" has been replaced by "saturated alcohols" in all text of the manuscript, tables and figures.

2-Page 1. Line 12. The next sentence has been included:

"These SAs are alcohols that could be used as fuel additives"

3-Page 1. Lines 17-21. The paragraph has been replaced by the following:

"The main products detected in the reaction of SAs with Cl atoms (absence/presence NOx), OH and NO_3 radicals were: E-4-methylcyclohexanone for the reactions of E-4-methyl-cyclohexanol, 3,3-dimethylbutanal for the reactions of 3,3-dimethyl-1-butanol and 3,3-dimethyl-2-butanone for the reactions of 3,3-dimethyl-2-butanol"

4-Page 1. Line 21. The sentence has been modified including "..of Cl atoms and OH radicals with.."

5-Page 1. Line 23. The next sentence has been included "In addition, the molar yields of the reaction products were estimated".

6-Page 1. Line 23. The sentence has been modified as follows

"The products detected, indicate a hydrogen atom abstraction mechanism at different sites on the carbon chain of alcohol…"

7-Page 1. Line 31 "Therefore, the use of saturated alcohols as additives in diesel-blends should be considered with caution"

8-Pages 2 and 3. The introduction has been reorganized.

9-Page 2. Line 17. A new reference has been included.

10-Page 7. Lines 31-37. The text has been modified as follows:

"These results show that the activating effect of the OH group of the SA is less important for the reaction with Cl atoms than with the OH radical, behavior that agrees with that established by the Structure Activity Relationships (SARs) methods (Kwok and Atkinson 1995; Calvert et al. 2011)."

12-Page 9. Lines 21, 22. The sentence has been removed.

13-Page 9. Lines 28-31. The sentence has been rewritten to more clarity as follows:

"Some of these compounds are products from the reactions of the SAs with oxidants. They can also be formed by decomposition of the employed precursors (Cl2, CH3ONO and N2O5) and in some cases, by heterogeneous reactions of these precursors with the Pyrex glass reactor walls."

14-Page 10. Lines 32. Part of the sentence has been modified as follows:

“Figure 5A shows the paths that explain the formation of organic compounds (carbonyl, hydroxycarbonyl, etc)..”

15-Page 12. Lines 1 and 2 have been modified to more clarity, as follows:

“..presented in Fig. 6, showing that in the absence of NOx the profiles of acetone and formaldehyde have two trends. It indicates that these compounds are formed as primary and secondary products.”

16-Page 12. Lines 13-18. The sentence has modified to more clarity, as follows:

“The higher yield of nitrated compounds in the reaction of 3,3DM1ButOH with nitrate radical could indicate an extra formation of nitrated compounds from secondary reactions..”.

17-Page 12. Lines 25-27. The paragraph has rewritten to more clarity, as follows:

“As it can see in Table 4, the estimated molecular yields of 3,3-dimethylbutanal (formed by H atom abstraction at the α–position of 3,3DM1BuOH) are very similar to the one predicted by the SARs method for the Cl and OH reactions.”

18-Page 13. Lines 15-17. The paragraph has rewritten to more clarity, as follows:

“Plots of concentration versus time for formaldehyde, acetone (Fig. S12A) and nitrated compounds in the reactions of Cl in the presence of NOx (Fig. S12B) show profiles with two trends. This type of profile indicates that formaldehyde and acetone could also be formed by degradation of 3,3-dimethyl-2-butanone (Fig. S13).”

19-Page 13. Lines 17-19. The sentence has been moved to Line 14.

20-Page 13. Line 33. The next sentence has been added to more clarity, as follows:

“It could justify the low estimated molecular yield for 3,3-dimethyl-2-butanone.”

21-Page 14. Lines 3-4. The paragraph has been eliminated

22-Page 15. Lines 30-32 The sentence has been rewritten as follows:

“Therefore, more kinetic studies of the NO_3 radical reaction with primary alcohols are necessary to quantify the effect of the OH group at the β–position (–CH2OH) and to update the SARs method developed by Kerdouci et al.”

23-Page 16. Lines 18-20. The sentence has been changed by:

“Therefore, the use of SAs as additives for diesel blends should be controlled, as poor handling could result in high concentrations of these alcohols in the atmosphere.”

24-Page 19. Lines 36-38. A new reference has been included:

“Li, F., Yi, B., Song, L., Fu, W., Liu, T., Hu, H., & Lin, Q. Macroscopic spray characteristics of long-chain alcohol-biodiesel fuels in a constant volume chamber. Proceedings of the Institution of Mechanical Engineers, Part A: JPE, 232(2), 195–207. https://doi.org/10.1177/0957650917721336, 2017.”

Atmospheric fate of a series of ~~Methyl~~ s~~S~~aturated a~~A~~lcohols ~~(MSA)~~: kinetic and mechanistic study

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Keywords. ~~Methyl~~ S~~s~~aturated alcohols, ~~;~~ additives, ~~;~~ biofuel, ~~;~~ atmosphere, ~~ric~~ reactivity.

Abstract. The atmospheric fate of a series of ~~Methyl~~ ~~S~~saturated a~~A~~lcohols (~~M~~SAs) has been evaluated through the kinetic and reaction product studies with the main atmospheric oxidants. These SAs are alcohols that could be used as fuel additives. Rate coefficients (in cm^3 $molecule^{-1}$ s^{-1} unit) measured at ~298K and atmospheric pressure (720 ± 20 Torr) were as follows: k_1 (E-4-methyl-cyclohexanol + Cl) = (3.70 ± 0.16) × 10^{-10}, k_2 (E-4-methyl-cyclohexanol + OH) = (1.87 ± 0.14) × 10^{-11}, k_3 (E-4-methyl-cyclohexanol + NO_3) = (2.69 ± 0.37) × 10^{-15}, k_4 (3,3-dimethyl-1-butanol + Cl) = (2.69 ± 0.16) × 10^{-10}, k_5 (3,3-dimethyl-1-butanol + OH) = (5.33 ± 0.16) × 10^{-12}, k_6 (3,3-dimethyl-2-butanol + Cl) = (1.21 ± 0.07) × 10^{-10} and k_7 (3,3-dimethyl-2-butanol + OH) = (10.50 ± 0.25) × 10^{-12}. The main ~~detected~~ products detected in the reaction of SAs with Cl atoms (absence/presence of NO_x), OH and NO_3 radicals were: E-4-methylcyclohexanone~~,~~ for the reactions of E-4-methyl-cyclohexanol, 3,3-dimethylbutanal for the reactions of 3,3-dimethyl-1-butanol and 3,3-dimethyl-2-butanone for ~~the reactions of E-4-methyl-cyclohexanol, 3,3-dimethyl-1-butanol and~~ the reactions of 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, 2,2-dimethylpropanal and acetone ~~also~~ have also been identified in the reactions of Cl atoms and OH radicals with 3,3-dimethyl-1-butanol and 3,3-dimethyl-2-butanol. In addition, the ~~The~~ molar yields~~s~~ of the~~se~~ reaction products ~~detected~~were estimated. The products detected, ~~S~~ indicate a hydrogen atom~~hydroge n~~ abstraction mechanism at different sites ~~of~~ on the carbon chain of alcohol~~the alkyl chain~~ in the case of Cl reactions and a predominant site in the case of OH and NO_3 reactions, confirming the predictions of Structure Activity Relationship~~s~~ (SAR) methods.

Tropospheric lifetimes (τ) of these ~~M~~SAs 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 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 calculated global tropospheric lifetimes ~~calculated~~, and the polyfunctional compounds detected as reaction products in this work, imply that the ~~Methyl~~ SAs~~sSaturated~~ a~~Alcohols~~ could contribute to the formation of ozone and nitrated compounds ~~formation~~ at

local, ~~but also~~ regional and even to global scale. Therefore, the use of ~~large~~ saturated alcohols as additives in diesel-blends ~~biofuels~~should ~~must~~ be considered~~taken~~ with caution.

1. Introduction

A m~~M~~ultitude of scientific studies ~~about~~on combustion emissions confirm that fossil fuels, especially diesel fuel, are the substances mainly responsible for air pollution. The loss of air quality and its consequences for~~on~~ health as well as for global warming are some of the most important problems caused by air pollution (www.iea.org). These consequences have led governments to set restrictive limits on~~for~~ the presence of certain pollutants in the atmosphere, such as~~is~~ the case of particulate matter (PM) (EURO 6) and to develop biofuels (Sikarwara et al., 2017) as alternatives to conventional ones.

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

~~The fact that the use of high alcohols is a good alternative to conventional fuels could suppose an important presence of these alcohols in the atmosphere. 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.~~

Alcohols are present in the atmosphere from a wide variety of anthropogenic and biogenic sources (Calvert et al., 2011). Methanol, ethanol and isopropanol are some of the main alcohols detected in urban areas such as Osaka and Sao Paulo cities (Nguyen et al., 2001) with concentrations of~~between~~ 5.8–8.2 ppbv and 34.1–176.3 ppbv respectively. Other alcohols, such as E-4-methylcyclohexanol, have been identified in the exhaust gas emissions resulting from~~of~~ burning fuel blends containing 7% v/v (B7) and 20% v/v (B20) of soy bean/palm biodiesel (84%/16%) (Lopes et al., 2014). 3,3-dimethyl-1-butanol is a glass-forming material~~,~~ used as a chemical intermediate in organic syntheses (www.capotchem.com). 3,3-dimethyl-2-butanol is a potential precursor for prohibited chemical weapons such as soman, a nerve agent (Murty et al., 2010). It is also used in conversion of ribose-and glucose- binding proteins into receptors for pinacolyl methyl phosphonic acid (Allert et al. 2004). The~~ fact that the~~ use of long-~~-~~chain ~~high~~ alcohols as biofuels~~as biofuels~~ ~~is a good alternative to conventional fuels c~~could~~ be~~~~suppose~~ present an additional~~ additional~~ important source ~~presence~~ of these alcohols in the atmosphere. Therefore, prior~~eviously~~ to~~ th~~ usee~~ir massive use as biofuels~~, it is necessary to study the~~ir~~ reactivity~~ of the large alcohols~~ of long-chain alcohols in atmospheric conditions~~,~~ in order to establish and to evaluate their ~~their~~ atmospheric impact.

In the case of small~~er~~ alcohols, the knowledge of their~~its~~ reactivity is well established and indicates~~ing~~ that the main degradation process~~ mechanism~~ of saturated alcohols~~ (SAs)~~ in the atmosphere is the reaction with hydroxyl~~OH~~ radicals (OH) during the daytime ~~is mainly initiated by the H-abstraction from C-H bond. The H-~~

~~abstraction from the OH group seems to be less favored~~ (Grosjean et al., 1997~~;,~~ Atkinson and Arey, 2003; Atkinson et al., 2006; Calvert et al., 2011; Caravan et al., 2015; Mellouki et al, 2015). ~~According to literature (Atkinson and Arey, 2003; Atkinson et al., 2006; Calvert et al., 2011; Caravan et al., 2015; Mellouki et al, 2015)., the main degradation route of saturated alcohols in the atmosphere is the reaction with OH radicals during daytime.~~ Kinetics with chlorine atoms (Cl) are expected to be high, therefore reactions with Cl could also be an important degradation route, especially in coastal areas where concentration peaks of Cl~~chlorine~~ atoms can be found. Reactions with ozone molecular (O_3) (k~~-~~ $\leq 10^{-20}$ cm^3 molecule^{-1} s^{-1}) and nitrate radical (NO_3) (~~~-~~10^{-15} cm^3 molecule^{-1} s^{-1}) are too low to make~~have~~ a significant contribution to their degradation. However, the determination of the rate coefficients and the reaction products of alcohols with the nitrate radical are also necessary to ~~better~~ understand better the general reactivity of alcohols in the atmosphere, since the reactions with this radical are a source of OH during the night-time (Finlayson-Pitts and~~-~~ Pitts, 2000).

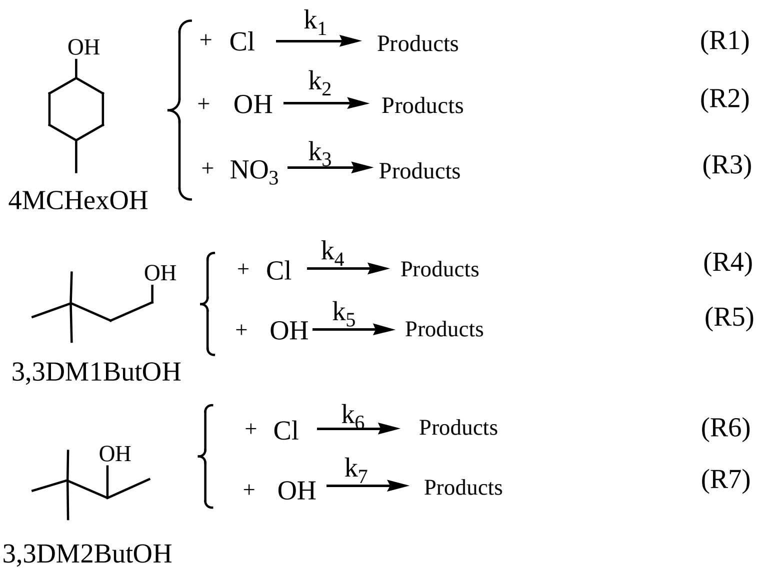
Although in ~~the~~ last years some studies into the~~about~~ reactivity of higher~~large~~ alcohols have been made (Ballesteros et al., 2007; Hurley et al., 2009; Andersen et al., 2010; Calvert et al., 2011; Moreno et al., 2012, 2014, Mellouki et al., 2015) the kinetic and mechanistic database is still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

Therefore, in the present work ~~, the~~ studies~~y~~ into the kinetics and the products of gas~~-~~-phase reactions of some ~~Methyl Saturated Alcohols (M~~SAs, such as~~):~~ E-4-methylcyclohexanol (4MCHexOH), 3,3-dimethyl-1-butanol (3,3DM1ButOH) and 3,3-dimethyl-2-butanol (3,3DM2ButOH) with Cl atoms and OH and NO_3 radicals~~the main atmospheric oxidants~~ haves been carried out.~~n done~~ These SAs have~~d~~ been chosen for their potential use as biofuels and because their reactivity has not yet been evaluated. So, our work will permit ~~us~~ to ~~in order to~~ complete the kinetic and mechanism database, to improve our knowledge of the atmospheric chemistry of higher~~long chain SAs~~ alcohols ~~in special saturated alcohols, and~~and to assess their environmental chemical impact in the case of their future use as biofuels.~~.~~

2. Experimental Section

2.1 Kinetic experiments

The reactions of a series of ~~Methyl Saturated Alcohols (M~~SAs~~)~~ with the main atmospheric oxidants have been studied:



Rate coefficients were determined using a relative rate method. This method relies on the assumption that the organic compound (~~M~~SA) and the reference compound (R), are removed solely by their reactions with the oxidants (Ox: OH and~~,~~ NO$_3$ radicals and Cl atoms):

Ox + ~~M~~SA → Products ($k_{\cancel{M}SA}$) (R8)

Ox + R → Products (k_R) (R9)

w~~W~~here $k_{\cancel{M}SA}$ and k_R are the rate coefficients of the ~~M~~SA and the reference compound, respectively.

On the assumption that the ~~M~~SA and the reference compound are only consumed by reaction with the oxidants, the kinetic treatment for the reactions expressed by R8 and R9 gives the following relationship;

$$\ln\left(\frac{[\cancel{M}SA]_0}{[\cancel{M}SA]_t}\right) = \frac{k_{\cancel{M}SA}}{k_R}\ln\left(\frac{[R]_0}{[R]_t}\right) \qquad (1)$$

where [~~M~~SA]$_0$, [R]$_0$, [~~M~~SA]$_t$, and [R]$_t$ are the initial concentrations and those at time *t* for the SA~~Methyl Saturated Alcohol~~ and the r~~R~~eference compound, respectively. Two reference compounds were used with each oxidant ~~were used~~ to ensure~~assure~~ that the reference compound~~ does not have~~ had no~~any~~ influence on overall rate coefficient. According to Eq (1), a plot of ln([~~M~~SA]$_0$/[~~M~~SA]$_t$) versus ln([R]$_0$/[R]$_t$) should be a straight line that passes through the origin. The slope of this plot gives the ratio of rate coefficients $k_{\cancel{M}SA}/k_R$. Therefore, the value of $k_{\cancel{M}SA}$ can be obtained if the rate coefficient k_R of the reference compound is known.

The experimental systems have been~~are~~ described in previous works (Tapia et al., 2011;~~,~~ Martin et al., 2013) and only a brief description is given~~shown~~ here. Kinetic measurements were performed at room temperature (~298 K) and atmospheric pressure (720 ± 20 Torr) by employing two separate~~d~~ experimental set-ups: 1) ~~—~~A~~n FTIR system formed by~~ 50 ~~-~~L Pyrex® glass reactor was coupled to an~~the~~ Fourier Transform Infrared~~ Radiation~~ spectrometer as a detection technique ("on~~-~~line" analysis). Inside of the Pyrex® glass reactor there is a multi-reflect~~x~~ion system with three mirrors that allows an infrared radiation path of 2.8~~–~~-200 m~~eters~~. This reactor is known as white cell (Saturn Series Multi-Pass cell). The FTIR spectrometer (Thermo Nicolet 6700) was~~is~~ equipped with a KBr beam splitter and liquid nitrogen-cooled MCT. Typically, for each spectrum, 60 interferograms were co-added over 98 ~~-~~s and approximately 30~~—~~40 spectra were recorded per experiment with a spectral resolution of 1 ~~-~~cm^{-1}. 2) ~~—~~A Teflon ® gas bag reactor of 500 L with s~~S~~olid p~~P~~hase m~~M~~icro e~~E~~xtraction ~~fiber~~ (SPME) ~~as a~~

~~fiber pre-concentration sample method, was~~ for sampling ~~followed by analysis on~~ and g~~G~~as c~~C~~hromatography —~~-~~m~~Mass~~ s~~Spectrometry system~~ with a t~~T~~ime of f~~F~~light mass spectrometer~~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 ºC 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 ºC; interface, 250 ºC; ~~oven~~ initial oven temperature, 40 ºC for 4 min; ramp, 30 ºC min~~-~~$^{-1}$ to 120 ºC, held for 6 min; second ramp, 30 ºC min~~-~~$^{-1}$ to 200 ºC, held for 3 min.

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

The kinetic experiments~~,~~ for the Cl and OH reactions~~,~~ were performed in the 50 L Pyrex® glass reactor coupled to an FTIR spectrometer~~the 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$_3$ with 4MCHexOH was studied using a 500 L Teflon~~-~~® reactor~~ of 500 L~~ in order to minimize the wall deposition and dilution effects of consecutive additions of N$_2$O$_5$. Chlorine atoms and OH radicals were obtained by photolysis of Cl$_2$ in N$_2$ and methyl nitrite, CH$_3$ONO, in the presence of NO in air. Methyl nitrite~~, CH$_3$ONO,~~ was synthesized in the laboratory as described elsewhere (Taylor et al., 1980).

Nitrate radicals were generated in situ in the dark by the thermal decomposition of N$_2$O$_5$ (Atkinson et al., 1984, 1988). N$_2$O$_5$ was obtained mixing O$_3$ with an excess of NO$_2$ (Scott and Davidson, 1958). Prior~~eviously~~ to the kinetic experiments a series of tests in the dark and photolytic~~sis~~ conditions were carried out to evaluate secondary reactions, such as wall depositions and photodegradation~~ processes~~ of all reactants.

The r~~R~~ange concentrations of reactants employed were as follows: 2–~~-~~16 ~~-~~ppm of 4MCHexOH, 3–~~-~~9 ~~-~~ppm of 3,3DM1ButOH and 3,3DM2ButOH, 9–~~-~~30 ~~-~~ppm of Cl$_2$, 4–~~-~~13 ~~-~~ppm of 1-butene and 2-methylpropene, 7–~~-~~14 ~~-~~ppm of propene and cyclohexene, 5–~~-~~7 ~~-~~ppm of isopropanol, 3–~~-~~5 ppm of 2-methyl-2-butanol, 26–~~-~~55 ~~-~~ppm of CH$_3$ONO, 20–~~-~~60 ~~-~~ppm of NO, 3–~~-~~4 ~~-~~ppm of 2-ethyl-1-hexanol, 4–~~-~~5 ~~-~~ppm of 1-butanol. For reactions of 4MCHexOH with nitrate radicals 2–~~-~~5 additions of N$_2$O$_5$ with concentrations between 8–~~-~~36 ~~-~~ppm were made per ~~each~~ experiment. ~~N$_2$ and synthetic air were used as bath gases for Cl, NO$_3$ and OH reactions, respectively.~~

2.2 Product experiments

The product study was carried out at room temperature (~ 298 K) and at a pressure of ~~(~~720 ± 20~~)~~ Torr of synthetic air employing the two experimental set-ups previously described~~mentioned above~~. 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 mixture was taken from this~~eis~~ reactor using the SPME and subsequently analyzed with GC-TOFMS. In addition, independent experiments using SPME/GC-TOFMS ~~technique~~ in a 150 ~~-~~L Teflon® reactor were developed. Product~~s~~ analyses were carried out using the same procedure as for the kinetic experiments, without the reference compound, and employing synthetic air as bath gas. O~~I~~n this occasion the heating of the oven was changed slightly in order to get a better separation and to detect the products generated. The temperature ramps of the oven employed in the chromatograph were: 40 ºC for 4 min; ramp, 25 ºC min~~-~~$^{-1}$ to 120 ºC, held for 10 min; second ramp, 25 ºC min~~-~~$^{-1}$ to 200 ºC, held for 4 min.

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

For the SPME/GC-TOFMS experiments, the NIST webbook (https://webbook.nist.gov/chemistry/) and the m~~M~~ass s~~S~~pectra database of the instrument were used to identify the products. Calibrated FTIR spectra and SPME/GC-TOFMS chromatograms were used for~~to~~ quantification in those cases where the product was commercially available.

The molecular yields of the reaction products were estimated from the slopes of plots of the concentration of ~~formed~~ product formed versus the amounts of ~~M~~SA (Δ[~~M~~SA]) consumed. In the cases where ~~it was observed~~ an important loss of the reaction product by reaction of the oxidant and/or by photolytic process was observed, the concentration of the product was corrected using the formulism of Tuazon et al. (1986) (See S1, S~~in s~~upplementary M~~m~~aterial). Range of concentrations of reactants employed were as follows: 2–~~-~~14 ~~-~~ppm of ~~M~~SA, 8–~~-~~31 ~~-~~ppm of Cl_2, 12–~~-~~57 ~~-~~ppm of NO, 19–~~-~~66 ~~-~~ppm of CH_3ONO and 6–~~-~~36 ~~-~~ppm of N_2O_5.

Chemicals used were as follows: 4MCHexOH (97~~-~~%, Aldrich), 3,3DM1ButOH and 3,3DM2ButOH (98~~-~~%, Aldrich); 1-butene, propene, 2-methyl-2-butanol, isopropanol, 2-methylpropene, 4-methylcyclohexanone and cyclohexene (≥~~-~~99~~-~~%, Aldrich), 2-ethyl-1-hexanol (≥ 99~~-~~%, Fluka), 1-butanol (99.8~~-~~%, Aldrich), 3,3-dimethylbutanal (95~~-~~%, Aldrich) and 3,3-dimethyl-2-butanone (98~~-~~%, Aldrich), NO (99~~-~~%, Praxair), Cl_2 (> 99.8 %, Praxair), synthetic a~~A~~ir (Praxair Ultrahigh purity 99.999~~-~~%~~,~~) and ~~,~~ N_2 (99.999~~-~~%, Praxair). For N_2O_5 synthesis, N_2O_4 was~~ere~~ used (>99.5~~-~~%) from Fluka, P_2O_5 (98~~-~~%, such as desiccant) from Fluka and O_3 was synthesized by a generator model TRCE-5000, 5 g_{O3} h^{-1} OZOGAS.

3. Results and D~~d~~iscussion

3.1 Kinetic study

Preliminary test experiments indicated that dark heterogeneous reactions and photolytic losses of ~~M~~SAs and reference compounds could~~an~~ be considered negligible in our experimental conditions (k ≈ ~~∼~~10^{-6} s^{-1}). T~~As mentioned above, t~~he kinetic study~~ of Cl atoms and OH radical with the MSA~~ was carried out at room temperature (∼~~–~~298 K) and at 720 ± 20 Torr of N_2 gas for Cl atoms reactions and synthetic air for OH radical reactions~~respectively~~. Nitrate radical experiments were performed using N_2 gas in a 500 ~~-~~L Teflon reactor and employing the ~~system~~ SPME/GC-TOFMS system. A number of injections of the unreacted mixture were carried out in order to determine the associated precision of~~with~~ the sampling method to be used in the error analysis (Brauers and Finlayson-Pitts, 1997). The standard deviations (σ) were as follows: 3.7~~-~~% for 4MCHexOH, 1.7~~-~~% for 1-butanol and 3.5~~-~~% for 2-ethyl-1-hexanol.

~~-~~Figure 1 shows examples of the kinetic data plotted according to Eq (1) for the reactions of ~~M~~SAs with different atmospheric oxidants.

A good correlation was obtained with an intercept close to zero, which indicated~~s~~ the absence of~~ other ~~secondary reactions~~processes~~. From the slopes of the plots ($k_{\cancel{M}SA}/k_R$) and knowing the values of the rate coefficients for the reference compounds employed (k_R), the value of the absolute rate coefficient for each~~ methyl~~ saturated alcohol ($k_{\cancel{M}SA}$) was~~has been~~ determined.

Rate coefficients of reactions of reference compounds~~,~~ with~~for~~ Cl atoms reactions (in 10^{-10} cm^3 molecule^{-1} s^{-1} units) were: 2-methylpropene (3.40 ± 0.28), 1-butene (3.38 ± 0.48), (Ezzel et al., 2002) and propene (2.23 ± 0.31) (Ceacero-Vega et al., 2009); with~~for~~ OH radicals~~ reactions~~ (in 10^{-11} cm^3 molecule^{-1} s^{-1} units): propene (2.66 ± 0.40) ~~,~~(Atkinson and Aschman, 1989), cyclohexene (6.77 ± 1.69) (Atkinson and Arey, 2003), isopropanol (0.51 ± 0.008) (IUPAC www.iupac-kinetic.ch.cam.ac.uk) and 2-methyl-2-butanol (0.36 ± 0.06) (Jiménez et al., 2005)~~.~~ a~~A~~nd with~~for~~ NO$_3$ radicals ~~eactions ~~(in 10^{-15} cm^3 molecule^{-1} s^{-1} units): 1-butanol (3.14 ± 0.97) and 2-ethyl-1-hexanol (2.93 ± 0.92) (Gallego-Iniesta et al., 2010).

~~-~~The ratios of the rate coefficients, $k_{\cancel{M}SA}/k_R$, the absolute rate coefficients and the weighted averages are shown in Table 1. The error of $k_{\cancel{M}SA}/k_R$ was~~are~~ given by two~~2~~ times the statistical deviation calculated from the least ~~-~~squares fit of the plot of Eq. (1). The uncertainties for rate coefficients of ~~M~~SA ($\sigma_{k\cancel{M}SA}$) were calculated from the uncertainty of slope of plots (σ_{slope}) and the uncertainty of the reference (σ_{kR}) by using the propagation of uncertainties. The average value of the rate coefficients obtained with different reference compounds and their~~its~~ associated errors were obtained by weighted average (See footnote, Table 1). ~~-~~The rate coefficients obtained in this work are the first kinetic data reported for these ~~M~~SAs~~,~~ therefore, the results obtained cannot be compared with literature values.

I~~As it has been mentioned in introduction section, i~~t is well established that the gas-phase reaction mechanism of saturated organic compounds (alkanes, alcohols, ethers, etc.) with~~ the~~ atmospheric oxidants (Cl atoms, OH and NO$_3$ radicals) are initiated ~~“~~via~~”~~ hydrogen atom abstraction from the organic compound to form a stable molecule and an alkyl radical (Finlayson-Pitts and Pitts, 2000; Atkinson and Arey, 2003; Calvert et al., 2011; Ziemann and Atkinson, 2012). The presence of the OH~~hydroxyl~~ group in saturated alcohols implies two types of hydrogens that can be abstracted:~~,~~ hydrogen bonded to a carbon (C−H) of the main chain or of an alkyl substituent and hydrogen bonded to oxygen of OH~~hydroxyl~~ group~~ (-OH)~~. Two literature reviews of the~~about~~ reactivity of saturated alcohols (Calvert et al., 2011; Mellouki et al., 2015) conclude that:

1 –) ~~–~~The reactions of aliphatic alcohols with atmospheric oxidants proceed mainly by H atom abstraction from various C−H groups in the alkyl chain,~~ being the~~ abstraction of H atom ~~abstraction ~~from the O−H group being negligible;~~.~~

2 –) ~~–~~Rate coefficients for the reactions of Cl, OH and NO$_3$ are higher for alcohols than those of the corresponding alkanes due to the activating effect of the OH group. This effect is extended over about four~~4~~ carbon atoms (Nelson et al., 1990); and~~.~~ ~~As will be discussed below, the activating effect of the OH group depends on the oxidant.~~

3 –) ~~–~~The attack percentage of a radical to the different sites of the alcohol (α, β, γ and δ) depends on the oxidant, the structure of saturated alcohol, the type and numbers of substituents, and temperature~~,~~ (Moreno et al., 2012, 2014; McGillen et al., 2013, 2016).

In order to verify~~check~~ these remarks, the reactivity of the~~ Methyl~~ SA~~saturated Alcohols~~ studied in this work were~~has been~~ analyzed and discussed by comparing~~ a)~~ the rate coefficients of the ~~M~~SAs obtained with ~~for the~~

different oxidants~~;, b)~~ comparing the rate coefficients of the ~~M~~SAs and the rate coefficients of their homologous alkanes available in literature, ~~bibliography~~ and comparing ~~c)~~ the rate coefficients obtained in the reaction of the same oxidant but with different alcohols. The data used in the ~~to~~ comparis~~on~~e are summarized in Table S1 in S~~s~~upplementary M~~m~~aterial.

From the analysis of all data shown in Table S1, it can be observed that:

a~~)~~) The trend in the reactivity of ~~M~~SAs in relation to the different oxidants is the same that ~~the~~ observed for other saturated alcohols: k_{Cl} (k ~~~~~ ≈ 10^{-10}) > k_{OH} (k ≈ ~~~~~ 10^{-11}) >> k_{NO3} (k ≈ ~~~~~ 10^{-15}), (k in cm^3 $molecule^{-1}$ s^{-1} units). This behavior could be explained by considering the geometry and ~~the~~ electronic density of each oxidant, together with ~~the~~ kinetic c~~C~~ollision t~~T~~heory. As the Cl atom has spherical electronic density distribution ~~of its density~~, any ~~, for the~~ collision ~~any~~ orientation is suitable~~adequate~~, in addition, the Cl atoms present~~s~~ low~~ess~~ steric hindrance. So ~~Then, comparatively~~ the Cl reaction is comparatively less selective and faster, with values for the rate coefficient~~s~~, 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 the OH radical~~,~~ must be specifically oriented toward the hydrogen of the ~~M~~SA that will be abstracted. The electronic density of nitrate radical is distributed around the three oxygens, which implies several appropriate orientations~~. However~~, but since~~as~~ the nitrate radical has a non-linear structure, the steric hindrance is much greater~~bigger~~ than for the OH radical, which~~and it~~ reduces the reactivity of NO_3 in relation to th~~at~~ose of OH ~~radical~~.

b~~)~~) The rate coefficient for the reaction of 4MCHexOH with Cl atoms is similar to the rate coefficient of its homologous alkane (E-1,4-dimethylcyclohexane): $k_{4MCHexOH+Cl} = 37.0 \times 10^{-11}$ ≈ ~~≃~~ $k_{E\text{-}1,4\text{-}dimethylcyclohexane+Cl} = 36.3 \times 10^{-11}$. In the case of the reaction with OH radical, the rate coefficient of 4MCHexOH is 1.5 times higher than with E-1,4-dimethylcyclohexane:~~;~~ $k_{4MCHexOH+OH} = 18.7 \times 10^{-12} > k_{E\text{-}1,4\text{-}dimethylcyclohexane+OH} = 12.1 \times 10^{-12}$ (Table S1). These results show that the activating effect of the ~~hydroxyl group (~~ OH group~~)~~ of the ~~M~~SA is less important for the reaction with Cl atoms than with the OH radical, behavior that agrees with that established by the Structure Activity Relationships (SARs) methods~~. The activating effect of hydroxyl group of the alcohols was quantified by different authors~~ (Kwok and Atkinson 1995;~~ Kerdouci et al, 2010;~~ Calvert et al. 2011). ~~taking into account the available kinetic data reported in bibliography, obtaining the factor of reactivity for the hydroxyl group, F(-OH)). This factor of reactivity is different for each oxidant, 1.18 for Cl reaction, 2.35 for reaction with OH (Calvert et al. 2011) and 18 for NO~~$_3$ ~~reaction (Kerdouci et al., 2010).~~ There are no ~~data of~~ rate coefficient datas for the reactions with NO_3 radical of the alkanes homologous to ~~alkanes of~~ the ~~M~~SAs studied in this work ~~with NO~~$_3$ ~~radical~~, and therefore it was~~is~~ not possible to check ~~out~~ the effect of OH ~~hydroxyl~~ group in the r~~reactivity of NO~~$_3$ ~~r~~eaction with NO_3. However, according to the SAR method developed by ~~factor of reactivity obtained by~~ Kerdouci et al. (2010) for the reactions of alcohols with NO_3, this effect is greater~~higher~~ than in the corresponding ~~to~~ Cl and OH reactions.

c~~)~~) ~~–~~The activating effect of the chain length ~~chain~~ in the reactivity of alcohols is also ~~more~~ different~~evident in~~ for the Cl and OH 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 in the ~~of~~ rate coefficient for Cl reaction can be observed ($k_{3M1BuOH+Cl} = 25.0 \times 10^{-11}$; $k_{3,3DM1ButOH+Cl} = 26.9 \times 10^{-11}$) together with~~and~~ an important decrease in ~~of~~ the rate coefficient for the OH reactions ($k_{3M1BuOH+OH} = 14 \times 10^{-12}$; $k_{3,3DM1ButOH+OH} = 5.33 \times 10^{-12}$). This behavior could be explained by the different order of reactivity of~~between~~ the two oxidants. So, ~~For~~ Cl atom, more reactive (k in the order of 10^{-10} cm^3 molecule^{-1} s^{-1}) but less selective than OH, an increase in the chain ~~of the~~ length ~~chain~~ or in the number of methyl groups in the SA~~s~~ implies more hydrogens available to be abstracted and therefore an increase in~~of~~ the rate coefficient. However, for OH radicals, less reactive (k in the order of 10^{-11}–10^{-12} cm^3 molecule^{-1}s^{-1}) and more selective than Cl, the attack for H-abstraction will be carried out at ~~in~~ a specific position in the SA~~place~~, so an increase in~~of~~ the chain length of the alcohol does~~has~~ not have a significant~~ative~~ effect on~~to~~ the reactivity;~~,~~ ~~even~~ the presence of a second methyl group even disfavors the reaction, probably due to ~~the~~ steric hindrance near ~~to~~ the attack position.

In addition, as can be seen in Table S1, the position of the OH~~hydroxyl~~ group of SA has a different effect on the reactivity 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 tho~~one~~se 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_3 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 the α–position available to be abstracted.

All these observations ~~(a, b and c)~~ could imply a different mechanism for~~in~~ the hydrogen abstraction process for Cl atoms versus the OH ~~and NO_3~~ radical~~s~~. Nelson et al. (1990) and Smith and Ravishankara (2002) indicate the possible formation of an intermediate adduct between the OH radical and the oxygen of the OH~~hydroxyl~~ group ~~via hydrogen bond~~ that will imply a specific orientation. Theoretical studies found in the literature~~bibliography~~ show this different hydrogen ~~-~~abstraction process in the reaction of saturated alcohols with Cl atoms (Garzon et al., 2006) and OH radical (Moc and Simmie, 2010). There are not enough rate coefficient data for the reaction of SAs with NO_3 radicals to establish conclusions about the mechanism.

Different mechanisms in the hydrogen atom abstraction process for each oxidant will imply different product distributions and molecular yields, as ~~it~~ will be shown ~~below,~~ in the section on~~f~~ product and mechanism ~~and mechanistic~~ study.

3.1.1 Estimation of rate coefficients

In order to estimate the rate coefficients of the reactions of organic compounds with the atmospheric oxidants, a multitude of methods have been proposed (Vereecken et al., 2018). The most popular and widely used is the SAR method developed initially by Kwok and Atkinson (1995) to estimate the rate coefficients at room temperature for gas-phase reactions with the OH radical. This method has been updated for OH reactions (Jenkin et al., 2018) and extended to reaction with NO_3 (Kerdouci et al., 2010, 2014) and Cl (Calvert et al., 2011; Poutsma 2013) ~~reactions~~. The EPA (United States Environmental Protection Agency) has developed the EPI Suite™-Estimation Program Interface that allows ~~to~~ estimation~~e~~ of the rate coefficients for the reactions of the OH radical with~~and~~ organic compounds using the AOPWIN v1.92 program.

In our work the rate coefficients of ~~M~~SAs with the three oxidants have been estimated using the SARs method (See S2, S~~s~~upplementary M~~m~~aterial). The results are shown in Table 2.

The estimated values of ~~estimated~~ rate coefficients agree with experimental data, with ~~ratios~~ k_{exp}/k_{SAR} ~~b~~ratios between 0.9 and 1.28, except for the case of 3,3DM1ButOH and NO_3 radical~~, with~~ which showed a k_{exp}/k_{SAR} ratio of 3.24. In general, the SARs method when applied to alcohols predicts better rate coefficients for the Cl atom~~s~~

and the OH radical than for the NO_3 radical, especially for primary alcohols. It is important to note that the kinetic database for the NO_3 reactions is more limited than for Cl and OH reactions, so the estimated rate coefficient for NO_3 radical should be treated with caution (Kerdouci et al. 2010, 2014; Calver et al., 2011).

It is known that organic compounds that~~which~~ react~~s~~ in the same way with different atmospheric oxidants~~,~~ present a correlation between their rate coefficients. In this sense, over~~along~~ the years, different correlations have been proposed to~~hat~~ allow ~~to~~ estimation of~~e~~ the unknown rate coefficient when the other ~~one~~ is known (Wayne, 1991, 2000; Atkinson, 1994; Calvert et al., 2011; Gallego-Iniesta et al., 2014). The ~~Correlations~~ logk$_{Cl}$–logk$_{OH}$ and logk$_{NO3}$–logk$_{OH}$ correlations have been built for a set of ~~alcohols,~~ ethers and saturated alcohols by Calvert et al., (2011) obtaining the following relationships:

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

(2)

$$\log(k_{NO3}/\mathrm{cm^3\ molecule^{-1}\ s^{-1}}) = 1.11 \times \log(k_{OH}/\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}) - 2.42 \qquad (r^2 = 0.66) \qquad (3)$$

These equations have been used to estimate the rate coefficients of the reactions of ~~M~~SAs with Cl and NO_3~~nitrate~~ radical using the experimental rate coefficients measured in this work for OH reactions. The estimated rate coefficients, k_{log}, according to~~with~~ Eqs (2) and~~ Eq~~ (3), and the ratios (k_{exp}/k_{log}), are also shown in Table 2. This estimation method obtains slightly better rate coefficient for 3,3DM1ButOH + NO_3 reaction ($k_{exp}/k_{log.}$ = 1.53) than the SAR method (k_{exp}/k_{SAR} = 3.24). However, for Cl reactions the~~ ratios~~ k_{exp}/k_{log} ratios are in the range of 0.6–1.97, indicating that~~ the~~ Eq (2) predicts ~~worse~~ the rate coefficients worse than SAR method. Again, this ~~fact~~ could be due to the different reaction mechanism~~ reaction~~ in the H-abstraction process for the Cl and OH reactions. ~~As Such as it has been indicated above, to apply these relationships both oxidants must react according to the same mechanism.~~ It is important to indicate that in the case of Cl reactions, other effects, such as thermochemistry and the polar effect, must be considered to estimate the rate coefficients for hydrogen abstraction reactions (Poutsma, 2013).

3.2 Product and m~~M~~echanistic s~~S~~tudy

A product study of the reaction of 4MCHexOH, 3,3DM1ButOH and 3,3DM2ButOH with chlorine atoms in the absence/presence of NO_x, hydroxyl and nitrate radicals has been performed. ~~by employing the two experimental set-ups mentioned above (FTIR and SPME/GC-TOFMS).~~ IR absorption bands of HCl, CO_2, CO, HNO_3, N_2O, NO_2, HCOOH, HCOH, ClNO, $ClNO_2$ and CH_3NO_3 were observed in the FTIR experiments. Some of t~~T~~hese compounds are products from the reactions of the SAs with oxidants. They can also be formed ~~bands are due~~ by~~to the~~ decomposition of the employed precursors~~ employed~~ (Cl_2, CH_3~~N~~ONO~~2~~ and N_2O_5) and in some cases,~~ are due~~ by~~to~~ heterogeneous reactions of these precursors with~~ the walls of~~ the Pyrex~~®~~ glass reactor walls. The formation of O_3 and N_2O_5 have also been observed after long~~t large~~ reaction times for the reactions of the ~~M~~SAs with Cl atoms in the presence of ~~+~~ NO_x, due to the high concentration of ~~the~~ NO_2 in the~~ medium of~~ reaction medium and the~~in~~ presence of radiation. Quantitative analysis was carried out by linear subtraction of a spectrum's absorption bands and the peak areas of GC chromatograms by~~with~~ the use of calibrated spectra and reference chromatograms. The experimental conditions and molecular yields of the main products formed in the reactions of ~~M~~SAs and analyzed by FTIR and SPME/GC-TOFMS~~ techniques~~ are given in Tables 3–6. Molecular yields could be affected by~~to~~ large errors associated with the SPME sampling method and due to the presence of interfering IR absorption bands, mainly associated with precursors of the OH and NO_3 radicals or by nitrated compounds formed.

3.2.1. ~~–~~4MCHexOH

E-4-methylcyclohexanone was identified in the reactions with Cl~~,~~ (absence/presence of NO_x)~~Cl + NO~~, OH~~ + NO~~ and NO_3~~ + NO_2~~. An example of the product spectra obtained by~~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 as sampling method and the ~~/~~GC-TOFMS as detection technique~~ system~~ were also carried out for the reactions of 4MCHexOH with Cl atoms and OH and NO_3 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. The peak (B) shown~~ed~~ 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 Cl~~chlorine~~ atoms (absence/presence of NO_x) 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 analysis for the reaction with Cl~~chlorine~~ atoms in the presence of NO_x are~~is~~ shown i~~o~~n Fig. S2. The concentrations of E-4-methylcyclohexanone, corrected according to Eqs (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 plots 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 was~~is~~ below to 50% for reactions with Cl and OH radical and ~60% for NO_3.

Residual spectra after subtraction of~~ the~~ E-4-methylcyclohexanone show IR absorption bands compatible with the presence of hydroxy–carbonyl compounds (~1750, 1720 and~~,~~ 1060 cm^{-1}) and nitrated organic compounds ($RONO_2$ ~1660, 1264 and 862 cm^{-1}, and/or $ROONO_2$ ~1720, 1300 and 760 cm^{-1}) (See residual spectra, Fig. S3 in S~~s~~upplementary M~~m~~aterial). The amount of nitrated compounds was estimated using the average integrated absorption coefficient of 1.2 × 10^{-17} cm molecule^{-1} of similar compounds corresponding to the IR range 1260–1305 cm^{-1} (Tuazon and Atkinson,1990). The calculated yields of $RONO_2$ were 20% and 60% for Cl (in the presence of ~~+~~ NO_x) and NO_3 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_x, present~~s~~ in the reaction medium~~,~~ reacts faster with the $CH_3O^•$ radical, (formed by~~in the reaction of~~ photolysis of CH_3ONO~~, with NO)~~ than other~~s~~ alcoxy radicals. Table 6 shows a summary of the average yields of reaction products quantified for 4MCHexOH reactions.

Considering the products detected here and the those 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 that~~o~~ explain the formation of organic compounds (carbonyl~~, or~~ hydroxy-carbonyl, etc)~~ compounds,~~ and Figure 5B shows an example of a path to explain the formation of nitrated organic compounds ($ROONO_2$ and $RONO_2$). Similar nitrated compounds could be formed by routes II–IV. The abstraction of hydrogen atom~~s~~ at the~~in~~ ~~α-~~α–position with respect to OH~~alcohols~~ group (route I) followed by the addition of oxygen, the formation of a peroxy radical and the fast decomposition of this radical explains the formation of E-4-methylcyclohexanone. Based on the molecular yield obtained for E-4-methylcyclohexanone for each oxidant (See Table 6), this route represents ∼25/~~, ∼~~ 30 %, ∼40 % and ∼60 % of the reaction mechanism of 4MCHexOH with Cl (absence/presence of NO_x),~~, and Cl + NO,~~ OH and NO_3, respectively. Percentages are two-fold~~times~~ higher than those predicted by the SARs method~~ prediction~~ in the case of the Cl ~~atoms~~ reactions and 1.3- and 1.5-fold~~ times~~ lower for the OH and NO_3 reactions, respectively. These data should be taken with caution, since they could include~~mply~~ many sources of error.

Apart from E-4-methylcyclohexanone, other carbonyl and hydroxy-carbonyl compounds could be formed by routes II, III and IV. The presence of these types ~~is kind~~ of compounds has~~ve~~ been observed in the reactions with Cl and OH. According to the e~~E~~lectron i~~I~~onization m~~M~~ass s~~S~~pectra (EI-MS) (Fig. S4, S~~s~~upplementary M~~m~~aterial) an assignation of peaks (C) and (D) shown in Fig. 3,~~ an assignation~~ to 2-hydroxy-5-methyl-cyclohexanone, 5-hydroxy-2-methylc~~-c~~yclohexanone and/or 3-methyl-1,6-hexanedial has been proposed. However, according to the atmospheric reactivity (Finlayson and Pitts, 2000; Calvert et al., 2011; Ziemann and Atkinson, 2012) and the study of Bradley et al.~~,~~ (2001), the compound that would be expected is~~ the~~ 3-methyl-1,6-hexanedial, which ~~come~~arises~~s~~ from the decomposition of the alkoxy radical formed in route II. However, confirmation was not possible since these compounds a~~we~~re not commercially available. The detection about 9% of HCOH ~~about 9 %~~ in the reaction with Cl atoms indicates that the elimination of the methyl group in route IV is minor~~ity~~.

In the case of nitrate radical, the only carbonyl compound detected was E-4-methylcyclohexanone~~ was detected as carbonyl compound~~, suggesting that ~~the~~ route I may be the dominant pathway for this radical. The large difference between the yields of E-4-methylcyclohexanone obtained using the SPME/GC-TOFMS system (∼75 %) or the FTIR (35 %) could be due to the different methods of adding ~~way to add~~ the precursor to the two~~in both~~ reactors (small aliquots of N_2O_5 in the Teflon® reactor versus one large addition in the Pyrex® glass 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 of 50 L reactor~~ of 50 L~~, favoring the formation of carbonyl compounds instead of nitrated organic compounds. Taking into account~~,~~ the yields of E-4-methylcyclohexanone and the nitrated compounds for the NO_3 reaction using FTIR analysis, a total carbon balance of 100% is obtained (See Table 6).

3.2.2. 3,3DM1ButOH

For the reaction of 3,3DM1ButOH with the three atmospheric oxidants, ~~Following the same procedure as above,~~ 3,3-dimethylbutanal was identified as the main reaction product. ~~in the reaction of 3,3DM1ButOH with the three atmospheric oxidants.~~ Figure S5A shows the FTIR spectra obtained for the reactions of 3,3DM1ButOH with Cl (absence/presence of NO_x)~~, Cl + NO~~, OH and NO_3~~ after subtraction~~.

Residual FTIR spectra after subtraction of 3,3-dimethylbutanal (Fig. S5B), the SPME/GC-TOFMS chromatograms (Fig. S6) and the EI-MS spectra (Fig. S7), show that other reaction products such as carbonyl, hydroxy-carbonyl and nitrated compounds are formed. These reaction products could be formaldehyde, 2,2-dimethylpropanal, glycolaldehyde, acetone, and peroxy-3,3-dimethyl-butyryl nitrate (P33DMBN) $(CH_3)_3CCH_2C(O)OONO_2$. These compounds can be formed as primary products (See Fig. 6) and/or secondary products from the degradation of 3,3-dimethylbutanal (See Fig. S8). The SPME/GC-TOFMS chromatograms show common peaks for the three oxidants, but the numbers of peaks and their distribution are very different, especially for OH reactions. In the case of the SPME/GC-TOFMS system, a set of experiment using f~~F~~ield i~~I~~onization was carried out in order to help~~ us to~~ establish the identification of reaction products.

Time–~~-~~concentration profiles of 3,3DM1ButOH, 3,3-dimethylbutanal and those reaction products positively identified by FTIR analysis were made ~~in order~~ to ~~establish~~ test whether~~if~~ the profiles correspond to~~with~~ ~~a~~ primary or secondary reaction products. An example of the reactions with Cl~~chlorine~~ atoms in the absence and presence of NO_x is presented~~shown~~ in Fig. 6, show~~observ~~ing that in the absence of NO_x the profiles of acetone and formaldehyde have~~show~~ two trends. It ~~profiles~~indicates~~ a typical profile of secondary reactions.~~ that these compounds are formed as primary and secondary products. This profile is clearly observed for nitrated compounds in the reaction with~~of~~ Cl atoms in~~-~~ the presence of NO_x (Fig. 6B).

A c~~C~~ommercial sample of 3,3-dimethylbutanal was used to estimate the molecular yields in both experimental systems. These~~e molecular yields~~ are shown in~~ the~~ Table 4. The yields of acetone and formaldehyde were calculated using an FTIR reference spectrum of a commercial sample and FTIR reference spectra from Eurochamp database (https://data.eurochamp.org/data-access/spectra/), respectively. An FTIR reference spectrum of 2-methylpropanal (from this same database) was~~has been~~ used to estimate the molecular yield of 2,2-dimethylpropanal.

The amounts of 3,3-dimethylbutanal formed were corrected by their reactions with Cl atoms, and with OH and NO_3 radicals~~ as is described previously,~~ using the rate coefficients available in literature~~bibliography~~ or for reactions of structurally similar compounds (see footnote, Table 4). Estimated yields of formaldehyde, acetone, 2,2-dimethylpropanal and nitrated compounds are summarized in Table 6 along with an average yield of 3,3-dimethylbutanal. The higher yield of nitrated compounds in the reaction of 3,3DM1ButOH with nitrate radical could indicate an extra formation of nitrated compounds from secondary~~ products~~ reactions (See Fig. S8). T~~A t~~otal of carbon yields ~~(nitrated compounds werehave not been accounted for)~~ of 60%, 81% and 36% have been justified for Cl~~ (in the absence and presence of NO)~~, OH and NO_3 reactions respectively. It ~~, but~~ must~~ it~~ be noted that there are reaction products that could not be quantified as dihydroxy~~carbonyl~~ or hydroxy-carbonyl compounds in the reactions with Cl~~ atoms~~ atoms~~reactions~~ in the absence of NO_x and primary nitrated compounds in the reactions with Cl atoms in the presence of NO_x~~+ NO~~ and with NO_3 radical.~~ reactions.~~

This work is the first study of the products of reaction ~~products~~ of 3,3DM1ButOH with~~ the~~ atmospheric oxidants, so there is no other~~any~~ study with which to compare. Figure 7 shows the reaction mechanism proposed based on ~~the~~ literature studies of~~ about~~ saturated alcohols reactions with Cl atoms and the OH radical (Cavalli et al., 2002; Hurley et al., 2009; McGillen et al., 2013; Welz et al., 2013) and considering the reaction products identified in ~~this~~ our work. Table S2~~,~~ in S~~s~~upplementary M~~m~~aterial, shows a summary of the reaction products, either~~ proposed in this mechanism~~ observed or tentatively identified~~ in~~ proposed in this mechanism of the reaction~~s~~ of 3,3DM1ButOH with the atmospheric oxidants.

As it can see in Table 4, the e~~E~~stimated molecular yields of 3,3-dimethylbutanal (formed by H atom -a~~A~~bstraction at the~~in~~ α–~~-~~position of 3,3DM1BuOH) are very similar to the one predicted by the SARs method for the Cl ~~(~40% without NO and 43% with NO)~~ and OH reactions. ~~(~(40-43) %, ~60 %) are very similar to the one predicted by the SAR method (40 % for Cl and 66 % for OHrespectively).~~ In the case of NO_3 radical a large difference between ~~both~~ yields was~~are~~ observed (36% estimated in this work, 86% predicted by SAR~~ method~~). This discrepancy could be explained by the fact that the SAR method applied to the NO_3 radical reaction with primary alcohols (Kerdouci et al., 2010, 2014) underestimates the attack of NO_3 at the~~in~~ β–~~-~~position, since it does not consider the possible activating effect of the -CH_2OH~~hydroxyl~~ group (See S2,Supplementary Material)~~- jointed to -CH_2-, (F(-CH_2OH))~~. This could also explain the large difference observed between the estimated and measured rate coefficients of the reaction of 3,3DM1ButOH with NO_3 as~~ was~~ shown in Table 2. On the other hand, ~~as it has been discussed above, ~~the volume of the reactor could also have an influence on formation of 3,3-dimethylbutanal.

According to the molecular yields of the products quantified and/or observed in the SPME/GC-TOFMS chromatograms, it can be concluded that for the OH radical reaction,~~ the~~ route I (attack at the~~in~~ α–~~–~~position) seems to be the main reaction route. For Cl atoms the three routes can occur to a significant extent~~with a high percentage~~. The major molecular yields of formaldehyde and acetone (route III) in the reactions with~~of~~ Cl atoms in the presence of NO_x versus those of ~~Cl atoms reactions ~~in the absence of NO_x could indicate that in the absence of NO_x the self reactions of peroxy radicals (RO_2·) ~~reaction “~~via the ~~”~~ molecular pathway~~channel~~ is more favored than ~~“~~via~~”~~ the radical pathway~~channel~~. For the NO_3 radical, routes I and II (attack at the~~in~~ β–~~–~~position) with the formation of nitrated compounds seem to be the major~~unique~~ routes.

3.2.3. ~~–~~3,3DM2ButOH

A~~The a~~nalysis of the FTIR spectra obtained for the reactions of 3,3DM2ButOH with Cl atoms~~,~~ in the presence and absence of NO_x, OH radical and NO_3 radical shows the formation of 3,3-dimethyl-2-butanone as a main product (see Fig. S9). Other compounds, such as formaldehyde, acetone, 2,2-dimethylpropanal and p~~P~~eroxya~~ A~~cetyl n~~N~~itrate (PAN), were ~~have ~~also ~~been ~~observed. The residual FTIR spectra after sub~~s~~traction of all known IR bands~~,~~ again shows the presence of carbonyl compounds (IR~~ bands~~ absorption in the range ~~of ~~1820–~~-~~1700 cm^{-1}); hydroxy compounds (1060–~~-~~1040 cm^{-1}) in the reaction with~~of~~ Cl atoms in the absence of NO_x, and also nitrated compounds ($RONO_2$; 1650, 1305–~~-~~1260, 890 cm^{-1}) in the reaction with~~of~~ Cl in the presence of NO_x~~ + NO~~ and NO_3 radical (Fig. S9C). The presence in the residual~~ an~~ FTIR spectra of an IR absorption band around 1800 cm^{-1} for the reaction with~~of~~ Cl atoms at long~~arge~~ reaction times could be due to the formation of chlorine compounds by reaction of 3,3-dimethyl-2-butanone with Cl_2 (Ren et al., 2018) or the formation of cyclic compounds such as hydrofurans. The SPME/GC-TOFMS chromatograms and MS spectra (Fig. S10 and S11) confirm the presence of other reaction products apart from 3,3-dimethyl-2-butanone in the case of Cl (absence/presence of NO_x) ~~, Cl + NO~~ and NO_3 reactions. Only one significant peak is observed in chromatograms of~~obtained for~~ the OH reactions.

The estimated molecular yields of 3,3-dimethyl-2-butanone for all individual experiments are given in Table 5, where the measured concentrations have been corrected for secondary reactions. Acetone, formaldehyde, 2,2-dimethylpropanal, nitrated compounds and acetaldehyde~~ have~~ were also ~~been ~~quantified. Plots of concentration versus time for formaldehyde, acetone (Fig. S12A) and nitrated compounds in the reactions of Cl in the presence of NO_x (Fig. S12B) show~~ typical~~ profiles with two trends. This type of profile indicates that ~~of secondary reactions for formaldehyde, acetone (Fig. S12A) and nitrated compounds in the reactions of Cl with NO (Fig. S12B).~~ formaldehyde and acetone ~~These compounds ~~could also be formed by degradation of 3,3-dimethyl-2-butanone (Fig. S13)~~. The estimated molecular yields of 3,3-dimethyl-2-butanone for all individual experiments are given in Table 5, where the measured concentrations have~~ again ~~been corrected again for secondary reactions~~. Table 6 summarizes the molecular yields of all quantified products.

~~A t~~Total carbon yields of ~60 %/~~,~~ 100 %, 90 % and 60 % have been accounted for Cl (in the absence and presence of NO_x), OH and NO_3 reactions, respectively (See Table 6). It is important to note that in the case of the reaction of Cl atoms in the absence of~~without~~ NO_x, where the total carbon yield was~~is~~ lower than 100 %, there were~~are~~ many reaction products that could not be quantified, such as dihydroxy~~carbonyl~~ and/or hydroxy–carbonyl compounds. In the reaction with ~~of~~ NO_3 radical, due to our experimental conditions, significant number ~~an important amount~~ of primary nitrated compounds was~~is~~ expected to be formed (Fig. S9C).

A mechanism of hydrogen atom abstraction at~~in~~ different positions on~~f~~ the carbon chain has been proposed for the reaction of 3,3DM2ButOH with Cl, OH and NO_3 ~~reactions~~. The mechanism is shown in Figure 8. Table S3, in S~~s~~upplementary M~~m~~aterial, shows a summary of the reaction products either observed or tentatively identified proposed by~~in~~ this mechanism ~~observed or tentatively identified in~~of the reactions of 3,3DM2ButOH with the atmospheric oxidants.

Molecular yields of 3,3-dimethyl-2-butanone obtained in this work imply ~~a~~ percentages of attack of the oxidant ~~i~~at the ~~n~~ α–position (route II) of: 43 %/~~and~~ 44 %~~,~~ in the case of Cl~~chlorine~~ atom (absence/presence of NO_x~~without and with NO respectively~~); 81 % for the OH radical and 58 % for the NO_3 radical. Percentages are very similar to th~~at~~ose predicted by SARs~~method~~ except for the NO_3 radical (See Table 5). High NO_2 concentration present in the reactions with NO_3 radical would greatly~~highly~~ favor the formation of nitrated compounds over~~versus~~ 3,3-dimethyl-2-butanone. It could justify the low estimated molecular yield for 3,3- dimethyl-2-butanone.

The main reaction products observed in the reaction with~~of~~ Cl atoms in the presence of NO_x (3,3-dimethyl-2-butanone, formaldehyde, 2,2-dimethylpropanal, acetone and~~,~~ acetaldehyde) confirm ~~that~~ the attack of Cl atoms ~~could attack in~~ at other sites ~~(~~apart from the~~of~~ α–position~~) with an important percentage~~. Based on the estimated molecular yield of acetone, ~~the~~ attack at the~~in~~ δ–position with abstraction of hydrogen atom from~~of~~ methyl groups (route III) could be ~58 %, and based on the estimated molecular yield of~~for~~ 2,2-dimethylpropanal, the attack ~~in~~ at the β–position (route I) could account ~~with a~~ for 10 %. These data agree with the SAR predictions for Cl atom reactions. On the other hand, the major molecular yields of acetone, formaldehyde and acetaldehyde (route III) in the reaction with~~of~~ Cl atoms in the presence of NO_x rather than in its absence ~~of NO~~ could indicate that in the presence of NO_x the self-reactions of peroxy radicals ~~self-reactions (RO_2) “~~via~~”~~ the molecular pathway~~channel~~ is negligible. The lower yield ~~(17 %)~~ estimated (17 %) ~~by~~ of acetaldehyde versus 58% of its coproduct (acetone) is due to its fast degradation by ~~Cl atoms~~ reaction with Cl atoms with the formation ~~of Peroxy acetyl nitrates~~ PAN as ~~it has been~~ observed in the FTIR experiments (See Fig. S9B). ~~Moreover, the molecular yield of acetone could be overestimated due to secondary reactions as can be seen in Figs. S12 and FigS13.~~

4. Atmospheric Implications

~~The p~~Pollutants in the atmosphere, can~~ould~~ create serious environmental problems, such ~~a~~ photochemical smog, acid rain and degradation of the ozone layer (Finlayson-Pitts and Pitts, 2000). So, it is important to evaluate the parameters that help us to understand~~know~~ the impact of the presence of these compounds in the atmosphere. These parameters are~~,~~ the time that such compounds remain~~s~~ in the atmosphere, their g~~G~~lobal w~~W~~arming p~~P~~otential (GWP) and their mechanisms of degradation, ~~mechanisms~~ in order to estimate the atmospheric effect of products formed.

The first important parameter of the environmental impact of ~~an O~~oxygenated v~~V~~olatile o~~O~~rganic c~~C~~ompounds in the atmosphere~~,~~ is the global lifetime, τ_{global}, which considers all the degradation processes that~~which~~ could affect~~suffer~~ these compounds in the t~~T~~roposphere. This parameter can be obtained from the sum of the individual sink processes such as reactions initiated by OH and NO_3 radicals, Cl atoms, and O_3 molecules; photolysis and dry and wet deposition, Eq (4):

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

The ~~T~~tropospheric lifetime (τ) of 4MCHexOH, 3,3DM1ButOH and 3,3DM2ButOH for each process have been estimated by considering Eqs (4) and (5):~~.~~

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

where k_{OX} and [Ox] are the rate coefficients obtained in this work for each oxidant and the typical atmospheric concentrations of the oxidants Cl, OH and NO_3, respectively. Concentrations employed were as follows: for 24 h~~ours~~ average: 1 × 10^3 atoms cm^{-3} (Platt and Janssen, 1995) for Cl~~chlorine atoms~~, 12 ~~-~~h~~ours~~ average day~~-~~time concentration of 1 × 10^6 radicals cm^{-3} for OH (Prinn et al., 2001) and 5 × 10^8 radicals cm^{-3} for NO_3 ~~radicals~~ (Atkinson, 2000), and a peak concentration of Cl~~chlorine atoms~~ of 1.3 × 10^5 atoms cm^{-3} in the coastal marine boundary layer at dawn (Spicer et al., 1998). Reactions with O_3 and photolysis are negligible loss processes for this type~~kind~~ of compound~~s~~ (Mellouki et al., 2015). Other processes are referred to as dry and wet deposition. ~~For~~ To estimate~~ing~~ the lifetime associated with wet deposition, Eq (6) proposed by (Chen et al. 2003) was~~has been~~ used:

$$\tau_{wet} = \frac{H_{atm}}{v_{pm} R T k_H} \qquad (6)$$

w~~W~~here k_H is the Henry's law constant, H_{atm} is the height of ~~in~~ the troposphere, taking a value of 630 ~~-~~m, v_{pm} is the average precipitation rate for Ciudad Real (Spain) (402 ~~-~~mm~~/~~ yr^{-1}~~ear~~) (www.aemet.es), R is the gas~~es~~ constant and T is the temperature, considered ~~as~~ to be constant and equal to 298 K. In the literature~~bibliography~~ there are~~is~~ only data of ~~the constant of~~ Henry's constant for 3,3DM2ButOH (5.6 × 10^{-1} mol m^{-3} Pa^{-1}) (Sander, 2015). Comparing the available data for similar compounds~~ it has been used an~~ approximated values of K_H of 3 ~~-~~mol m^{-3} Pa^{-1} and 0.4 ~~-~~mol m^{-3} Pa^{-1} for 4MCHexOH and 3,3DM1ButOH, respectively have been used. The calculated l~~L~~ifetimes ~~calculated~~ of the three ~~studied~~ alcohols studied in this work are shown in ~~the~~ Table 7. It can be seen that the dominant tropospheric loss process for the three alcohols is clearly their reaction with OH radicals followed by their reaction with NO_3 radicals at night. However, in places where there is a peak concentration of chlorine atoms (coastal areas) the reaction of these alcohols with chlorine atoms may compete with that with OH radicals as~~becoming~~ their main degradation process.

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

Their degradation products (mostly carbonyl-containing compounds and nitro-compounds in polluted areas) must be considered. Thus, the nitrated compounds generated can act as NOx reservoir species especially during the night (Altshuller, 1993) and could have an influence at the global scale. Moreover, since 4MCHexOH, 3,3DM1ButOH and 3,3DM2ButOH react quickly with Cl~~chlorine~~ atoms and OH radicals, their contribution to the formation of photochemical smog might be important. For that reason, the contribution of these three alcohols to the formation of smog was estimated by obtaining the average ozone production during 99~~-~~% of their reactions with OH radical, using the equation indicated by Dash and Rajakumar (2013). The values obtained were 3.24, 0.90 and 1.69 ~~-~~ppm for 4MCHexOH, 3,3DM1ButOH and 3,3DM2ButOH, respectively. These values suggest that these compounds may be ~~a~~ potential generators of tropospheric ozone and could contribute significantly to the formation of photochemical smog ~~(~~depending on their ~~-~~concentrations in the atmosphere~~)~~.

5. Conclusions

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

– ~~-~~The kinetic and product study support that: 1 – ~~-~~The atmospheric degradation mechanism for ~~M~~SAs, and possibly for other~~the rest of~~ unstudied saturated alcohols, proceeds by abstraction of ~~the~~ a hydrogen atom bonded to a carbon rather than a~~instead of~~ hydrogen atom~~s~~ bonded to the oxygen atom of the alcohol group, and~~.~~ 2 – ~~-~~The reaction mechanism in the H atom ~~-~~abstraction process depends on the oxidant. Cl~~hlorine~~ atoms abstract any type of~~ alkyl~~ hydrogen (α, β, δ) from SAs~~saturated alcohols~~ with a high percentage~~,~~ compared to the OH~~hydroxyl radical~~ and the NO$_3$ ~~nitrate~~ radicals. The OH and NO$_3$ radicals abstract mainly the hydrogen atom at~~in~~ the α–position, if the saturated alcohols are secondary. For primary alcohols, the abstraction of a hydrogen atom at the~~in~~ β–~~-~~position could~~ be~~ also be important in the reaction with NO$_3$ radical. Therefore, more kinetic studies of the~~for~~ NO$_3$ radical reaction with primary alcohols are necessary to quantify the effect of the OH group at the β–position (–CH$_2$OH) and to update the SAR method developed by Kerdouci et al.~~,~~ ~~and to quantify the effect of the OH group at thein β position, (– -CH$_2$OH).~~

– ~~-~~Theoretical ab-initio studies of the reactions of ~~M~~SAs with atmospheric oxidants should be performed~~done~~ in order to obtain more information about their reaction mechanisms in the H atom ~~-~~abstraction process.

– ~~-~~The atmospheric conditions determine the reaction mechanism and therefore the reaction products obtained in the degradation of ~~methyl saturated alcohol~~SAs. So, in polluted environments with high concentrations of NOx, the peroxy radicals ~~(RO$_2$·)~~ react~~s~~ mainly with NO to form the alkoxy radical instead of molecular compounds. In these conditions, nitrated organic compounds (RONO$_2$) are formed as well as~~apart from~~ polyfunctional organic compounds. Also, when the concentration of NO$_2$ is higher than that of NO~~ concentration~~, ozone is formed. In a clean atmosphere, as in the case of the experiments with ~~of~~ Cl atoms in the absence of NO$_x$, the reaction products are different because, ~~of~~ peroxy radicals ~~(RO$_2$·)~~ could react mainly ~~"~~via~~"~~ a self-reaction molecular pathway~~channel~~ instead of ~~to "~~via~~"~~ a self-reaction radical pathway with formation of dihydroxy and hydroxycarbonyl compounds~~channel~~.

– -The unquantified~~counted~~ polyfunctional organic compounds could explain the low carbon balance obtained in the Cl or NO$_3$ reactions. The carbon balance must be taken with caution since the calculated molecular yields have a high degree of uncertainty.

– -Calculated lifetimes for~~ methyl~~ saturated alcohols (in the order of ~1 day) imply that these compounds are pollutants at a local–~~-~~regional scale, but it is also important to indicate that ~~M~~SAs are sources of stable nitrated compounds (ROONO$_2$), depending on environmental conditions, that can travel~~ to~~ large distances from their sources and contribute~~ing~~ to form ozone in clean areas, for example in forest or rural areas.

– -The main products of~~coming from~~ the degradation of the ~~M~~SAs, aldehydes and ketones, develop a very important secondary chemistry with the formation of products of special relevance, such as the PAN observed in the degradation of 3,3-dimethyl-2-butanol. More experiments should be carried out~~done~~ using other detection techniques~~,~~ in order to evaluate the formation of secondary ~~S~~organic ~~O~~aerosol (SOA)~~A~~ because it is well known that polyfunctional organic compounds are important SOA precursors.

– -From the environmental point of view, this work shows that the degradation of ~~M~~SAs is an important source of pollutants in the atmosphere of~~with~~ greater or lesser impact depending on the environmental conditions and the quantities of these alcohols present in the atmosphere. Therefore, the use of ~~M~~SAs as additives in the production of biofuels ~~as biofuels~~ should be controlled, ~~avoiding that a bad~~ as poor handling could result~~involves~~ in high concentrations of these alcohols in the atmosphere.

– -The r~~R~~ate coefficients and reaction products~~ measured~~ reported in this work are the first available data, so this work contributes to a better understanding of the atmospheric chemistry of oxygenated compounds, expands~~ing~~ the kinetic and mechanistic database, and ~~additionally it~~ contributes to develop~~-~~ing or to improving~~e~~ predictive~~on~~ models that~~ which~~ help us to avoid or mitigate the effects of climate change or air quality. However, kinetic experiments in the tropospheric temperature range are necessary to obtain more information about the reaction mechanism and to extrapolate the ~~data of~~ rate coefficient~~s~~ data to other typical atmospheric conditions and thus be able to better establish the atmospheric impact of these alcohols.

6. Supplementary material.

Attached in a separated file.

7. Author contribution

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

8. Competing interests

The authors declare that they have no conflict of interest.

9. Acknowledgment

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Table 1. Rate coefficient ratios, absolute rate coefficients and average rate coefficients for the reactions of a series of ~~M~~SAs with Cl atoms and OH and NO_3 radicals at 298 K and 720 ± 20 Torr of pressure. Rate coefficients, k, in cm^{3-} molecule^{-1} s^{-1}.

Reaction	Reference	$(k_{\cancel{M}SA}/k_R)\pm2\sigma$	$(k_{\cancel{M}SA}\pm2\sigma)^a/10^{-10}$	$(\bar{k}_{\cancel{M}SA}\pm2\sigma)^b/10^{-10}$
3,3DM1ButOH + Cl	1-butene	0.85 ± 0.03	2.89 ± 0.42	2.69 ± 0.16
		0.79 ± 0.02	2.68 ± 0.38	
		0.76 ± 0.02	2.58 ± 0.37	
	Propene	1.18 ± 0.02	2.63 ± 0.37	
		1.21 ± 0.03	2.70 ± 0.38	
		1.22 ± 0.03	2.71 ± 0.38	
3,3DM2ButOH + Cl	1-butene	0.42 ± 0.01	1.42 ± 0.21	1.21 ± 0.07
		0.35 ± 0.01	1.17 ± 0.17	
		0.41 ± 0.01	1.38 ± 0.20	
	Propene	0.48 ± 0.01	1.08 ± 0.15	
		0.50 ± 0.02	1.12 ± 0.16	
		0.56 ± 0.03	1.26 ± 0.19	
4MCHexOH + Cl	2-methylpropene	1.08 ± 0.03	3.69 ± 0.32	3.70 ± 0.16
		1.16 ± 0.02	3.95 ± 0.33	
		0.98 ± 0.05	3.35 ± 0.32	
	1-butene	1.14 ± 0.03	3.86 ± 0.56	
		1.12 ± 0.03	3.78 ± 0.55	
		1.15 ± 0.04	3.90 ± 0.57	

Reaction	Reference	$(k_{\cancel{M}SA}/k_R)\pm2\sigma$	$(k_{\cancel{M}SA}\pm2\sigma)/10^{-12}$	$\bar{k}_{\cancel{M}SA}\pm2\sigma/10^{-12}$
3,3DM1BuOH + OH	Isopropanol	1.00 ± 0.04	5.09 ± 0.20	5.33 ± 0.16
		1.13 ± 0.09	5.78 ± 0.47	
		1.12 ± 0.08	5.72 ± 0.40	
	2-methyl-2-butanol	1.60 ± 0.09	5.78 ± 1.01	
		1.57 ± 0.08	5.65 ± 1.00	
		1.61 ± 0.09	5.79 ± 1.02	
3,3DM2BuOH + OH	Isopropanol	2.33 ± 0.09	11.90 ± 0.48	10.50 ± 0.25
		2.05 ± 0.08	10.50 ± 0.45	
		1.95 ± 0.08	9.95 ± 0.43	
	2-methyl-2-butanol	2.39 ± 0.09	8.61 ± 1.50	
		2.92 ± 0.09	10.50 ±1.78	
		2.25 ± 0.09	8.12 ± 1.34	
4MCHexOH + OH	Propene	0.64 ± 0.01	17.10 ± 2.59	18.70 ± 1.42
		0.76 ± 0.03	20.30 ± 3.19	
		0.76 ± 0.02	20.40 ± 3.10	
	Cyclohexene	0.27 ± 0.01	18.20 ± 4.55	
		0.27 ± 0.01	18.40 ± 4.62	
		0.27 ± 0.01	18.00 ± 4.46	

Reaction	Reference	$(k_{\cancel{M}SA}/k_R)\pm2\sigma$	$(k_{\underline{SA}\cancel{NO3}}\pm2\sigma)/10^{-15}$	$\bar{k}_{\underline{SA}\cancel{NO3}}\pm2\sigma/10^{-15}$
4MCHexOH + NO_3	1-butanol	1.08 ± 0.12	3.39 ± 1.11	2.69 ± 0.37
		1.81 ± 0.15	5.70 ± 1.82	
		0.79 ± 0.07	2.51 ± 0.80	
	2-ethyl-1-hexanol	0.71 ± 0.10	2.08 ± 0.72	
		1.00 ± 0.10	2.93 ± 0.96	
		0.86 ± 0.08	2.52 ± 0.82	

[a] The uncertainties for rate coefficients of ~~M~~SAs ($\sigma_{\cancel{k}\cancel{M}SA}$) were calculated from the uncertainty of slope of plots (σ_{slope}) and the uncertainty of the reference ($\sigma_{\underline{k}\cancel{K}R}$) by using the propagation of uncertainties. [b] Weighted average according to the equation $(w_1k_1+ w_2k_{2+}\ldots)/(w_1+ w_2\ldots)$; $(w_i=1/\sigma_i^2)$. The uncertainty of weighted average (σ) was given by $(1/w_1+1/w_2+\ldots)^{-0.5}$

Table 2. Estimated and experimental rate coefficients (k_{SAR}, k_{log} and k_{exp}) for the reaction of ~~M~~SAs with atmospheric oxidants and ratio of rate coefficients (k_{exp}/k_{SAR} and k_{exp}/k_{log}). $k_{Cl}/10^{-11}$, $k_{OH}/10^{-12}$ and $k_{NO3}/10^{-15}$ in cm^3 molecule^{-1} s^{-1} units.

	4MCHexOH			**3,3DM1ButOH**			**3,3DM2ButOH**		
	k_{Cl}	k_{OH}	k_{NO3}	k_{Cl}	k_{OH}	k_{NO3}	k_{Cl}	k_{OH}	k_{NO3}
k_{exp}	37.0[a]	18.7[a]	2.69[a]	26.9[a]	5.33[a]	1.78[b]	12.1[a]	10.5[a]	3.4[b]
k_{SAR}	34.2[c]	19.2[c]	2.27[c]	21.0[c]	6.08[c]	0.55[c]	15.2[c]	9.16[c]	3.86[c]
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[d]	-	4.69[d]	13.9[d]	-	1.16[d]	21.4[d]	-	3.19[d]
k_{exp}/k_{log}	1.21	-	0.57	1.94	-	1.53	0.57	-	1.07

[a] Data obtained in this work

[b] Data obtained by Moreno et al., 2014

[c] See S2 S~~s~~upplementary M~~m~~aterial

[d] Estimated using the correlations log$_{Cl}$-log$_{OH}$ (Eq. (2)) and log$_{NO3}$-log$_{OH}$ (Eq. (3)) described by Calvert et al, 2011.

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

~~M~~SA	Oxidant	Exp	[~~M~~SA] (ppm)	[Precursor] (ppm)	[NO] (ppm)	Carbonyl compound ^{d}Yield (%)	Technique	Average^{f} (%)	SAR Yield (%)
4MCHexOH	Cl^{a}	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^{e}		
	Cl^{a} + 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^{e}		
	OH^{b}	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^{e}		
	NO_3^{c}	1	3	6	-	56.8±11.4	SPME/GC-TOFMS^{e}	58.0±23.5	86
		2	6	34	-	88.3±7.0	SPME/GC-TOFMS^{e}		
		3	4	30	-	77.1±4.6	SPME/GC-TOFMS^{e}		
		4	4	21	-	34.6±0.5	FTIR		
		5	7	10	-	33.4±0.6	FTIR		

[a] Rate coefficient k (in cm^3 molecule^{-1} s^{-1} unit) used to correct the concentration of E-4-methylcyclohexanone by loss with the reaction of Cl atoms = 11.2 ×10^{-11} (data of 2-methylcyclohexanone and Cl atoms (Herath et al., 2018)). Photolysis rate coefficient estimated for E-4-methylcyclohexanone under our experimental conditions, k_p =5 × 10^{-5} s^{-1}

[b] Rate coefficient k (in cm^3 molecule^{-1} s^{-1} unit) used to correct the concentration of E-4-methylcyclohexanone by loss with the reaction of OH radical =13.7 × 10^{-12} (estimated using AOPWIN, v1.92). Photolysis rate coefficient estimated for E-4-methylcyclohexanone under our experimental conditions, k_p =5 × 10^{-5} s^{-1}

[c] Rate coefficient k (in cm^3 molecule^{-1} s^{-1} unit) used to correct the concentration of E-4-methylcyclohexanone by loss with the reaction of NO_3 radical = 2.28 × 10^{-16} (estimated using SAR method, Kerdouci et al., 2014)

[d] Indicated errors are the associated error to the slope of plots obtained in the least squares analysis

[e] Experiment using a Teflon gas b~~B~~ag of 150L

[f] Standard deviations 1σ

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

~~M~~SA	Oxidant	Exp	[~~M~~SA] (ppm)	[Precursor] (ppm)	[NO] (ppm)	Carbonyl compound [f]Yield (%)	Technique	Average[g] (%)	SAR Yield (%)
3,3DM1ButOH	Cl[a]	1	11	24	-	40.3±0.2	FTIR		
						41.8±4.6	SPME/GC-TOFMS[d]	39.4±15.0	
		2	2.6	8	-	19.6±0.5	SPME/GC-TOFMS[e]		
		3	6	25	-	55.9±1.7	FTIR		
	Cl[a] + NO	1	10	21	21	61.6±3.4	FTIR		40
						34.7±4.4	SPME/GC-TOFMS[d]	43.3±17.7	
		2	4	9	8	23.0±4.2	SPME/GC-TOFMS[e]		
		3	10	25	25	48.8±0.6	FTIR		
	OH[b]	1	10	60	36	82.1±4.2	FTIR		
						40.8±2.7	SPME/GC-TOFMS [d]	62.2±15.0	66
		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		
	NO_3[c]	1	11	36	-	29.2±0.5	FTIR		
						53.9 [h]	SPME/GC-TOFMS[d]	36.2±14.6	86
		2	11	32	-	26.5±1.6	FTIR		

[a] Rate coefficient k (in cm^3 molecule^{-1} s^{-1} unit) used to correct the concentration of 3,3-dimethylbutanal by loss with the reaction of Cl atoms = 1.7 × 10^{-10} (data of iso-Butyraldehyde and Cl atoms (Thevenet et al., 2000)). Photolysis rate coefficient estimated for 3,3-dimethylbutanal under our experimental conditions, $k_p = 1 \times 10^{-4}$ s^{-1}

[b] Rate coefficient k (in cm^3 molecule^{-1} s^{-1} unit) used to correct the concentration of 3,3-dimethylbutanal by loss with the reaction of OH radical = 2.73 × 10^{-11} (Aschmann et al., 2010). Photolysis rate coefficient estimated for 3,3-dimethylbutanal under our experimental conditions, $k_p = 1 \times 10^{-4}$ s^{-1}

[c] Rate coefficient k (in cm^3 molecule^{-1} s^{-1} unit) used to correct the concentration of 3,3-dimethylbutanal by loss with the reaction of NO_3 radical = 1.27 × 10^{-14} (D'Anna, 2001).

[d] Experiment using a FTIR g~~G~~as c~~C~~ell of 50 L

[e] Experiment using a Teflon gas b~~B~~ag of 150 L

[f] Indicated errors are the associated error to the slope of plots obtained in the least squares analysis

[g] Standard deviations 1σ

[h] Yield estimated using only one data

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

~~M~~SA	Oxidant	Exp	[~~M~~SA] (ppm)	[Precursor] (ppm)	[NO] (ppm)	Carbonyl compound [f]Yield (%)	Technique	Average[g] (%)	SAR Yield (%)
3,3DM2ButOH	Cl[a]	1	14	31	-	42.8±0.7	FTIR		
						45.2±1.1	SPME/GC-TOFMS[d]	43.2±1.8	
		2	2.3	8	-	41.7±3.2	SPME/GC-TOFMS[e]		
	Cl[a] + NO	1	14	28	20	36.7±5.0	FTIR		40
						49.6±4.5	SPME/GC-TOFMS[d]	44.2±7.4	
		2	3	7	6	39.0±6.1	SPME/GC-TOFMS[e]		
		3	8	28	27	51.5±3.9	FTIR		
	OH[b]	1	8	55	42	82.8±3.1	FTIR		
						71.2±2.6	SPME/GC-TOFMS[d]	80.7±6.5	91
		2	5	66	36	85.4±5.8	FTIR		
		3	11	28	29	83.6±3.0	FTIR		
	NO_3[c]	1	12	30	-	66.7±2.05	FTIR		
						45.9±1.6	SPME/GC-TOFMS[d]	58.0±10.9	99
		2	9	30	-	61.5±1.4	FTIR		

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

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

[c] No corrected

[d] Experiment using a FTIR g~~G~~as c~~C~~ell of 50 L

[e] Experiment using a Teflon gas b~~B~~ag of 150 L

[f] Indicated errors are the associated error to the slope of plots obtained in the least squares analysis

[g] Standard deviations 1σ

Table 6: Summary of molecular yields (%) of reaction products identified in the reaction of ~~M~~SAs with atmospheric oxidants and the total carbon balance (%).

Product	**~~M~~SA**			
	4MCHexOH			
	Cl	**Cl + NO**	**OH**	**NO_3**
E-4-methylcyclohexanone[1]	25.2 ± 1.9	29.5 ± 0.7	40.2 ± 5.4	58.0 ± 23.5
HCOH[2]	9	-	-	-
Nitrated compounds	-	20	10	60
Total Carbon[3]	26	50	50	~100
	3,3DM1ButOH			
	Cl	**Cl + NO**	**OH**	**NO_3**
3,3-dimethylbutanal[1]	39.4 ± 15.0	43.3 ± 17.7	62.2 ± 15.0	36.2 ± 14.6
HCOH[2]	10	22	-	-
2,2-dimethylpropanal[2]	22	8	23	-
Acetone[2]	5	17	-	-
Nitrated compounds	-	40[5]	35[6]	200[7]
Total Carbon[3,4]	61	62	81	36
	3,3DM2ButOH			
	Cl	**Cl + NO**	**OH**	**NO_3**
3,3-dimethyl-2-butanone[1]	43.2 ± 1.8	44.2 ± 7.4	80.7 ± 6.5	58.0 ± 10.9
HCOH[2]	10	64	-	-
2,2-dimthylpropanal[2]	14	10	14	-
Acetone[2]	3	58	-	-
Acetaldehyde[2]	-	17	-	-
Nitrated compounds	-	30	20	120
Total Carbon[3,4]	~60	98	93	58

[1] Average Tables 3-5; [2] Molecular yield obtained in earlier step of the reaction~~.~~;

$$^{3}Total\ Carbon\ (\%) = \sum_{1}^{i}\left(\frac{n^{o}\ of\ carbon\ of\ product_{i}}{n^{o}\ of\ carbon\ of\ \sout{M}SA} \times molar\ yield_{i}(\%)\right)$$

[4] Nitrate compounds were not accounted for~~Without accounting nitrated compounds~~; [5] From analysis of the experiment number 3 for the reaction of Cl~~ +~~ in the presence of NO_x; [6] From average of experiments number 2, 3 and 4 for the reaction with OH; [7] From analysis of the experiments number 1 and 2 for reaction with NO_3.

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

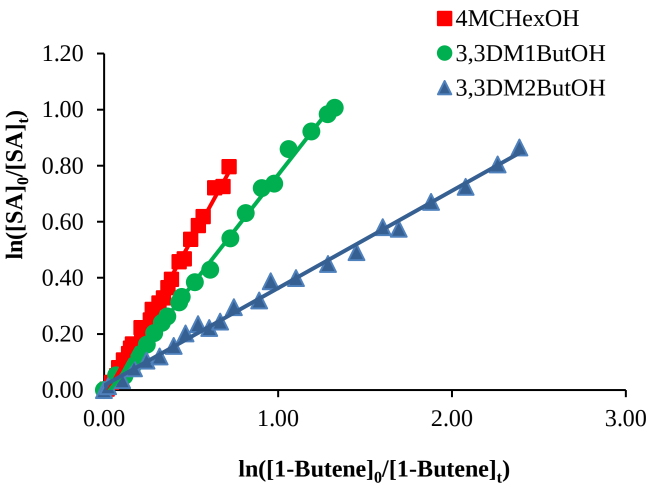
	τ_{OH} (days)	τ_{Cl} [a](days)	τ_{Cl} [b](days)	τ_{NO3} (days)	τ_{wet} (years)	τ_{global}[a](days)
4MCHexOH	0.62	31.28	0.24	8.61	~2.1	0.58
3,3DM1ButOH	2.17	43.03	0.33	13[c]	~15.8	1.78
3,3DM2ButOH	1.10	95.65	0.74	6.73[c]	11.3	0.94

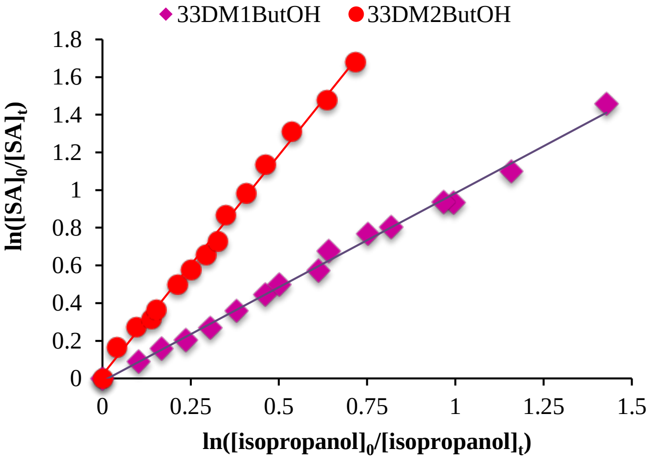
[a] Determined with the 24 hours average of chlorine atoms.

[b] Determined with the peak concentration of chlorine atoms.

[c] Determined using the rate coefficient obtained by Moreno ~~A.~~ et al., 2014.

A)


4MCHexOH
3,3DM1ButOH
3,3DM2ButOH
1.20
1.00
0.80
0.60
0.40
0.20
0.00
0.00
1.00
2.00
3.00
ln([SA]$_0$/[SA]$_t$)
ln([1-Butene]$_0$/[1-Butene]$_t$)


33DM1ButOH
33DM2ButOH
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
0.25
0.5
0.75
1
1.25
1.5
ln([SA]$_0$/[SA]$_t$)
ln([isopropanol]$_0$/[isopropanol]$_t$)

B)

C)

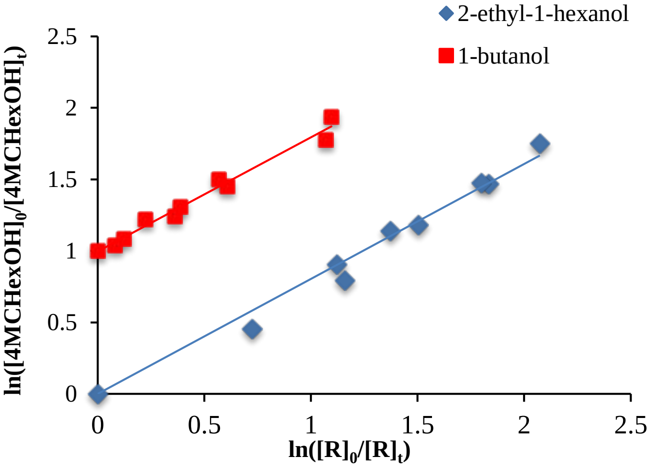

2-ethyl-1-hexanol
1-butanol
2.5
2
1.5
1
0.5
0
0
0.5
1
1.5
2
2.5
ln([4MCHexOH]$_0$/[4MCHexOH]$_t$)
ln([R]$_0$/[R]$_t$)

Fig.1: Relative rate plots for the reaction of (A) ~~M~~SAs with chlorine atoms employing 1-butene as a reference compound (B) 3,3-d~~D~~imethylbutanols and OH radical with isopropanol as a reference compound and (C) 4MCHexOH and NO_3 with two reference compounds. Data for 1-butanol have been vertically displaced for clarity.

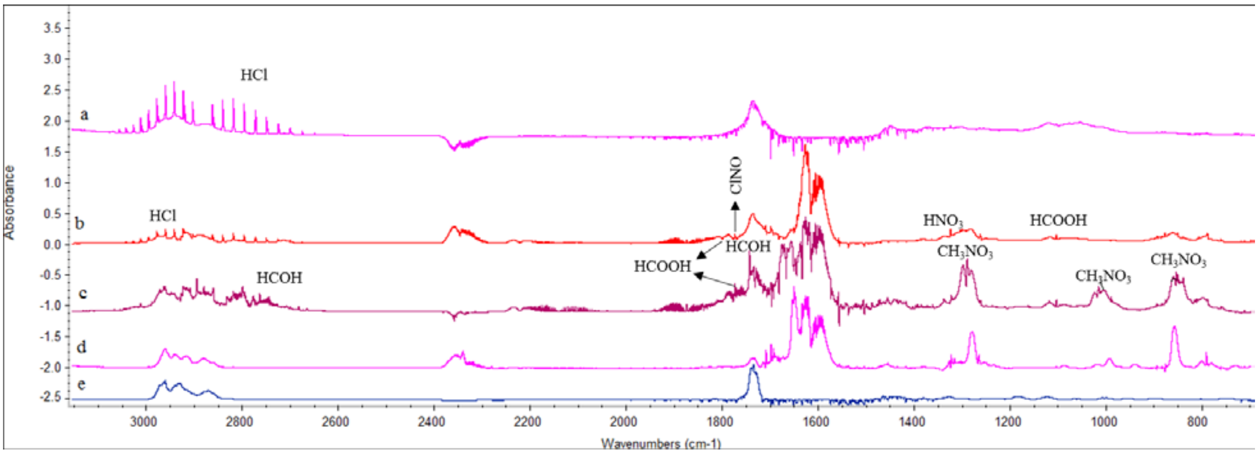


Fig. 2: Product spectra for reaction of 4MCHexOH with: (a) chlorine atoms at 10 min (x 2 to clarit~~f~~y), (b) Cl atoms in presence of ~~and~~ NOx at 7 min. (c) OH radical at 40 min and (d) NO_3 radical at 32 min. (e) Spectrum of 4-methylcyclohexanone commercial sample.

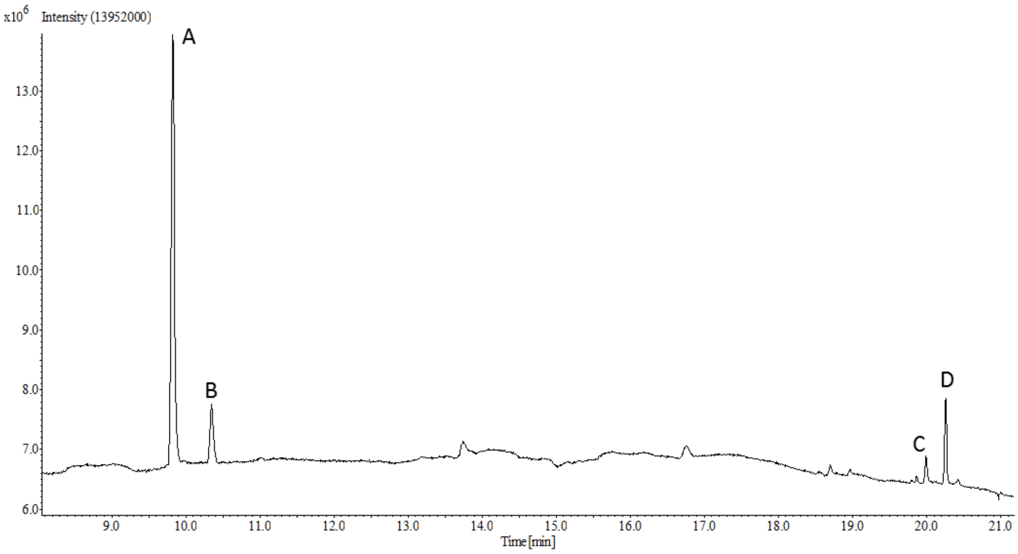


Fig. 3: SPME/GC-TOFMS chromatogram for the reaction of 4MCHexOH with Cl atoms after 15 minutes of reaction. Peak (A) 4MCHexOH. Peak (B) E-4-methylcyclohexanone. Peaks (C) and (D) reaction products.

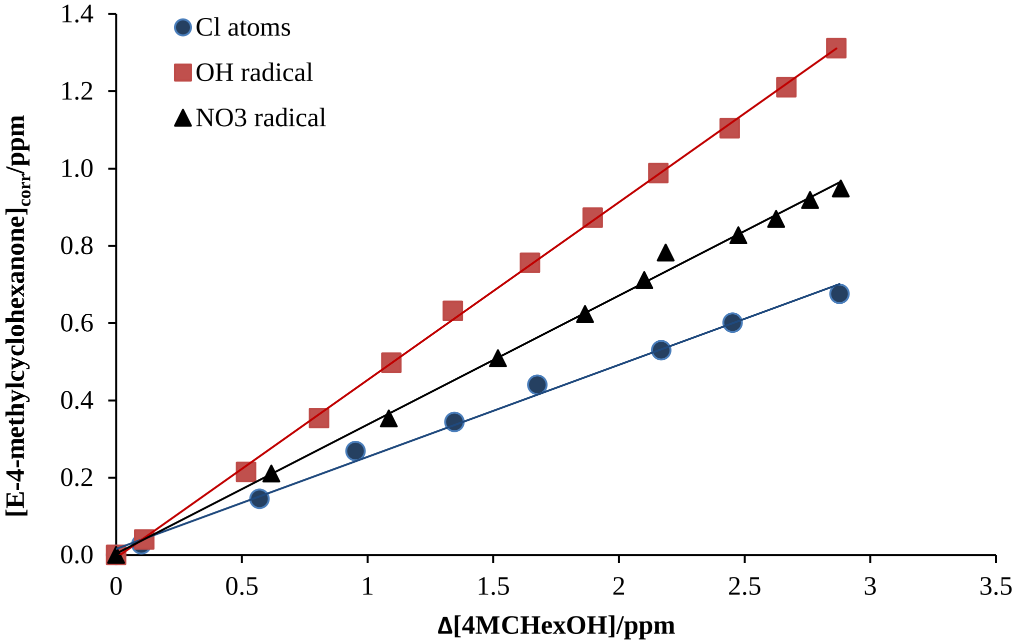


Fig. 4: Plots of corrected concentration of E-4-methylcyclohexanone ([E-4-methylcyclohexanone]$_{corr}$) against 4MCHexOH consumed (Δ[4MCHexOH]) for Cl atoms (in the absence of NOx) and OH and NO_3 radical reactions.

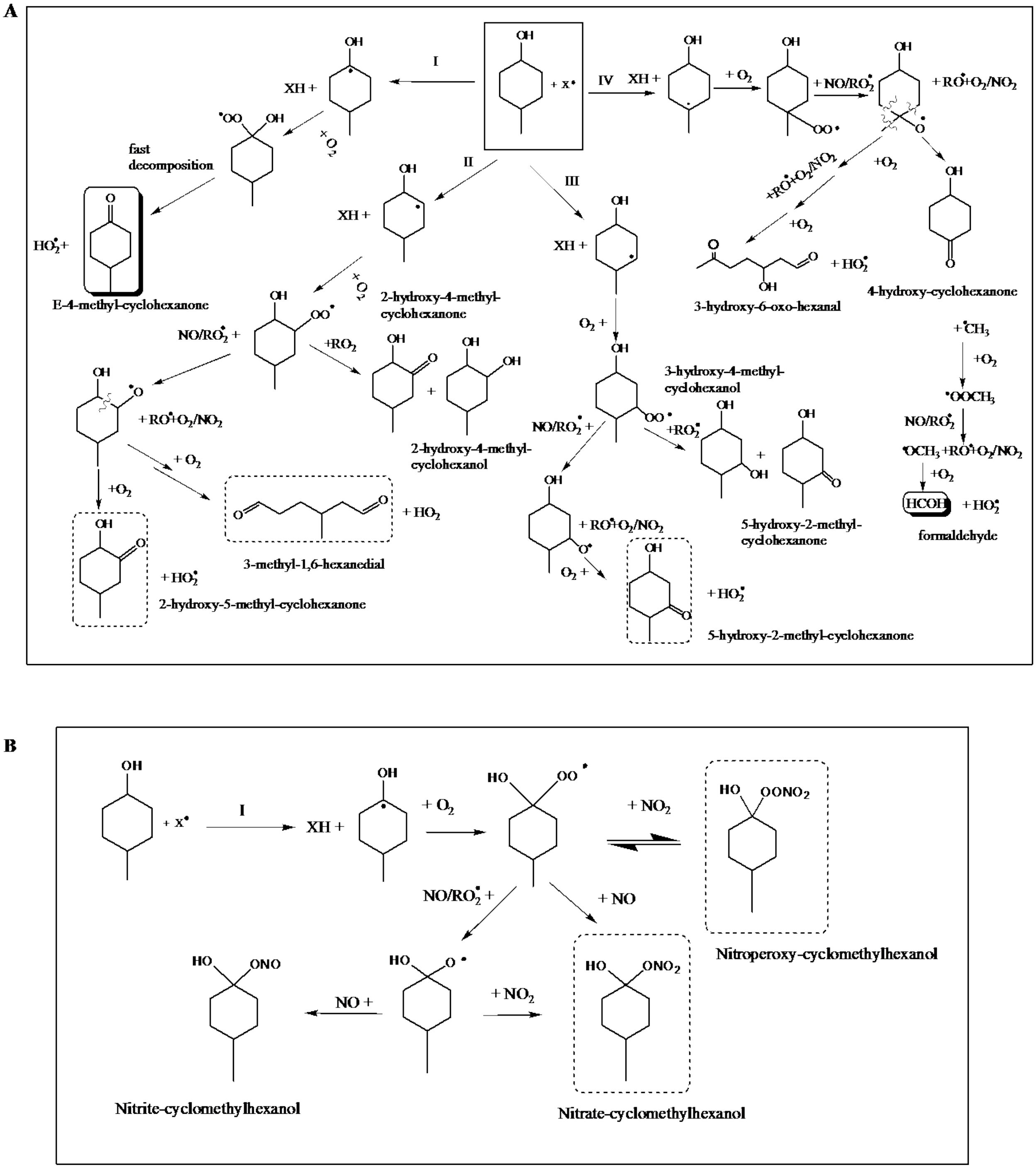


Fig. 5: Reaction mechanism for the degradation of 4MCHexOH with X (Cl atom, OH and NO_3 radicals). (A) Mechanism for the formation of carbonyl compounds, (B) Mechanism for the formation of nitrated compounds. Compounds marked with solid line are positively identified. Compounds marked with dotted~~shaded~~ lines are not positively identified.

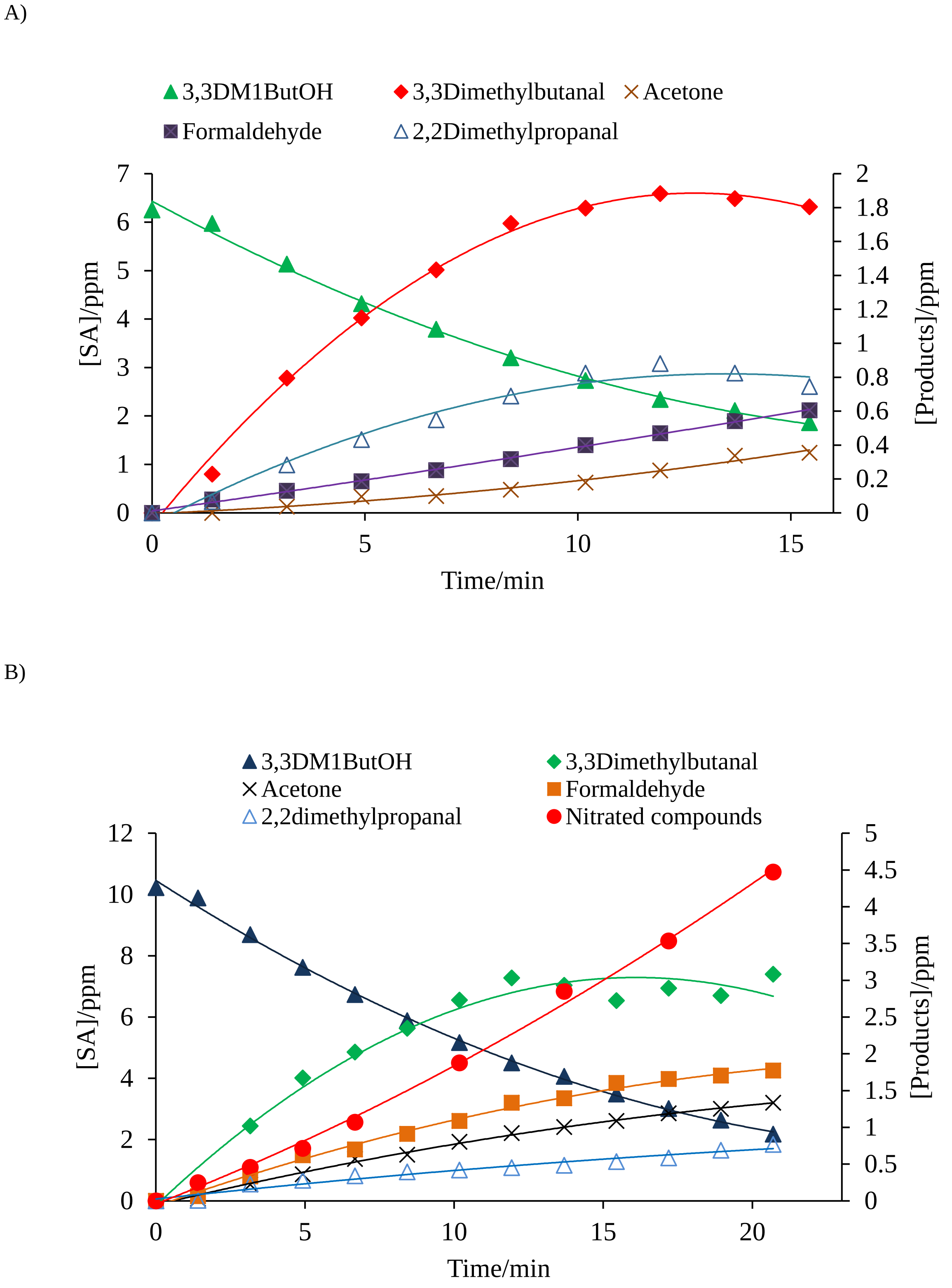


Fig. 6: Concentration-time profiles of ~~M~~SA (3,3DM1ButOH) and reaction products formed in the reaction of 3,3DM1ButOH with Cl atoms in the absence (A) and in the presence of NO_x (B).

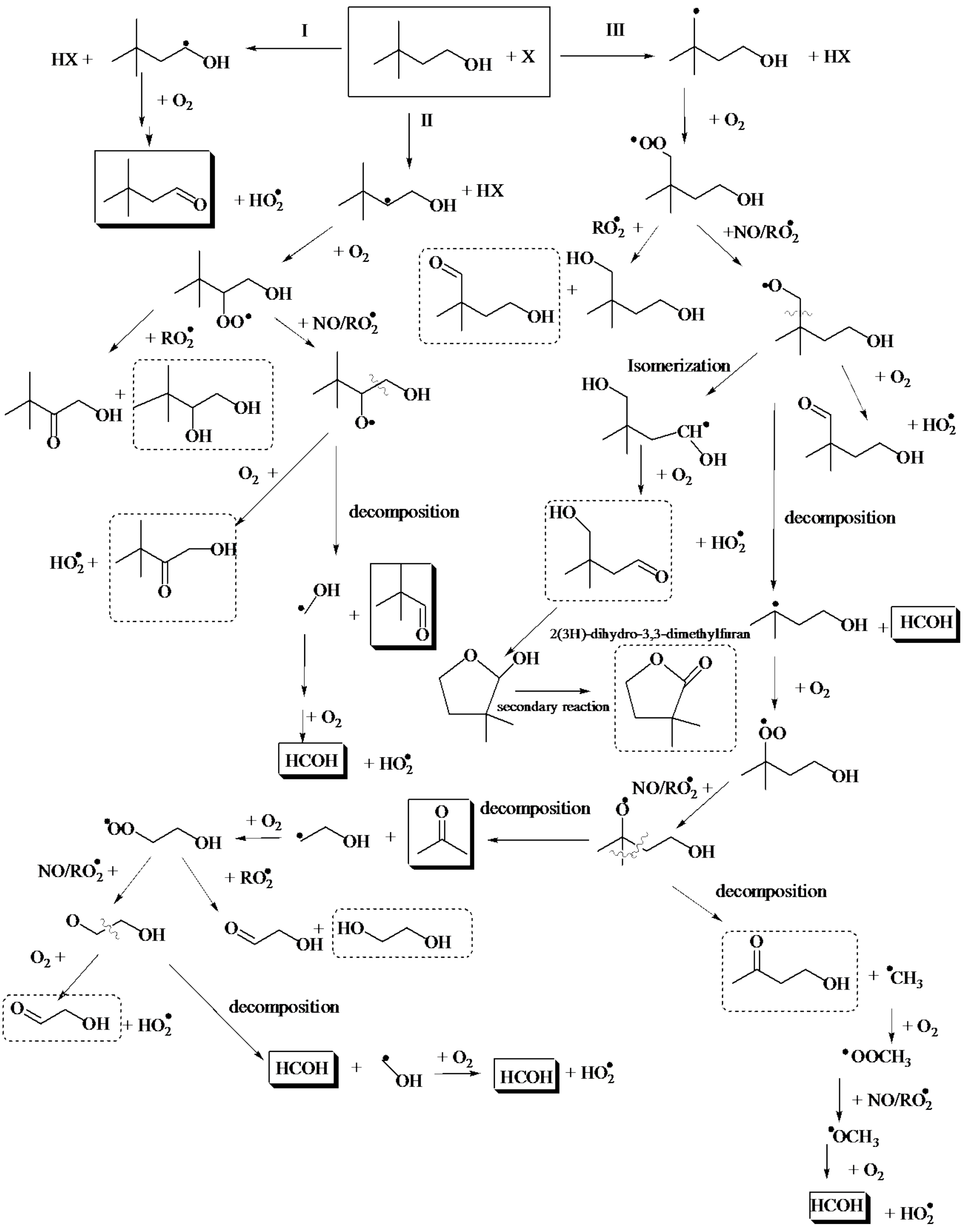


Fig. 7: Reaction mechanism for the degradation of 3,3DM1ButOH with X (Cl atom, OH and NO$_3$ radical). Mechanism for the formation of carbonyl compounds. Compounds marked with solid line are positively identified. Compounds marked with ~~shaded~~ dotted lines are not positively identified.

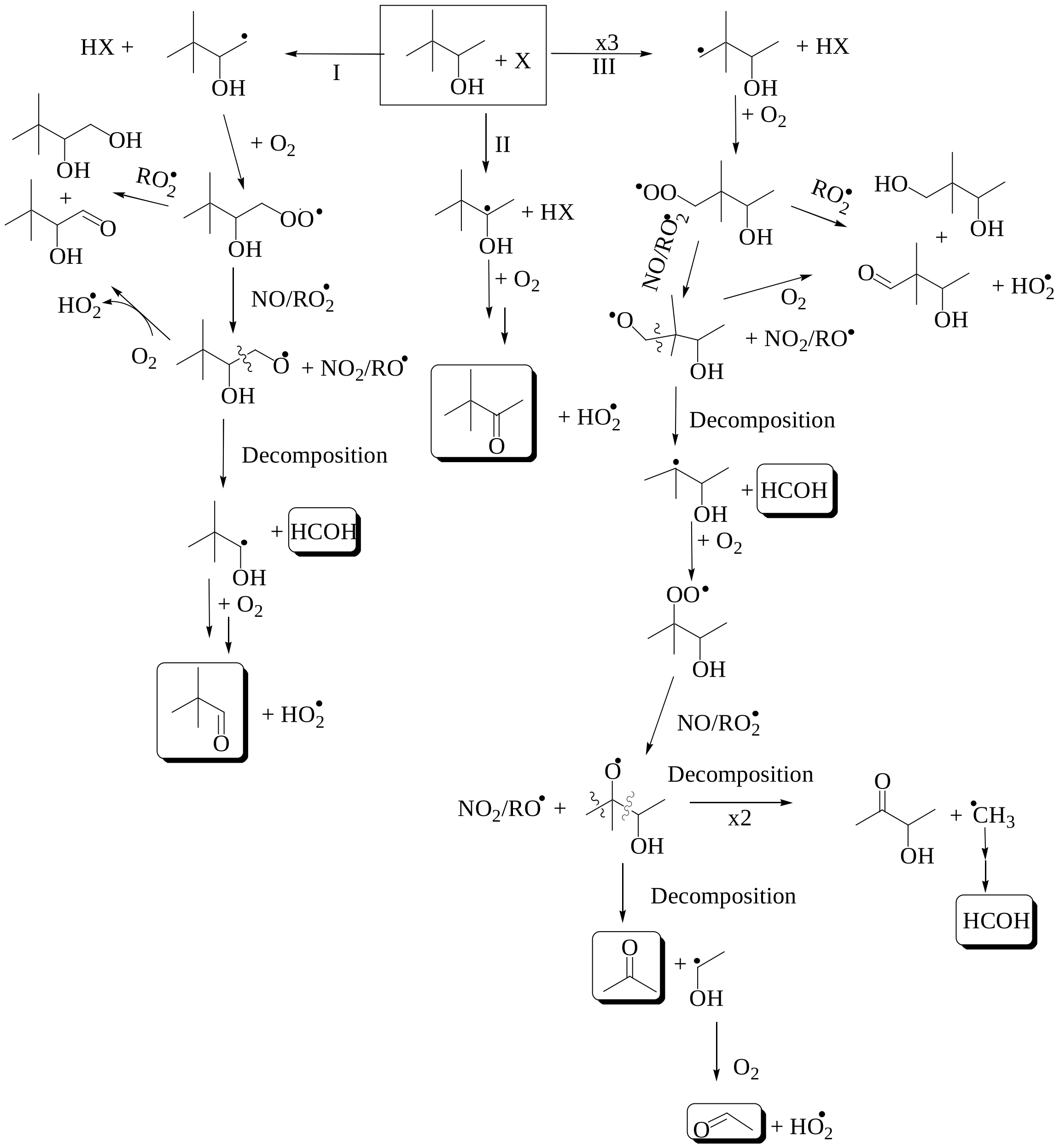


Fig. 8: Reaction mechanism for the degradation of 3,3DM2ButOH with X (Cl atom, OH and NO_3 radical). Mechanism to form carbonyl compounds. Compounds marked with solid line are positively identified. Compounds marked with dotted~~shaded~~ lines are not positively identified.

Supplementary material

S1. Tuazon formalism

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

$\cancel{M}$SA + Ox $\rightarrow \Sigma$ Y product1 (k_S) (RS1)
Product1 + Ox $\rightarrow$ Product2 (k_p) (RS2)
Product1 + hν $\rightarrow$ Product3 (k_1) (RS3)

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:

$$[\cancel{M}\mathrm{SA}]_{t_2} = [\cancel{M}\mathrm{SA}]_{t_1} \cdot e^{-(k_S \cdot [\mathrm{Ox}])(t_2 - t_1)} \qquad \text{(S1)}$$

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:

$$[\mathrm{product1}]_{t_2} = [\mathrm{product1}]_{t_1} \cdot e^{-(k_p \cdot [\mathrm{Ox}] + k_1)(t_2 - t_1)} + \frac{Y_{t_1 - t_2} \cdot [\cancel{M}SA]_{t_1} \cdot k_S [Ox]}{\{(k_P - k_S) \cdot [Ox] + k_1\}} \cdot [e^{-(k_S \cdot [Ox]) \cdot (t_2 - t_1)} - e^{-(k_P [Ox] + k_1) \cdot (t_2 - t_1)}] \qquad \text{(S2)}$$

Where [~~M~~SA]$_{t1}$, [product1]$_{t1}$ and [~~M~~SA]$_{t2}$, [product1]$_{t2}$ are the observed concentrations of the ~~methyl~~ saturated alcohol and the products at times t_1 and t_2 respectively, and Y$_{t1\text{-}t2}$ 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$_{t1\text{-}t2}$ can be calculated. The concentration of the reaction products, corrected for the reaction with radical and other processes of loss is given by:

$$[product1]_{t_2}^{corr} = [product1]_{t_1}^{corr} + Y_{t_1 - t_2} \cdot ([\cancel{M}SA]_{t_1} - [\cancel{M}SA]_{t_2}) \qquad \text{(S3)}$$

Where [product1]$^{corr}_{t1}$ and [product1]$^{corr}_{t2}$ 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.

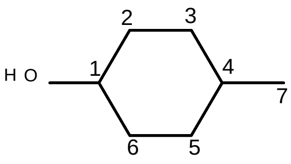
S2. Structure-Activity Relationship (SAR) method

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 ~~M~~SAs are obtained from the sum of the rate coefficients for the H-atom abstraction from the primary (k_{prim} (CH_3-)), secondary ($k_{sec,}$ (-CH_2-)) and tertiary (k_{tert} (-CH<)) groups and from the alcohol (k_{OH} (-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).

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

At 298K rate coefficients for H-atom abstraction (in units of $cm^3 molecule^{-1} s^{-1}$) and the reactivity factor for the reaction with OH are $k_{prim} = 1.36 \times 10^{-13}$; $k_{sec} = 9.34 \times 10^{-13}$; $k_{tert} = 1.94 \times 10^{-12}$ and $k_{OH} = 1.4 \times 10^{-13}$; $F(CH_3) = 1$; $F(-CH_2-) = F(-CH<) = F(>C<) = 1.23$ and $F(-OH) = 3.5$ from AOPWIN. The parameters for the reaction with Cl atoms are $k_{prim} = 2.84 \times 10^{-11}$; $k_{sec} = 8.95 \times 10^{-11}$; $k_{tert} = 6.48 \times 10^{-11}$ (in units of $cm^3 molecule^{-1} s^{-1}$); $F(CH_3) = 1$; $F(-CH_2-) = F(-CH<) = 0.8$ and $F(-OH) = 1.18$ from Calvert et al. 2011. By last, the parameters used for the reaction with NO_3 radicals are $k_{prim} = 1 \times 10^{-18}$; $k_{sec} = 2.56 \times 10^{-17}$; $k_{tert} = 1.05 \times 10^{-16}$ and $k_{OH} = 2 \times 10^{-17}$ (in units of $cm^3 molecule^{-1} s^{-1}$); $F(CH_3) = 1$; $F(-CH_2-) = 1.02$; $F(-CH<) = 1.61$; $F(>C<) = 2.03$ and $F(-OH)=18$ from Kerdouci et al. 2010, 2014.

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



$k_1 = k_{tert} \times F(-OH) \times F(-CH_2-) \times F(-CH_2-)$

$k_2 = k_3 = k_5 = k_6 = k_{sec} \times F(-CH<) \times F(-CH_2-)$.

$k_4 = k_{tert} \times F(-CH_3) \times F(-CH_2-) \times F(-CH_2-)$

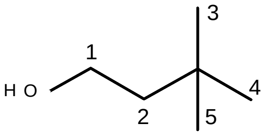
$k_7 = k_{prim} \times F(-CH<)$

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

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

$k_{4MCHexOH+NO3} = 2.27 \times 10^{-15}\ cm^3 molecule^{-1} s^{-1}$

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



$k_1 = k_{sec} \times F(-OH) \times F(-CH_2-)$

$k_2 = k_{sec} \times F(>C<) \times F(-CH_2-)$

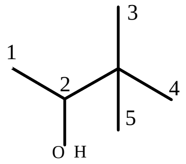
$k_3 = k_4 = k_5 = k_{prim} \times F(>C<)$

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

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

$k_{3,3DM1ButOH\ +NO3} = 0.55 \times 10^{-15}\ cm^3 molecule^{-1} s^{-1}$

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



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

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

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

$k_{3,3DM2ButOH+Cl} = 1.52 \times 10^{-10}$ cm^{3}molecule^{-1}s^{-1}

$k_{3,3DM2ButOH\ OH} = 9.16 \times 10^{-12}$ cm^{3}molecule^{-1}s^{-1}

$k_{3,3DM2ButOH\ +NO3} = 3.86 \times 10^{-15}$ cm^{3}molecule^{-1}s^{-1}

Tables

Table S1: Rate coefficients at 298 K for Cl, OH and NO_3 reactions with alkanes, saturated alcohols and saturated compounds with a similar structure of ~~M~~SAs studied in~~,~~ this work. k in cm^3 $molecule^{-1}$ s^{-1} unit.

Compound	$\mathbf{k_{Cl}\times10^{11}}$	$\mathbf{k_{OH}\times10^{12}}$	$\mathbf{k_{NO3}\times10^{15}}$
	Alkanes		
Methane	0.01	0.0064	<0.001[f]
Ethane	5.70[a]	0.24[f]	<0.01[f]
Propane	12.7[a]	1.09[f]	<0.07[f]
Butane	19.4[a]	2.36[f]	0.046[f]
Pentane	25.0[a]	3.80[f]	0.087[f]
Hexane	30.5[a]	5.20[f]	0.110[f]
Heptane	36.5[a]	6.76[f]	0.150[f]
Octane	40.9[a]	8.11[kf]	0.190[f]
Nonane	46[b]		0.220[b]
Decane	52.7[b]		0.260[b]
2-Methylpropane	13.0[a]	2.12[f]	0.106[f]
2-Methylbutane	19.6[a]	3.60[f]	0.162[f]
2-Methylpentane	25.8[a]	5.2[f]	0.180[f]
3-Methylpentane	26.9[b]	5.2[f]	0.220[f]
2-Methylhexane	31.2[a]	6.72[e]	-
2,3-Dimethylbutane	20[a]	5.78[f]	0.44[f]
2,2-Dimethylbutane	-	22.3[f]	-
2,2,4-trimethylpentane	22.5[a]	3.34[f]	0.09[f]
Cyclopentane	32.6[c]	4.97[f]	-
Cyclohexane	33[d]	6.97[f]	0.14[f]
Methylcyclohexane	35.1[e]	9.5[e]	-
Trans-1,4-dimethylcyclohexane	36.3[e]	12.1[e]	-
Ethylcyclohexane	38.8[e]	11.8[e]	-
	Saturated Alcohols		
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[g]
2-butanol	12[h]	8.7	2.51[q]
1-pentanol	24[i]	11[i]	-
2-pentanol	22[i]	11.8[i]	-
3-pentanol	20[i]	13[i]	-
1-hexanol	31[i]	13[i]	-
2-hexanol	-	12[i]	-

1-heptanol	37[i]	13[i]	-
4-heptanol	-	-	<6.2
1-octanol	42[i]	13[i]	-
2-methyl-1-propanol	20.6[j]	11.4[j]	-
2-methyl-2-propanol	3.26[k]	1.07[k]	-
2-ethyl-1-hexanol	18.8[l]	11.3[l]	2.93[l] ~~-~~
2-methyl-1-butanol	-	-	2.32[g]
2-methyl-2-butanol	7[h]	3.64[n]	1.57[q]
3-methyl-1-butanol	25[i]	14[i]	2.09[g]
3-methyl-2-butanol	11.7[h]	12.5[o]	3.06[q]
2-methyl-2-pentanol	-	7.1[i]	-
4-methyl-2-pentanol	-	17[i]	-
2,2-dimethyl-1-propanol	-	5.5[i]	-
3,3-dimethyl-1-butanol	**26.9**	**5.33**	1.78[g]
3,3-dimethyl-2-butanol	**12.1**	**10.50**	3.44[g]
2,3-dimethyl-2-butanol	10.3[h]	9.1[n]	3.64[q]
2,4-dimethyl-2-pentanol	-	11[i]	-
3,5-dimethyl-3-hexanol	-	13[i]	-
cyclopentanol	-	10.7[k]	-
cyclohexanol	32.1[m]	19.0[p]	-
4MCHexOH	**37.0**	**18.7**	**2.69**

Data obtained from IUPAC Subcommittee on Gas Kinetics Data Evaluation and the following references: [a]Hooshiyar and Niki, 1995; [b]Calvert et al., 2015; [c]Wallington et al., 1989; [d]Calvert et al., 2008; [e]Began et al., 2018; [f]Atkinson, 2003; [g]Moreno et al., 2014; [h]Ballesteros et al., 2007; [i]Calvert et al., 2011; [j]Andersen et al., 2010; [k]Wallington et al., 1988; [l]Gallego-Iniesta et al., 2010; [m]Ceacero-Vega et al., 2012; [n]Jiménez et al., 2005; [o]Mellouki et al., 2004; [p]Bradley et al., 2001; [q]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 p~~P~~roduct of reaction mechanism	**FTIR**				**GC-MS**				
	Cl	Cl + NO	OH	NO_3	Cl	Cl + NO	OH	NO_3	t_R/min
				Route I					
3,3-dimethylbutanal	X	X	X	X	X	X	X	X	6.00
				Route II					
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*	-		-	-	-	-
				Route III					
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 Ionization (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 mechanism	**FTIR**				**GC-MS**				
	Cl	**Cl + NO**	**OH**	**NO_3**	**Cl**	**Cl + NO**	**OH**	**NO_3**	**Retention time (min)**
				Route I					
3,3-dimethyl-1,2-butanediol	-	-	-	-	-	-	-	-	-
3,3-dimethyl-2-hydroxybutanal	-	-	-	-	-	-	-	-	-
Formaldehyde	X	X	X*		-	-	-	-	-
2,2-dimethylpropanal	X	X	X	-	-	-	/	/	5.39
				Route II					
3,3-dimethyl-2-butanone	X	X	X	X	X	X	X	X	6.04
				Route III					
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 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.

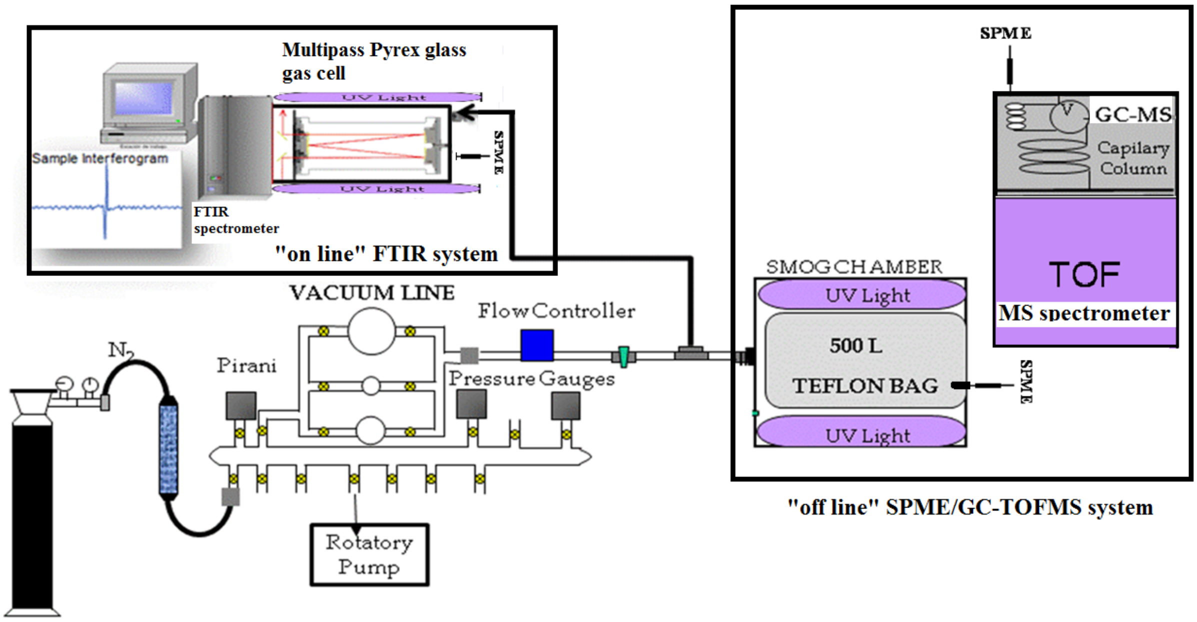


Fig.S1 Schematic diagram of experimental system: FTIR and SPME/GC-TOFMS.

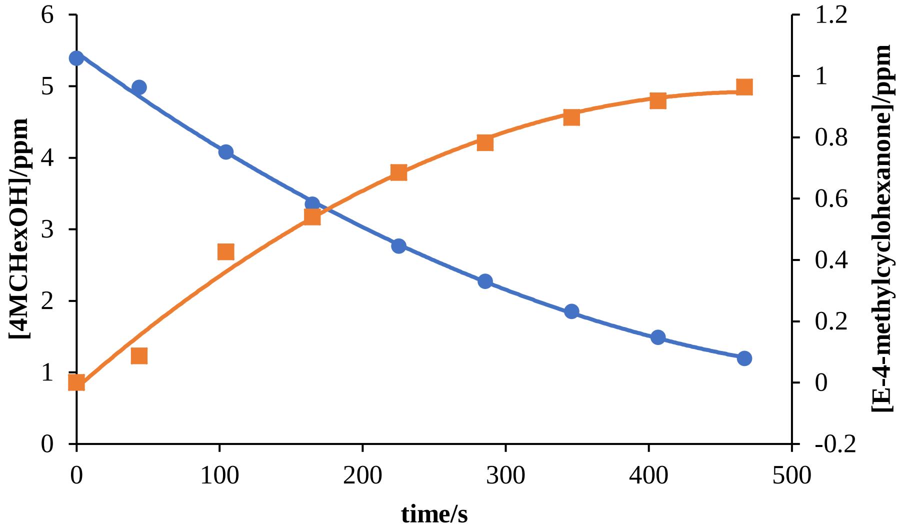


Fig. S2. Time-concentration profiles of 4MCHexOH ● and 4-methylcyclohexanone ■, for the reaction of 4MCHexOH with chlorine atoms in the presence of NOx obtained by FTIR.

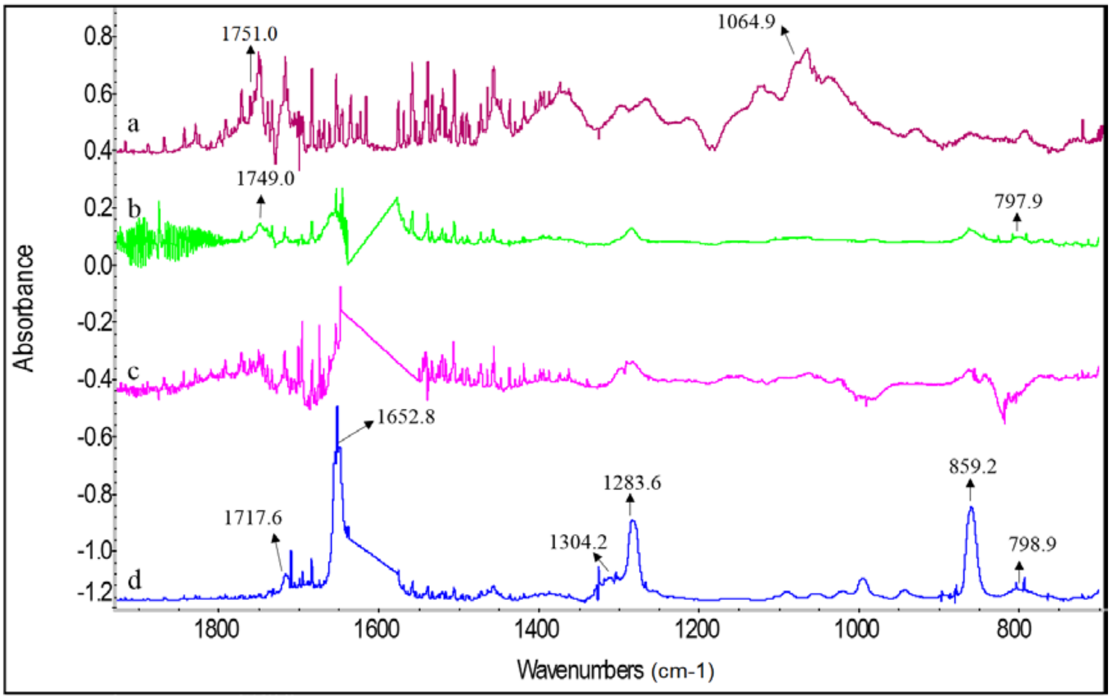


Fig. S3. Residual FTIR spectra obtained in the reaction of 4MCHexOH with (a) Cl atoms ~~(a)~~, (b) ~~Cl + NO (c), H~~OH radicals, (c) ~~(b)~~ Cl atoms in the presence of NO, and (d) NO_3 radicals ~~(d)~~. The gap in the range of 1650-1590 cm^{-1} corresponds to NO_2 absorption.

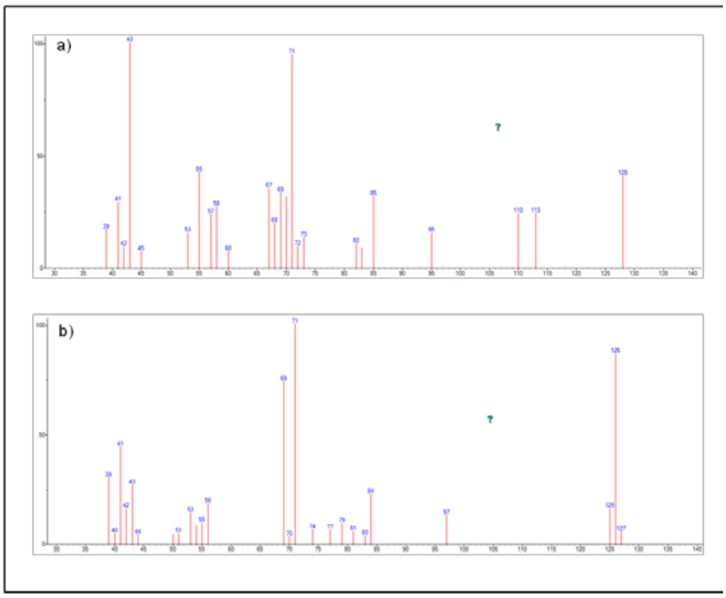


Fig. S4. EI MS spectra of peak C (a) and D (b) observed at 20 and 23 min of retention time in the reaction of 4MCHexOH with Cl atoms. Tentatively assigned to 2-hydroxy-5-methyl cyclohexanone, 5-hydroxy-2-methyl-cyclohexanone and or 3-methyl-1,6-hexanedial.

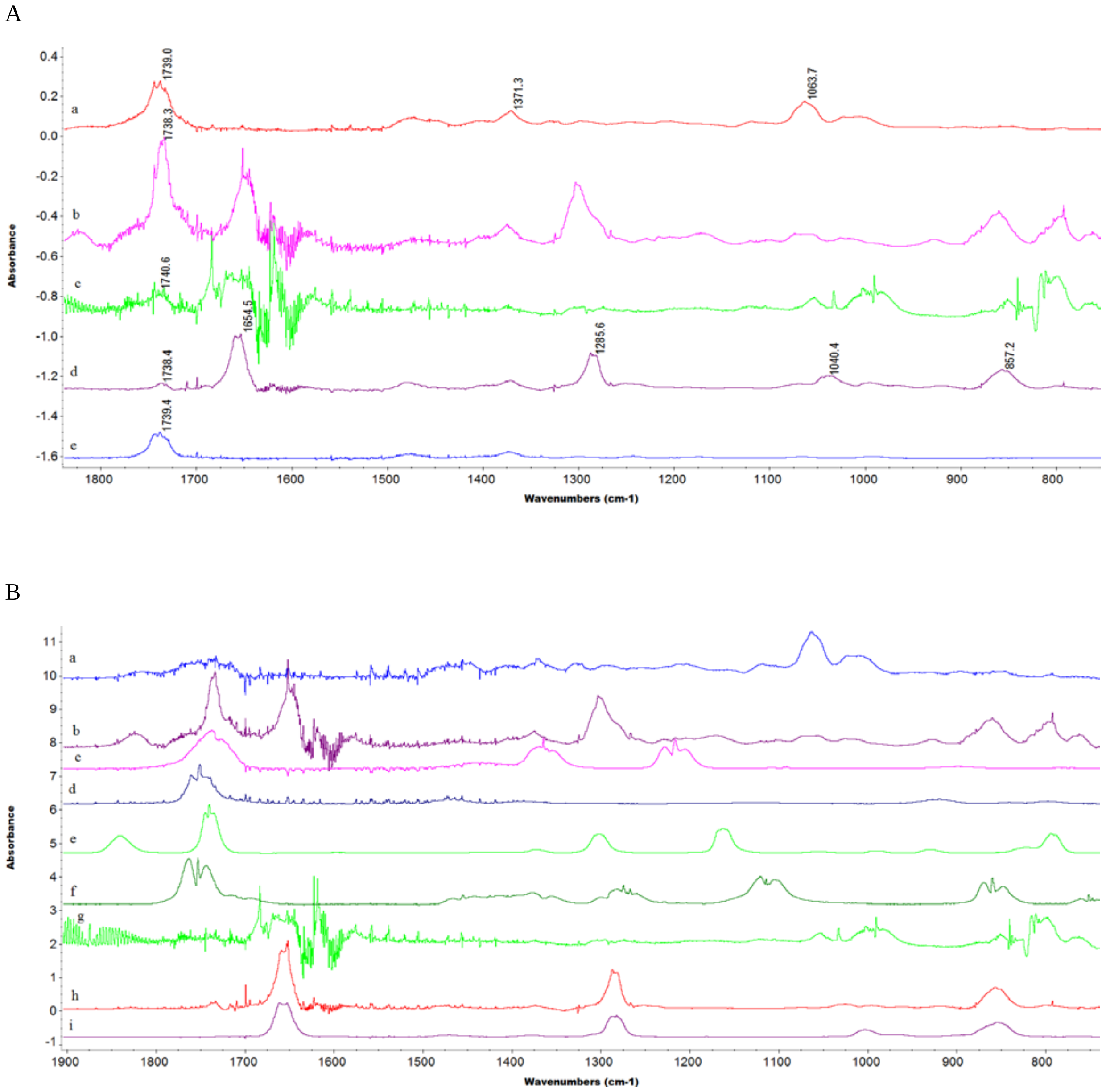


Fig. S5. A) Residual FTIR spectra obtained in the reaction of 3,3DM1ButOH with (a) Cl atoms ~~(a)~~, (b) Cl atoms in the presence of ~~+~~ NO ~~(b)~~, (c) OH radicals and (d) ~~(c)~~ NO$_3$ radicals ~~(d)~~. The IR absorption bands subtracted were:3,3DM1ButOH, HCl, ClNO$_2$, ClNO, HCOH, HCOOH, HONO, NO$_2$, NO, N$_2$O and peroxy nitric acid (for Cl in the absence and presence of NO~~and Cl + NO reactions~~); N$_2$O$_5$, HNO$_3$, NO$_2$ (for NO$_3$ reactions) and HCOH, HCOOH, HNO, NO$_2$, CH$_3$ONO and CH$_3$ONO$_2$ (for OH reactions). (e) FTIR reference spectrum of 3,3-dimethylbutanal**. B)** Residual FTIR spectra: (a) Cl atoms ~~(a)~~, (b) Cl atoms in the presence of ~~+~~ NO, (g) ~~b), H~~OH radicals ~~(g)~~ and (h) NO$_3$ radicals~~(h)~~ without 3,3-dimethylbutanal. Reference spectra (c) ~~of~~ acetone ~~(c)~~ from a commercial sample; (d) 2-methylpropanal ~~(d)~~; (e) PAN ~~(e)~~; (f) g~~G~~lycolaldehyde ~~(f)~~; and (i) isobutylnitrate ~~(i)~~ from Eurochamp 2020 database.

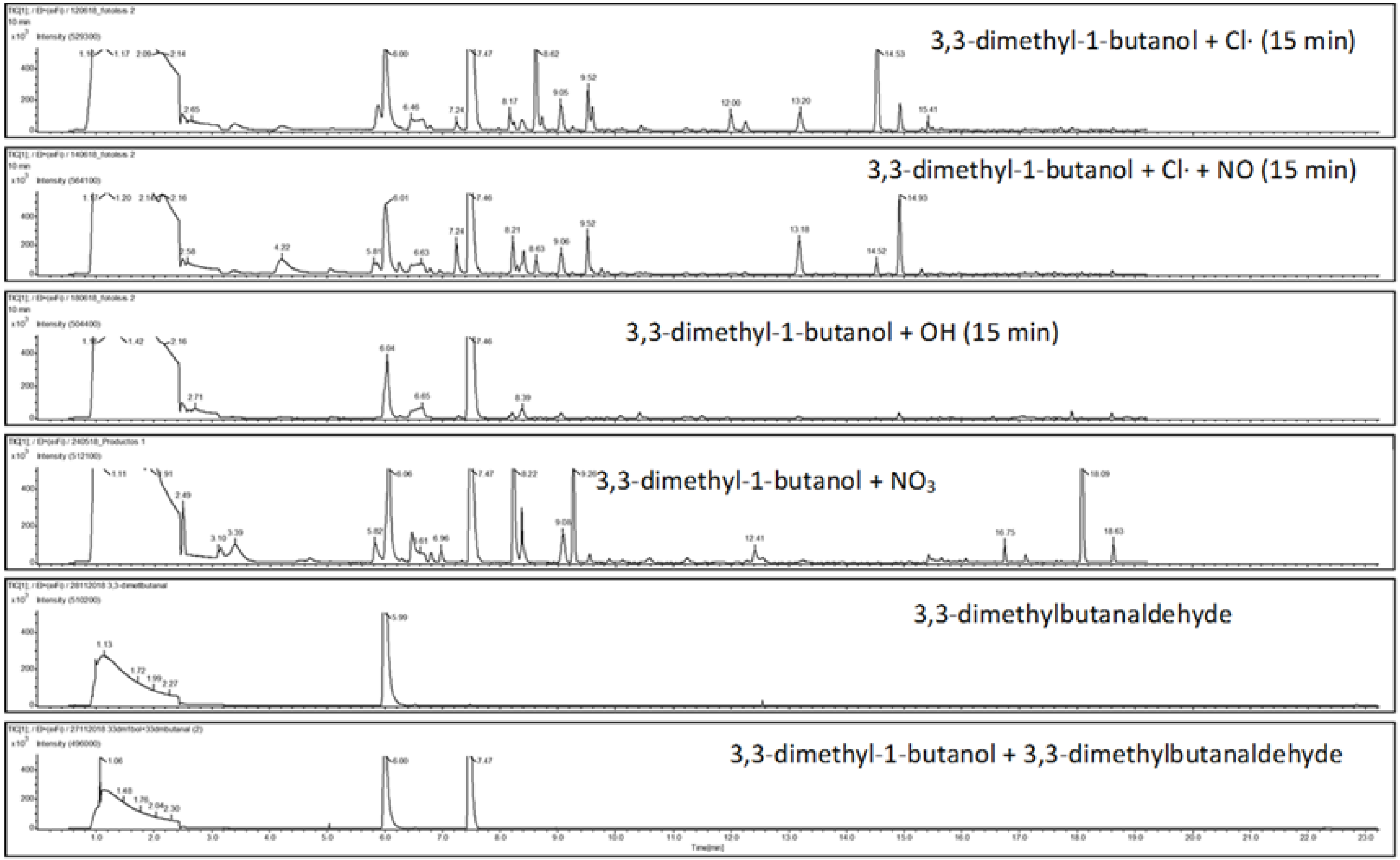
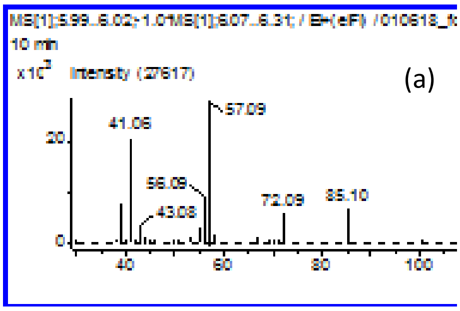
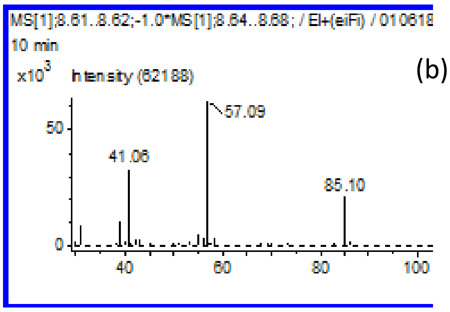
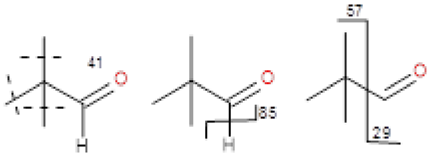
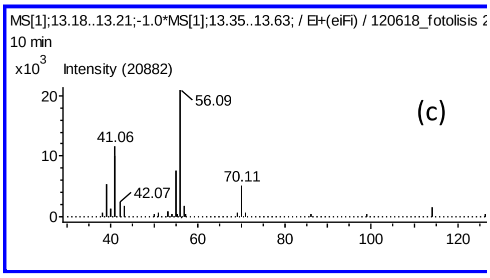


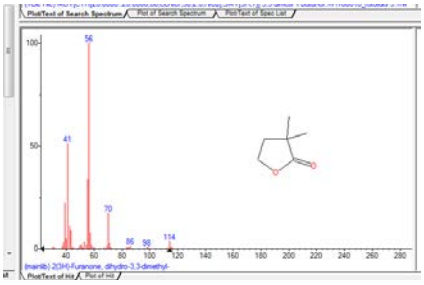
Fig. S6. SPME/GC-TOFMS chromatograms obtained for the reaction of of 3,3DM1ButOH with Cl atoms , Cl atoms in the presence of~~+~~ NO, OH radicals~~HO~~ and NO$_3$ radicals (30 min) and reference chromatograms of 3,3DM1ButOH and 3,3-dimethylbutanaldehyde.

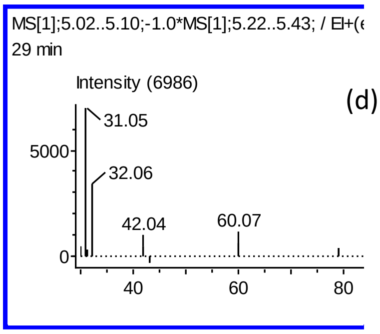


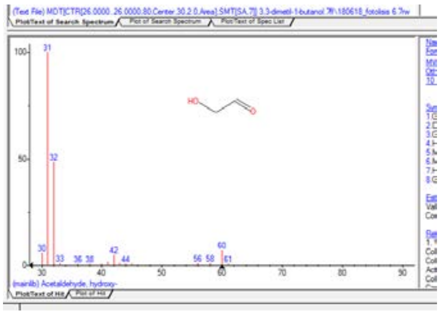


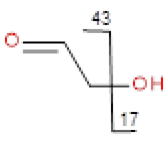












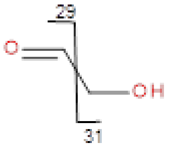


Fig. S7. EI-MS spectra of the peaks of chromatograms shown in Fig. S6 obtained for the reaction of of 3,3DM1ButOH with Cl atoms, Cl atoms in the presence of NO~~+ NO~~, ~~H~~OH radicals and NO$_3$ radicals. (a) t_R= 6.00 min; (b) t_R= 8.61 min; (c) t_R= 13.17 min; (d) t_R= 5.05 min).

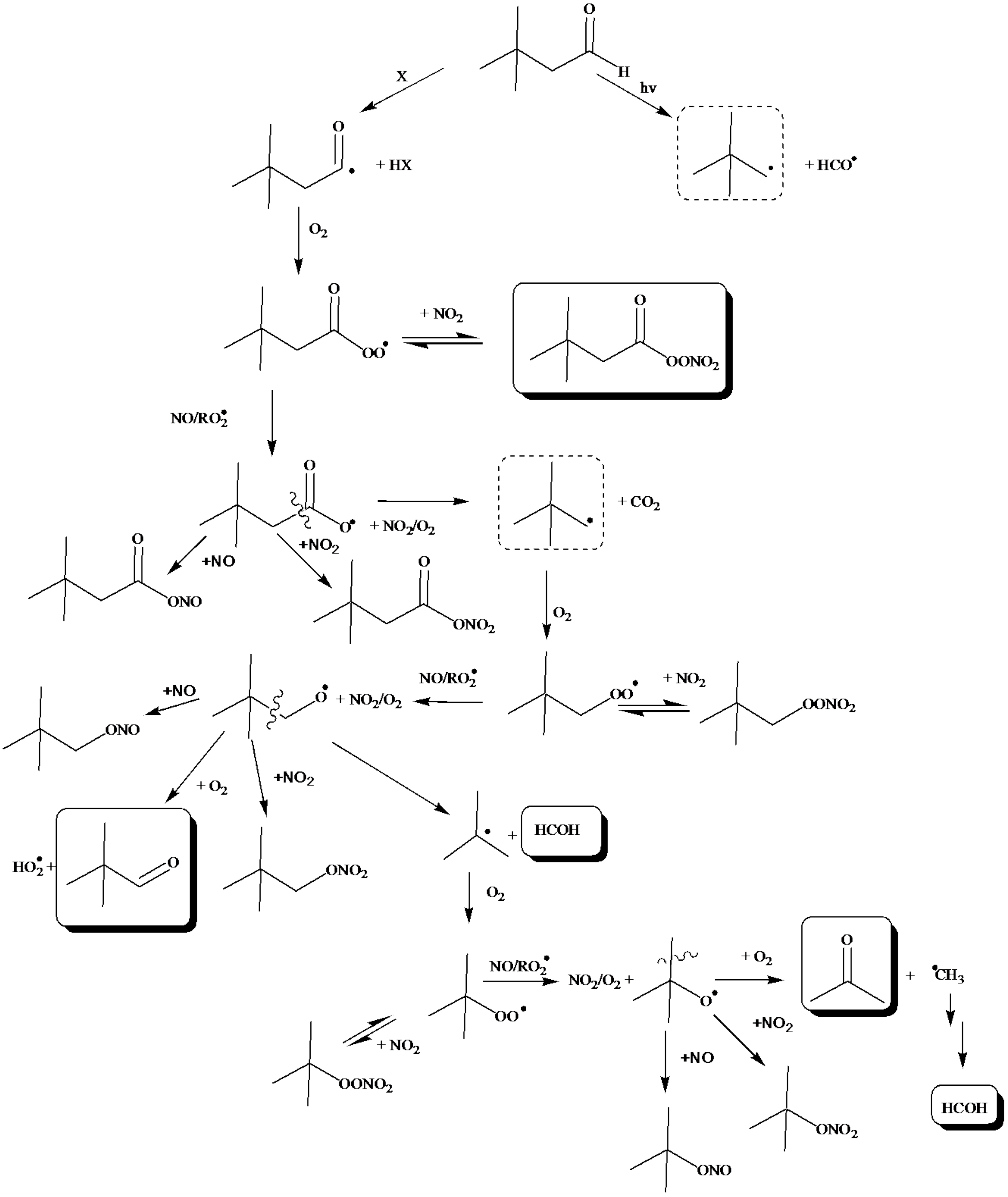


Fig. S8. Reaction mechanism for degradation of 3,3-dimethylbutanal with the atmospheric oxidants in presence of NOx. H-Atom abstraction from the -COH group in 3,3-dimethylbutanal. Aschamnn et al., 2010.

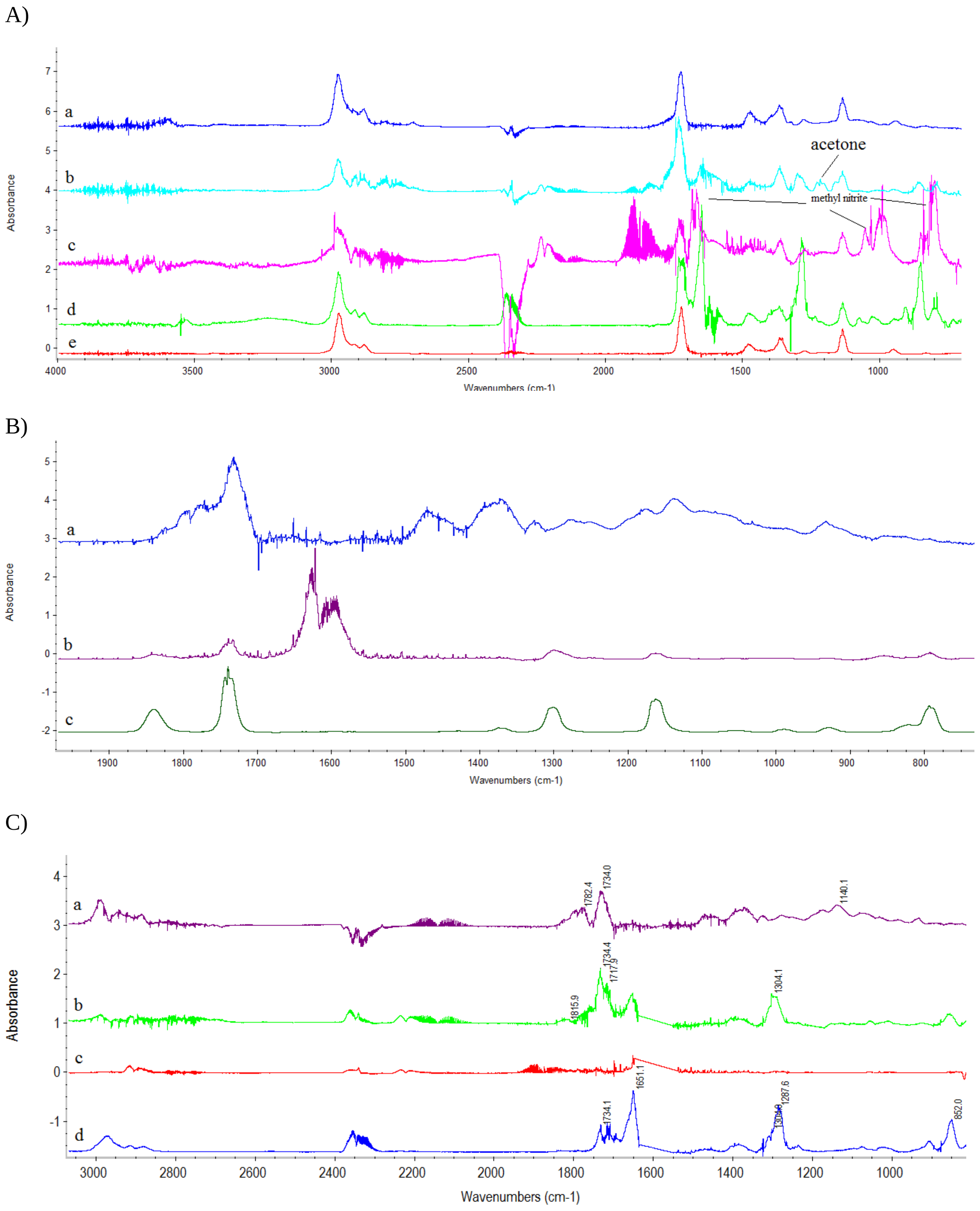


Fig. S9. A) FTIR spectra obtained in the reaction of 3,3DM2ButOH with (a) Cl atoms~~(a)~~, (b) Cl atoms in the presence of ~~+~~ NO, ~~(b),~~ (c) OH radials and (d) ~~(c)~~ NO$_3$ radicals~~(d)~~ at 5 minutes of reaction. (e) FTIR reference spectrum of 3,3-dimethyl-2-butanone. B) FTIR spectra obtained in the reaction of 3,3-dimethyl-2-butanol with (a) Cl atoms~~(a)~~, (b) Cl atoms in the presence of NO ~~+ NO (b)~~, 25 minutes and 35 minutes of reactions respectively. (c) IR PAN spectrum. C) Residual FTIR spectra after subtraction of all known bands. (a) Cl atoms ~~(a)~~, (b) Cl atoms in the presence of ~~+~~ NO ~~(b)~~, (c) ~~H~~OH ~~(~~ radicals ~~c)~~ and (d) NO$_3$ radicals~~(d)~~.

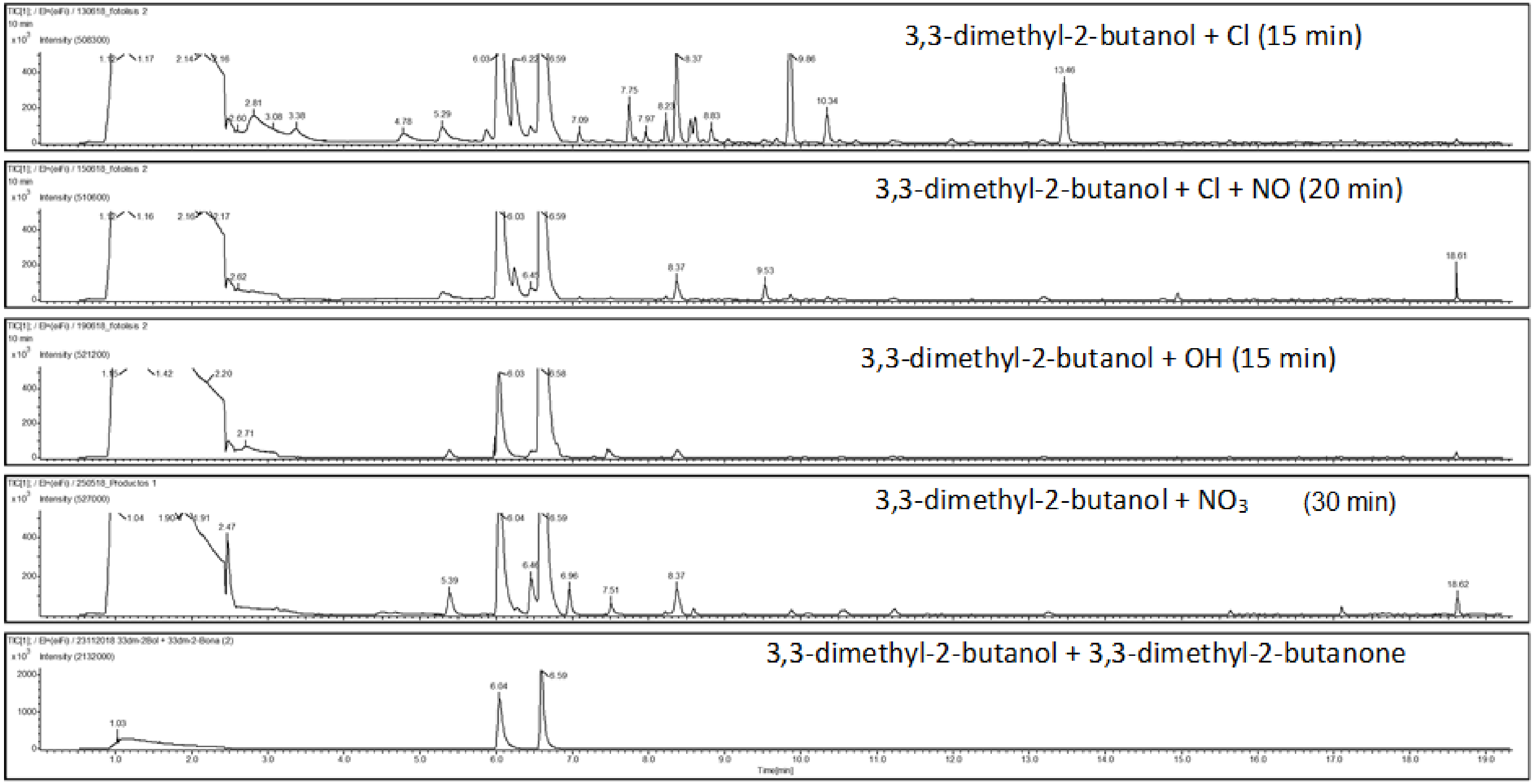


Fig. S10. SPME/GC-TOFMS chromatograms obtained for the reaction of of 3,3DM2ButOH with Cl atoms, Cl atoms in the presence of ~~+~~ NO, ~~H~~OH and NO$_3$ radicals and reference chromatograms of 3,3DM2ButOH and 3,3-dimethyl-2-butanone.

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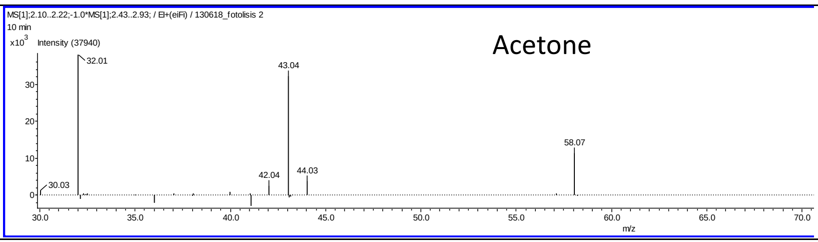

Acetone
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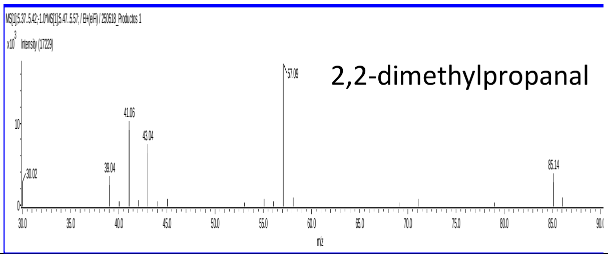
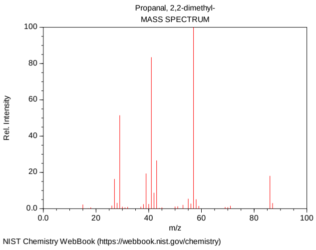


2,2-dimethylpropanal



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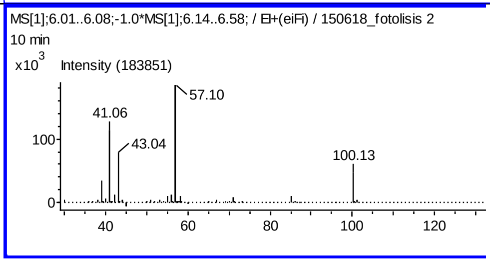

3,3-dimethyl-2-butanone
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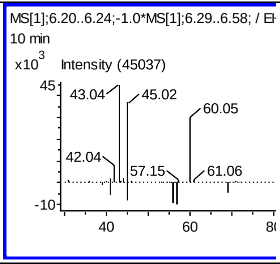

Acetic Acid (SI 80%)
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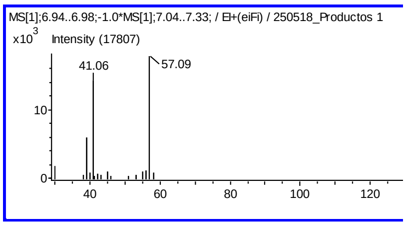

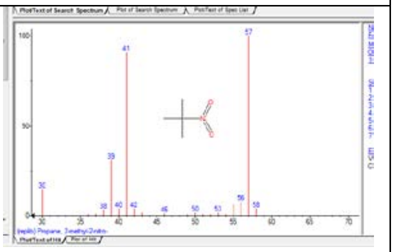

Nitrated compound
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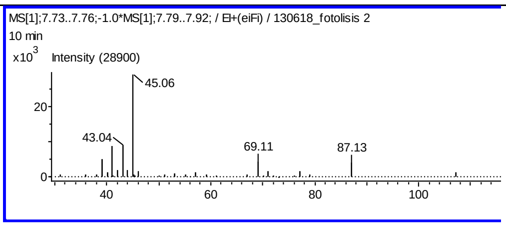

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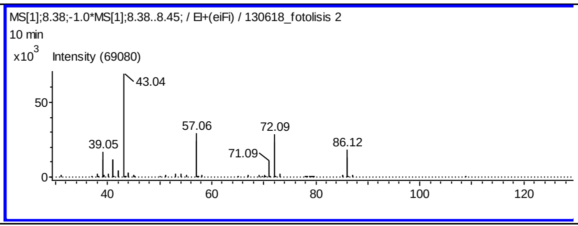

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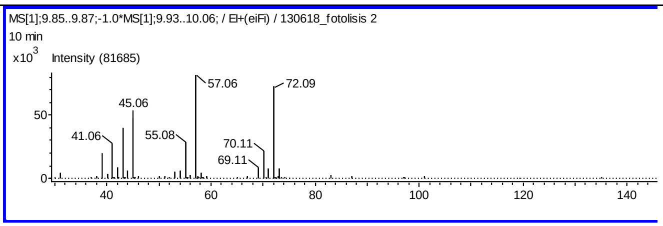
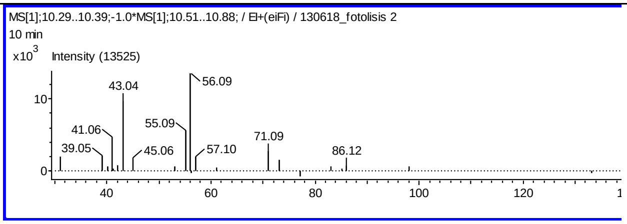
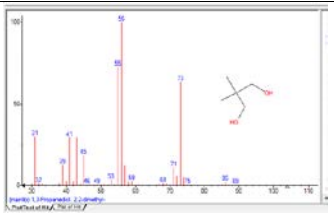
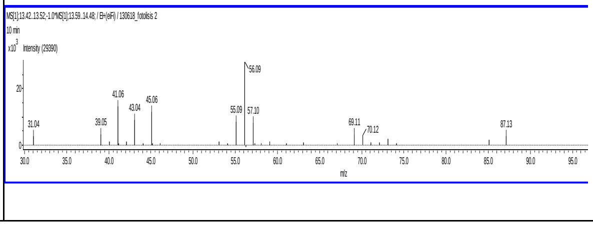
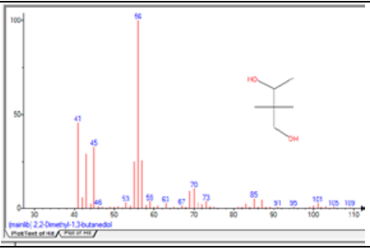
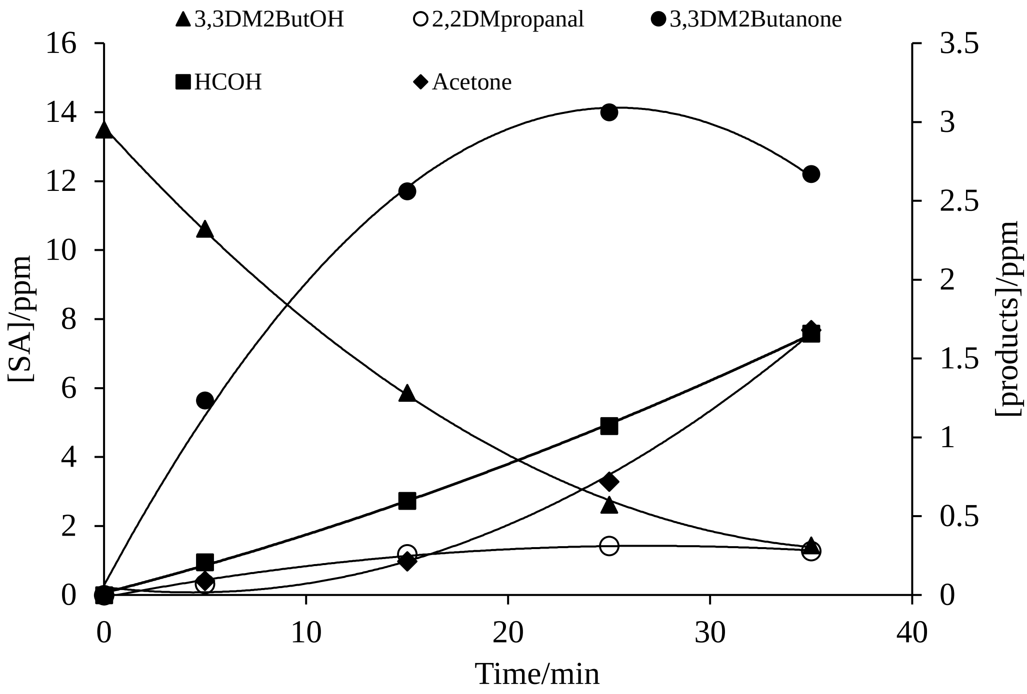
9.86		
10.34		
13.46		

Fig. S11. EI-MS spectra of the peaks of chromatograms shown in Fig. S10 obtained for the reaction of 3,3DM2ButOH with Cl atoms ~~,~~ Cl atoms in the presence of ~~+~~ NO, ~~H~~OH and NO$_3$ radicals,~~.~~

A)



(B)

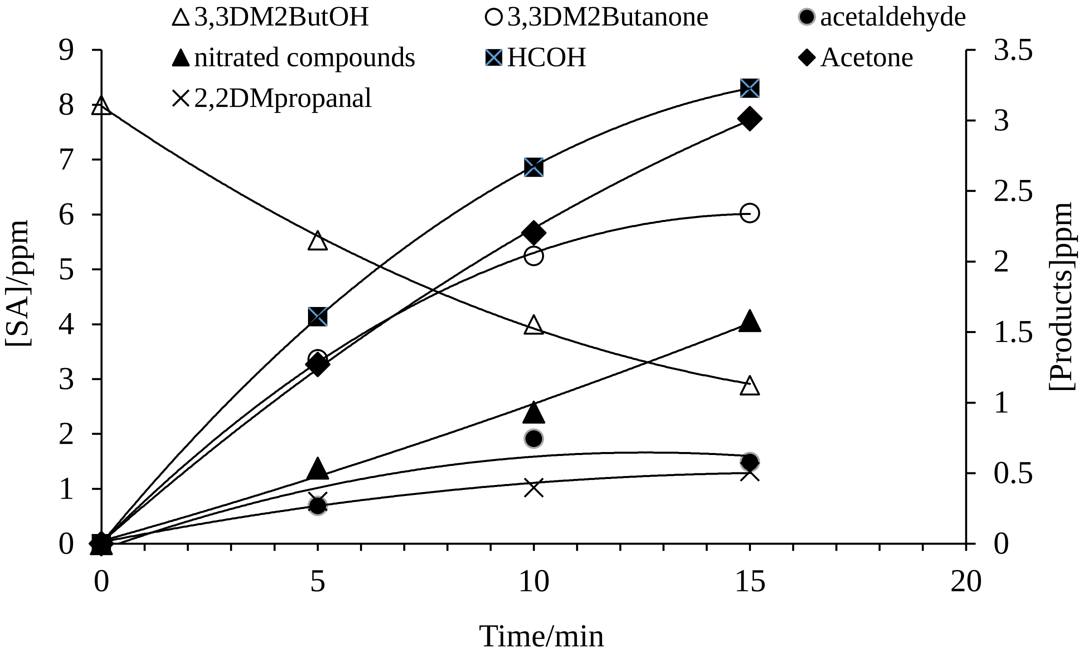


Fig. S12. Concentration-time profiles of 3,3DM2ButOH and reaction products formed for the reaction of 3,3DM2ButOH with Cl atoms in the absence (A) and the presence of NO (B).

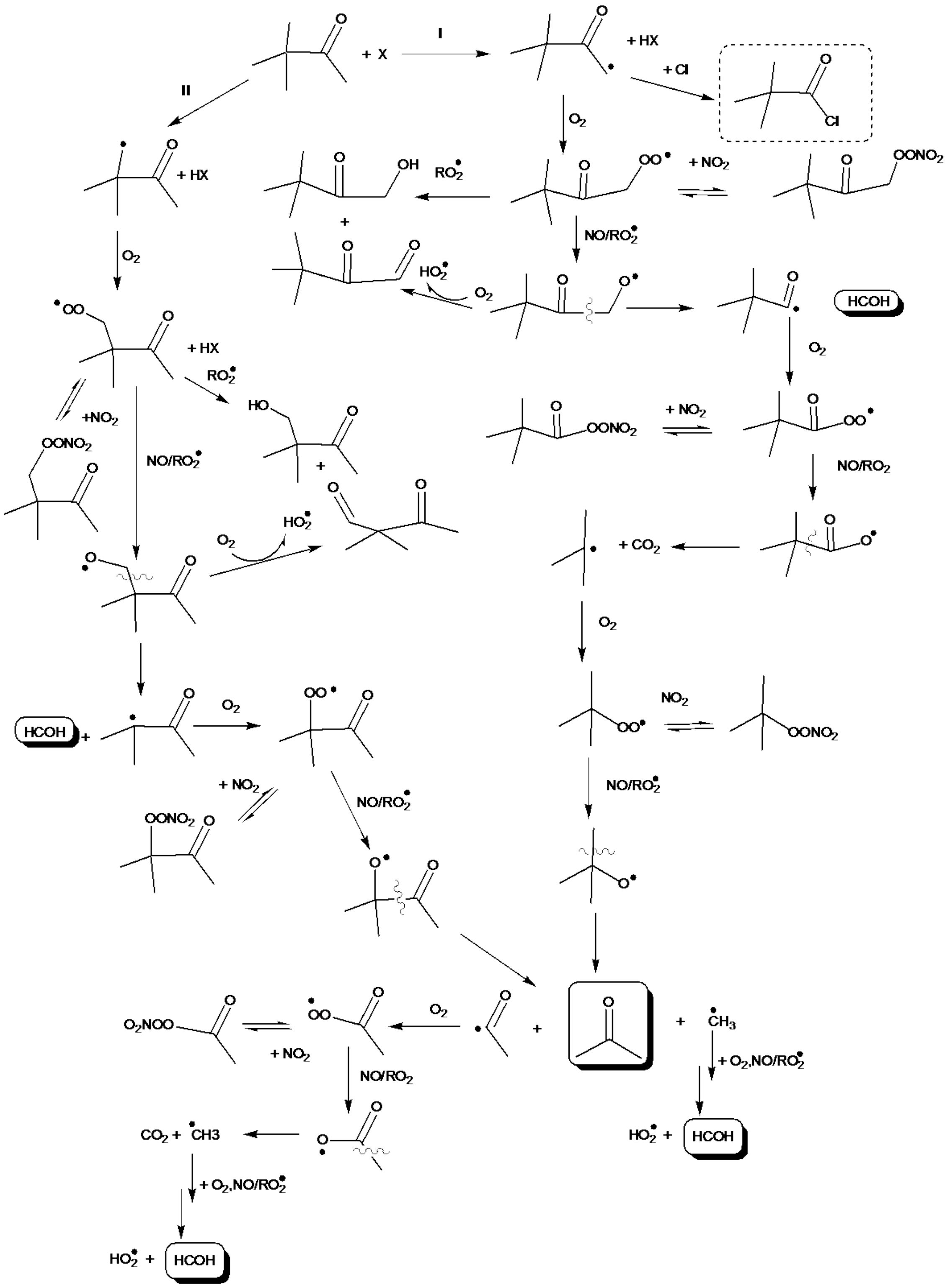


Fig. S13. Reaction mechanism for degradation of 3,3-dimethyl-2-butanone with the atmospheric oxidants in presence of NOx.

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