Atmospheric fate of a series of Methyl Saturated Alcohols (MSA): kinetic and mechanistic study

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Abstract. The atmospheric fate of a series of Methyl Saturated Alcohols (MSA) has been evaluated through the kinetic and reaction product studies with the main atmospheric oxidants. Rate coefficients (in 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) = $(3.70 \pm 0.16) \times 10^{-10}$, k_2 (E-4-methyl-cyclohexanol + OH) = $(1.87 \pm 0.14) \times 10^{-11}$, k_3 (E-4-methyl-cyclohexanol + NO_3) = $(2.69 \pm 0.37) \times 10^{-15}$, k_4 (3,3-dimethyl-1-butanol + Cl) = $(2.69 \pm 0.16) \times 10^{-10}$, k_5 (3,3-dimethyl-1-butanol + OH) = $(5.33 \pm 0.16) \times 10^{-12}$, k_6 (3,3-dimethyl-2-butanol + Cl) = $(1.21 \pm 0.07) \times 10^{-10}$ and k_7 (3,3-dimethyl-2-butanol + OH) = $(10.50 \pm 0.25) \times 10^{-12}$. The main detected products were 4-methylcyclohexanone, 3,3-dimethylbutanal and 3,3-dimethyl-2-butanone for the reactions of E-4-methyl-cyclohexanol, 3,3-dimethyl-1-butanol and 3,3-dimethyl-2-butanol respectively with the three oxidants. A tentative estimation of molecular yields has been done obtaining the following ranges (25-60) % for 4-methylcyclohexanone, (40-60) % for 3,3-dimethylbutanal and (40-80) % for 3,3-dimethyl-2-butanone. Other products such as formaldehyde, 2,2-dimethylpropanal and acetone have been identified in the reaction of 3,3-dimethyl-1-butanol and 3,3-dimethyl-2-butanol. The yields of these products indicate a hydrogen abstraction mechanism at different sites of the alkyl chain in the case of Cl reaction and a predominant site in the case of OH and NO_3 reactions, confirming the predictions of Structure Activity Relationships (SAR) methods.

Tropospheric lifetimes (τ) of these MSA have been calculated using the experimental rate coefficients. Lifetimes are in the range of 0.6-2 day**s** 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 global tropospheric lifetimes calculated, and the polyfunctional compounds detected as reaction products in this work, imply that the Methyl Saturated Alcohols could contribute to ozone and nitrated compound formation at local, but also regional and even to global scale. Therefore, the use of large saturated alcohols as additives in biofuels must be taken with caution.

1. Introduction

Multitude of scientific studies about combustion emissions confirm that fossil fuels, especially diesel fuel, are the main responsible for air pollution. The loss of air quality and its consequences on health as well as 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 for the presence of certain pollutants in the atmosphere, such is the case of particulate matter (PM) (EURO 6) and to develop biofuels (Sikarwara et al., 2017) as alternative to conventional ones.

Biodiesel are obtained from a transesterification process of 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 showing advantages as the reduction of the smoke, due to the presence of 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, 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). Other alternative is the use of longer alcohols (propanol, n-butanol, isobutanol and n-pentanol) with superior fuel properties than lower alcohols mixed with diesel fuel (Cheung, et al. 2014; Kumar and Saravanan, 2016).

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 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 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).

In the case of smaller alcohols, the knowledge of its reactivity is well established indicating that the degradation mechanism of saturated alcohols 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, Calvert et al., 2011). 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 are expected to be high, therefore reactions with Cl could also be an important degradation route, especially in coastal areas where concentration peaks of chlorine can be found. Reactions with ozone ($k \leq 10^{-20}$ cm^3 molecule^{-1} s^{-1}) and nitrate radical ($\sim 10^{-15}$ cm^3 molecule^{-1} s^{-1}) are too low to 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 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).

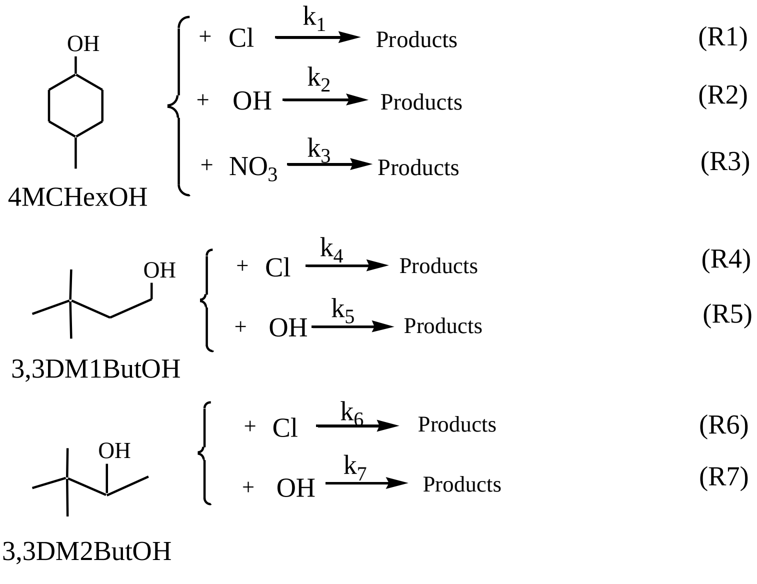
Although in the last years some studies about reactivity of large alcohols have been made (Ballesteros et al., 2007; Hurley et al., 2009; Andersen et al. 2010; Calvert et al, 2011; Moreno et al., 2012, 2014, Mellouki et al, 2015) the kinetic and mechanistic database is still scarce. In the case of the 3,3-dimethyl-1-butanol and 3,3-dimethyl-2-butanol (derives from 1-butanol, 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 for cyclohexanol (Bradley et al., 2001; Ceacero-Vega et al., 2012) and OH for cyclopentanol (Wallington et al., 1988) have been reported.

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

2. Experimental Section

2.1 Kinetic experiments

The reactions of a series of Methyl Saturated Alcohols (MSA) 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 (MSA) and the reference compound (R), are removed solely by their reactions with the oxidants (Ox: OH, NO_3 radicals and Cl atoms):

$$\text{Ox} + \text{MSA} \rightarrow \text{Products } (k_{MSA}) \qquad \text{(R8)}$$

$$\text{Ox} + \text{R} \rightarrow \text{Products } (k_{R}) \qquad \text{(R9)}$$

Where k_{MSA} and k_R are the rate coefficients of the MSA and the reference compound respectively.

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

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

where $[MSA]_0$, $[R]_0$, $[MSA]_t$, and $[R]_t$ are the initial concentrations and those at time *t* for the Methyl Saturated Alcohol and the Reference compound, respectively. Two reference compounds with each oxidant were used to assure that the reference compound does not have any influence on overall rate coefficient.

According to Eq (1), a plot of $\ln([MSA]_0/[MSA]_t)$ 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_{MSA}/k_R. Therefore the value of k_{MSA} can be obtained if the rate coefficient k_R of the reference compound is known.

The experimental systems are described in previous works (Tapia et al 2011, Martin et al. 2013) and only a brief description is shown here. Kinetic measurements were performed at room temperature (~ 298 K) and atmospheric pressure (720 ± 20 Torr) by employing two separated experimental set-ups: 1) - A FTIR system formed by 50 L Pyrex® glass reactor couple to the Fourier Transform Infrared Radiation spectrometer as a detection technique ("on line" analysis). Inside of Pyrex® glass reactor there is a multi-reflexion system with three mirrors that allows an infrared radiation path of 2.8-200 meters. This reactor is known as white cell (Saturn Series Multi-Pass cell). The FTIR spectrometer (Thermo Nicolet 6700) is equipped with a KBr beam splitter and liquid nitrogen-cooled MCT. Typically, for each spectrum, 60 interferograms were co-added over 98 s and approximately 30-40 spectra were recorded per experiment with a spectral resolution of 1 cm^{-1}. 2) - A Teflon ® gas bag reactor of 500 L with Solid Phase Micro Extraction fiber (SPME) as a pre-concentration sample method, followed by analysis on a Gas Chromatography - Mass Spectrometry system with a Time of Flight analyzer (SPME/GC-TOFMS) (AccuTOF 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 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 are injected into the reactors from a vacuum line by dragging with a stream of carrier gas used in the reaction. Both reactors are inside of a metallic housing in which walls there is a rack of actinic lamps (Philips, TL-40W, Actinic BL, λ_{max} = 360 nm). A scheme of the experimental systems is shown in Fig. S1 of supplementary material.

The kinetic experiments, for the Cl and OH reactions, were performed in 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 Teflon ® reactor of 500 L in order to minimize the wall deposition and dilution effects of consecutive additions of N_2O_5. Chlorine atoms and OH radicals were obtained by photolysis of Cl_2 in N_2 and methyl nitrite in the presence of NO in air. Methyl nitrite, CH_3ONO, 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_2O_5 (Atkinson et al., 1984, 1988). N_2O_5 was obtained mixing O_3 with excess of NO_2 (Scott and Davidson, 1958). Previously to the kinetic experiments a series of tests in dark and photolysis conditions were carried out to evaluate secondary reactions such as wall depositions and photodegradation processes of reactants.

Range 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, 3-5ppm of 2-methyl-2-butanol, 26-55 ppm of CH_3ONO, 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_2O_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 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 was taken from this reactor using the SPME and subsequent analyzed with GC-TOFMS. In addition, independent experiments using SPME/GC-TOFMS technique in a 150 L Teflon® reactor were developed. Products analyses were carried out using the same procedure as for the kinetic experiments, without the reference compound, and employing synthetic air as bath gas. In 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 provides 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 Mass Spectra database of the instrument were used to identify the products. Calibrated FTIR spectra and SPME/GC-TOFMS chromatograms were used 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 versus the amounts of MSA (Δ[MSA]) 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, the concentration of the product was corrected using the formulism of Tuazon et al. (1986) (See S1 in supplementary material). Range concentrations of reactants employed were as follows: 2-14 ppm of MSA, 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 Air (Praxair Ultrahigh purity 99.999 %,), N_2 (99.999 %, Praxair). For N_2O_5 synthesis, N_2O_4

were used (>99.5 %) from Fluka, P_2O_5 (98 %, such as desiccant) from Fluka and O_3 synthesized by a generator model TRCE-5000, 5 g_{O3} h^{-1} OZOGAS.

3. Results and discussion

3.1 Kinetic study

Preliminary test experiments indicated that dark heterogeneous reactions and photolytic losses of MSA can be considered negligible in our experimental conditions ($k \sim 10^{-6}$ s^{-1}). As mentioned above, the 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 and synthetic air respectively. Nitrate radical experiments were performed using N_2 gas in a 500 L Teflon reactor and employing the system SPME/GC-TOFMS. A number of injections of the unreacted mixture were carried out in order to determine the associated precision 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 MSA with different atmospheric oxidants.

A good correlation was obtained with an intercept close to zero, which indicates the absence of other secondary processes. From the slopes of the plots (k_{MSA}/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_{MSA}) has been determined.

Rate coefficients of reference compounds, for Cl atom 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); for OH radical 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). And for NO_3 reactions (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_{MSA}/k_R, the absolute rate coefficients and the weighted average are shown in Table 1. The error of k_{MSA}/k_R are given by 2 times the statistical deviation calculated from the least-square fit of the plot of Eq. (1). The uncertainties for rate coefficients of MSA (σ_{kMSA}) were calculated from the uncertainty of slope of plots (σ_{slope}) and the uncertainty of the reference (σ_{kR}) by using the propagation of uncertainties. The average value of the rate coefficient obtained with different reference compounds and its associated error were obtained by weighted average (See footnote Table 1). The rate coefficients obtained in this work are the first kinetic data reported for these MSA, therefore the results obtained cannot be compared with literature values.

As it has been mentioned in introduction section, it 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 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 hydroxyl group (-OH). Two literature reviews 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 H atom abstraction from the O−H 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 4 carbon atoms (Nelson et al., 1990). 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, structure of saturated alcohol, type and numbers of substituents, and temperature, (Moreno et al., 2012, 2014; McGillen et al., 2013, 2016).

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

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

a) -The trend in the reactivity of MSA in relation to the different oxidants is the same that the observed for other saturated alcohols: k_{Cl} ($k \sim 10^{-10}$) > k_{OH} ($k \sim 10^{-11}$) >> k_{NO3} ($k \sim 10^{-15}$), (k in cm^3 $molecule^{-1}$ s^{-1} units). This behavior could be explained considering the geometry and the electronic density of each oxidant, together with the kinetic Collision Theory. As Cl atom has spherical distribution of its density, for the collision any orientation is adequate, in addition the Cl atoms presents less steric hindrance. Then, comparatively the Cl reaction is less selective and faster with values for the rate coefficients, k, in the collision limit. However, the OH radical presents an asymmetric electron density located mostly over its oxygen atom. Therefore, for the OH reaction the oxygen of OH radical, must be specific oriented to the hydrogen of the MSA that will be abstracted. The electronic density of nitrate radical is distributed around the three oxygens which implies several appropriate orientations. However, as the nitrate radical has a non-linear structure, the steric hindrance is much bigger than for the OH and it reduces the reactivity of NO_3 in relation to those 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): $k_{4MCHexOH+Cl} = 37.0\times10^{-11} \simeq k_{E\text{-}1,4\text{-}dimethylcyclohexane+Cl} = 36.3 \times 10^{-11}$. In the case of the reaction with OH radical, the rate coefficient of 4MCHexOH is 1.5 times higher than 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 hydroxyl group (-OH) of the MSA is less important for the Cl than OH. 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 coefficients for the reactions of the homologous alkanes of the MSA studied in this work with NO_3 radical, and therefore it is not possible to check out the effect of hydroxyl group in the reactivity of NO_3 reaction. However, according to the factor of reactivity obtained by Kerdouci et al. (2010) for the reactions of alcohols with NO_3, this effect is higher than the corresponding to Cl and OH reactions.

c) - The activating effect of the length chain in the reactivity of alcohols is more evident in Cl reactions than OH reactions (See Table S1). Furthermore, if the rate coefficients of 3-methyl-1-butanol (3M1ButOH) and 3,3DM1ButOH with Cl and OH reactions are compared, it can be observed a slight increase of rate coefficient for Cl reaction ($k_{3M1BuOH+Cl}$ = 25.0 × 10^{-11}; $k_{3,3DM1ButOH+Cl}$ = 26.9 × 10^{-11}) and an important decrease of the rate coefficient for OH reactions ($k_{3M1BuOH+OH}$ = 14 × 10^{-12}; $k_{3,3DM1ButOH+OH}$ = 5.33 × 10^{-12}). This behavior could be explained by the different order of reactivity between the oxidants. For Cl atom, more reactive (k order of 10^{-10} cm^3 $molecule^{-1}$ s^{-1}) but less selective, an increase of the length chain or in the number of methyl groups implies more hydrogens available to be abstracted and therefore an increase of the rate coefficient. However, for OH radicals, less reactive and more selective, the attack for H-abstraction will be carried out in a specific place, so an increase of the chain has not a significative effect to the reactivity, even the presence of a second methyl group disfavor the reaction probably due to the steric hindrance near to the attack position.

In addition, as can be seen in Table S1, the position of hydroxyl group has a different effect depending on the oxidant. In the case of the Cl atom reactions, the rate coefficients for primary alcohols (1-propanol, 1-butanol, 1-pentanol, 3-methyl-1-butanol and 3,3-dimethyl-1-butanol) are higher than the ones of the secondary alcohols (2-propanol, 2-butanol, 2-pentanol, 3-methyl-2-butanol and 3,3-dimethyl-2-butanol) contrary to the OH and NO_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 α position available to be abstracted.

All these observations (a, b and c) could imply a different mechanism in the hydrogen abstraction process for Cl atoms versus OH and NO_3 radicals. 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 hydroxyl group via hydrogen bond that will imply a specific orientation. Theoretical studies found in 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).

Different mechanisms in the hydrogen abstraction process for each oxidant will imply different product distributions and molecular yields as it will be shown below, in the section of product 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, multitude of methods have been proposed (Vereecken et al. 2018). The most popular and 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 OH radical. This method has been updated for OH reactions (Jenkin et al., 2018) and extended to 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 estimate the rate coefficient for the reaction of OH radical and organic compounds using the AOPWIN v1.92 program. In our work the rate coefficients of MSA with the three oxidants have been estimated using the SAR method (See S2 supplementary material). The results are shown in Table 2.

The values of estimated rate coefficients agree with experimental data with ratios k_{exp}/k_{SAR} between 0.9 and 1.28, except for the case of 3,3DM1ButOH and NO_3 radical with a k_{exp}/k_{SAR} of 3.24. In general, the SAR method applied to alcohols predicts better rate coefficients for Cl atoms and OH radical than for 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 which reacts in the same way with different atmospheric oxidants, present a correlation between their rate coefficients. In this sense, along the years, different correlations have been proposed that allow to estimate the unknown rate coefficient when the other one is known (Wayne, 1991, 2000; Atkinson, 1994; Calvert et al., 2011; Gallego-Iniesta et al., 2014). Correlations $\log k_{Cl}$ -$\log k_{OH}$ and $\log k_{NO3}$-$\log k_{OH}$ have been built for a set of alcohols, ethers and saturated alcohols by Calvert et al., (2011) obtaining the following relationships:

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

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

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

3.2 Product and Mechanistic Study

A product study of 4MCHexOH, 3,3DM1ButOH and 3,3DM2ButOH with chlorine atoms in 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. These bands are due to the decomposition of the precursors employed (Cl_2, CH_3NO_2 and N_2O_5) and in some cases are due to heterogeneous reactions of these precursors with the walls of the Pyrex® reactor. The formation of O_3 and N_2O_5 have also been observed at large reaction times for the reactions of the MSA with Cl atoms + NO, due to the high concentration of the NO_2 in the medium of reaction and in presence of radiation. Quantitative analysis was carried out by linear subtraction of a spectrum's absorption bands and peak areas of GC chromatograms with the use of calibrated spectra and reference chromatograms.

The experimental conditions and molecular yields of the main products formed in the reactions of MSA and analyzed by FTIR and SPME/GC-TOFMS techniques are given in Tables 3-6. Molecular yields could be affected 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 reaction with Cl, Cl + NO, OH + NO and NO_3 + NO_2. An example of the product spectra obtained in the FTIR system is shown in Fig. 2. Formation of the E-4-methylcyclohexanone was confirmed by introducing a sample of the commercial product (spectrum (e)). A set of experiments using the SPME/GC-TOFMS system were also carried out for the reaction of 4MCHexOH with Cl atoms and OH and NO_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) showed in Fig. 3 was assigned to E-4-methylcyclohexanone and confirmed by comparing with the retention time and MS spectrum of a commercial sample. In the reactions with chlorine atoms (absence/presence of NO_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 for the reaction with chlorine atoms in presence of NOx is shown on Fig. S2. The concentrations of E-4-methylcyclohexanone, corrected according to Eq (S1), (S2) and (S3), were plotted versus the amounts of 4MCHexOH consumed in order to obtain the yield of 4-methylcyclohexanone from the slope. An example of the obtained plots is shown in Fig. 4. Molecular yields, Y (%), of E-4-methylcyclohexanone obtained in all experiments are listed in Table 3. Based on the average molecular yield of E-4-methylcyclohexanone, the carbon balance is below to 50 % for reactions with Cl and OH radical and ~ 60 % for NO_3.

Residual spectra after subtraction of the E-4-methylcyclohexanone show IR absorption bands compatible with the presence of hydroxy carbonyl compounds (~1750, 1720, 1060 cm^{-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 supplementary material). 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 + NO 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, presents in the reaction medium, reacts faster with the $CH_3O^\bullet$ (formed in the reaction of CH_3ONO with NO) than others alcoxyradicals. Table 6 shows a summary of the average yields of reaction products quantified for 4MCHexOH reactions.

Considering the products detected here and the detected in the study of Bradley et al., (2001) relative to cyclohexanol with OH radical reactions, a degradation mechanism for 4MCHexOH with the atmospheric oxidants has been proposed. Figure 5A shows the paths to explain the formation of carbonyl or hydroxy carbonyl compounds and Figure 5B shows an example of a path to explain the formation of nitrated organic compounds ($ROONO_2$ and $RONO_2$). Similar nitrated compounds could be formed by routes II-IV. The abstraction of hydrogen atoms in α-position with respect to alcohols group (route I) followed by the addition of oxygen, formation of a peroxy radical and 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 and Cl + NO, OH and NO_3, respectively. Percentages are two times higher than SAR method prediction in the case of Cl atoms reactions and 1.3 and 1.5 times lower for OH and NO_3 reactions respectively. These data should be taken with caution, since they could imply 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 this kind of compounds have been observed in the reactions with Cl and OH. According to the Electron Ionization Mass Spectra (EI MS) (Fig. S4, supplementary material) of peaks (C) and (D) shown in Fig. 3, an assignation to 2-hydroxy-5-methyl-cyclohexanone, 5-hydroxy-2-methyl-cyclohexanone 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 comes from the decomposition of the alkoxy radical formed in route II. However, confirmation was not possible since these compounds were not commercially available. The detection of HCOH about 9 % in the reaction with Cl atoms indicates that the elimination of the methyl group in route IV is minority.

In the case of nitrate radical only 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 way to add the precursor in both reactors (small aliquots of N_2O_5 in the Teflon® reactor versus one large addition in the Pyrex® reactor). This procedure causes a lower initial concentration of nitrated inorganic species (NO_3, NO_2, HNO_3) in reactor of 150 L than in reactor of 50 L, favoring the formation of carbonyl compounds instead of nitrated organic compounds. Taking into account, the yields of E-4-methylcyclohexanone and the nitrated compounds for the NO_3 reaction using FTIR, a total carbon balance of 100% is obtained (See Table 6).

3.2.2 -3,3DM1ButOH

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, 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 EI MS spectra (Fig. S7), show that other reaction products as carbonyl, hydroxy carbonyl and nitrated compounds are formed. These reaction products could be formaldehyde, 2,2-dimethylpropanal, glycolaldehyde, acetone, 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) or secondary products from degradation of 3,3-dimethylbutanal (See Fig. S8). The SPME/GC-TOFMS chromatograms show common peaks for the three oxidants, but the number of peaks and their distribution are very different, especially for OH reactions. In the case of SPME/GC-TOFMS system a set of experiment using Field Ionization 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 if the profiles correspond with a primary or secondary reaction products. An example of the reactions with chlorine atoms in the absence and presence of NOx is shown in Fig. 6, observing that in the absence of NO the profiles of acetone and formaldehyde show a typical profile of secondary reactions. This profile is clearly observed for nitrated compounds in the reaction of Cl atoms in presence of NO (Fig. 6B).

Commercial sample of 3,3-dimethylbutanal was used to estimate the molecular yields in both experimental systems. These molecular yields are shown in the Table 4. The yields of acetone and formaldehyde were calculated using a FTIR reference spectrum of commercial sample and FTIR reference spectra from Eurochamp database (https://data.eurochamp.org/data-access/spectra/), respectively. A FTIR reference spectrum of 2-methylpropanal (from this same database) 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 OH and NO_3 radicals as is described previously using the rate coefficients available in 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 secondary products (See Fig. S8). A total of carbon yield (nitrated compounds have not been accounted) of 60 %, 81 % and 36 % have been justified for Cl (absence and presence of NO), OH and NO_3 reaction respectively, but must be noted that there are reaction products that could not be quantified as carbonyl or hydroxy carbonyl compounds in the Cl atoms reactions and primary nitrated compounds in the Cl + NO and NO_3 radical reactions.

This work is the first study of reaction products of 3,3DM1ButOH with the atmospheric oxidants, so there is no any study to compare. Figure 7 shows the reaction mechanism proposed based on the literature studies about saturated alcohols reactions with Cl atoms and 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 work. Table S2, in supplementary material, shows a summary of the reaction products proposed in this mechanism observed or tentatively identified in the reactions of 3,3DM1ButOH with the atmospheric oxidants.

Estimated molecular yields of 3,3-dimethylbutanal (formed by H-Abstraction in α position of 3,3DM1BuOH) for Cl and OH reaction (~(40-43) %, ~60 %) are very similar to the one predicted by the SAR method (40 % and 66 % respectively). In the case of NO_3 radical a large difference between both yields are observed (36 % estimated in this work, 86 % predicted by SAR method). This discrepancy could be explained by the fact that the SAR method (Kerdouci et al., 2010, 2014) underestimates the attack of NO_3 in β-position, since it does not consider the possible effect of the hydroxyl group jointed to $-CH_2-$, $(F(-CH_2OH))$. This could also explain the large difference observed between the estimated and measured rate coefficient as was shown in Table 2. On the other hand, as it has been discussed above, the volume of the reactor could also have 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 OH radical reaction, the route I (attack in α position) seems to be the main reaction route. For Cl atoms the three routes can occur with a high percentage. The major molecular yield of formaldehyde and acetone (route III) in the reactions of Cl atoms in presence of NO versus Cl atoms reactions in absence of NO could indicate that in absence of NO the self peroxy radical reaction “via” molecular channel is more favored than “via” radical channel. For NO_3 radical, routes I and II (attack in β position) with formation of nitrated compounds seem to be the unique routes.

3.2.3 -3,3DM2ButOH

The analysis of FTIR spectra obtained for the reactions of 3,3DM2ButOH with Cl atoms, in presence and absence of NO, 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 Peroxy Acetyl Nitrate (PAN), have also been observed. The residual FTIR spectra after substraction 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 of Cl atoms in absence of NO and also nitrated compounds ($RONO_2$; 1650, 1305-1260, 890 cm^{-1}) in the reaction of Cl + NO and NO_3 radical (Fig. S9C). The presence in the residual FTIR spectra of a IR absorption band around 1800 cm^{-1} for the reaction of Cl atoms at large 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 as hydrofurans. The SPME/GC-TOFMS chromatograms and MS spectra (Fig. S10 and S11) confirm other reaction products apart from 3,3-dimethyl-2-butanone in the case of Cl, Cl + NO and NO_3 reactions. Only one significant peak is observed in chromatograms obtained for the OH reactions.

Acetone, formaldehyde, 2,2-dimethylpropanal, nitrated compounds and acetaldehyde have also been quantified. Plots of concentration versus time show typical profiles of secondary reactions for formaldehyde, acetone (Fig. S12A) and nitrated compounds in the reactions of Cl with NO (Fig. S12B). 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 been corrected again for secondary reactions. Table 6 summarizes the molecular yields of all quantified products.

A total carbon yields of ~60 %, 100 %, 90 % and 60 % have been accounted for Cl (absence and presence of NO), OH and NO_3 reaction, respectively (Table 6). It is important to note that in the case of the reaction of Cl atoms without NO where the total carbon yield is lower than 100 % there are many reaction products that could not be quantified, as carbonyl and/or hydroxy carbonyl compounds. In the reaction of NO_3 radical, due to our experimental conditions, an important amount of primary nitrated compounds is expected to be formed (Fig. S9C).

A mechanism of hydrogen abstraction in different positions of 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 supplementary material, shows a summary of the reaction products proposed in this mechanism observed or tentatively identified in the reactions of 3,3DM2ButOH with the atmospheric oxidants.

Molecular yields of 3,3-dimethyl-2-butanone obtained in this work imply a percentage of attack of the oxidant in α position (route II) of: 43 % and 44 %, in the case of chlorine atom; 81 % for OH radical and 58 % for NO_3 radical. Percentages are very similar to that predicted by SAR method except for NO_3 radical. High NO_2 concentration present in the reaction would highly favor the formation of nitrated compounds versus 3,3-dimethyl-2-butanone. The main reaction products observed in the reaction of Cl atoms in presence of NO (3,3-dimethyl-2-butanone, formaldehyde, 2,2-dimethylpropanal, acetone, acetaldehyde) confirm that the Cl atoms could attack in other sites (apart of α position) with an important percentage. Based on the estimated molecular yield of acetone, the attack in δ position with abstraction of hydrogen of methyl groups (route III) could be ~58 %, and based on the estimated molecular yield for 2,2-dimethylpropanal, the attack in β position (route I) could account with a 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 of Cl atoms in presence of NO than in absence of NO could indicate that in presence of NO the peroxy self-reactions (RO_2) “via” molecular channel is negligible. The lower yield (17 %) estimated by acetaldehyde versus 58% of its coproduct (acetone) is due to its fast degradation by Cl atoms reaction with formation of Peroxy acetyl nitrates 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 FigS12 and FigS13.

4. Atmospheric Implications

The pollutants in the atmosphere, could 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 know the impact of the presence of these compounds in the atmosphere. These parameters are, the time that such compounds remains in the atmosphere, the Global Warming Potential (GWP) and their degradation mechanisms in order to estimate the atmospheric effect of products formed.

The first important parameter of the environmental impact of an Oxygenated Volatile Organic Compounds in the atmosphere, is the global lifetime, τ_{global}, which considers all the degradation processes which could suffer these compounds in the Troposphere. 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):

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

Tropospheric lifetime (τ) of 4MCHexOH, 3,3DM1ButOH and 3,3DM2ButOH for each process have been estimated considering Eq (4) and (5).

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

where k_{OX} and [Ox] are the rate coefficient obtained in this work for each oxidant and typical atmospheric concentration of the oxidants Cl, OH and NO_3, respectively. Concentrations employed were as follows: for 24 hours average: 1×10^3 atoms cm^{-3} (Platt and Janssen, 1995) for chlorine atoms, 12-hours 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 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 kind of compounds (Mellouki et al., 2015). Other processes are referred to dry a wet deposition. For estimating the lifetime associated with wet deposition, Eq (6) proposed by (Chen et al. 2003) has been used:

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

Where k_H is the Henry’s law constant, H_{atm} is the height in the troposphere taking a value of 630 m, v_{pm} is the average precipitation rate for Ciudad Real (Spain) (402 mm/year) (www.aemet.es), R is the gases constant and T is the temperature considered as constant and equal to 298 K. In bibliography there is only data of the constant of Henry 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 value of K_H of 3 mol m^{-3} Pa^{-1} and 0.4 mol m^{-3} Pa^{-1} for 4MCHexOH and 3,3DM1ButOH respectively.

Lifetime calculated of the three studied alcohols 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 OH radicals 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 MSA do not have a significant contribution to radiative forcing of climate change (Mellouki et al., 2015), which is supported through the estimation of their GWP values. For time-horizon of 20 years, the values estimated 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 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 influence at global scale. Moreover, since 4MCHexOH, 3,3DM1ButOH and 3,3DM2ButOH react quickly with 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 the present study, are the following:

-The kinetic and product study support that: 1 -The atmospheric degradation mechanism for MSA, and possibly for the rest of unstudied saturated alcohols, proceeds by abstraction of the hydrogen atom bonded to a carbon instead of hydrogen atoms bonded to the oxygen atom of the alcohol group. 2 -The reaction mechanism in the H-abstraction process depends on the oxidant. Chlorine atoms abstract any type of alkyl hydrogen from saturated alcohols with a high percentage, compared to the hydroxyl radical and the nitrate radical. OH and NO_3 radicals abstract mainly the hydrogen in the α position, if the saturated alcohols are secondary. For primary alcohols, the abstraction of a hydrogen in β position could be also important in the reaction with NO_3 radical. Therefore, more kinetic studies for NO_3 radical with primary alcohols are necessary to update the SAR method developed by Kerdouci et al., and to quantify the effect of the OH group in β position, ($-CH_2OH$).

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

-The atmospheric conditions determine the reaction mechanism and therefore the reaction products obtained in the degradation of methyl saturated alcohols. So, in polluted environments with high concentrations of NOx, the peroxyradicals ($RO_2\cdot$) reacts mainly with NO to form the alkoxy radical instead of molecular compounds. In these conditions, nitrated organic compounds ($RONO_2$) are formed apart from polyfunctional organic compounds. Also, when the concentration of NO_2 is higher than NO concentration, ozone is formed. In clean atmosphere, as in the case of the experiments of Cl atoms in absence of NO, the reaction products are different because of peroxyradicals ($RO_2\cdot$) could react mainly “via” self-reaction molecular channel instead to “via” self-reaction radical channel.

-The uncounted polyfunctional organic compounds could explain the low carbon balance obtained in Cl or NO_3 reaction. 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 (the order of ~1 day) imply that these compounds are pollutants at local-regional scale, but it is also important to indicate that MSA are sources of stable nitrated compounds ($ROONO_2$), depending on environment conditions, that can travel to large distances from their sources contributing to form ozone in clean areas, for example in forest or rural areas.

-The main products coming from the degradation of the MSA, aldehydes and ketones, develop a very important secondary chemistry with formation of products of special relevance such as the PAN observed in the degradation of 3,3-dimethyl-2-butanol. More experiments should be done using other detection techniques, in order to evaluate the formation of SOA 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 MSA is an important source of pollutants in the atmosphere with greater or lesser impact depending on the environmental conditions and the quantities of these alcohols present in the atmosphere. Therefore, the use of MSA as additives in the production of biofuels should be controlled, avoiding that a bad handling involves high concentrations of these alcohols in the atmosphere.

-Rate coefficients and reaction products measured in this work are the first available data, so this work contributes to a better understanding of atmospheric chemistry of oxygenated compounds, expanding the kinetic and mechanistic database, and additionally it contributes to develop or to improve prediction models 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 coefficients to other typical atmospheric conditions and thus be able to better establish the atmospheric impact of the 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 MSA 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**	**$(k_{MSA}/k_R)\pm2\sigma$**	**$(k_{MSA}\pm2\sigma)^a/10^{-10}$**	**$(\bar{k}_{MSA}\pm2\sigma)^b/10^{-10}$**
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**	**$(k_{MSA}/k_R)\pm2\sigma$**	**$(k_{MSA}\pm2\sigma)/10^{-12}$**	**$\bar{k}_{MSA}\pm2\sigma/10^{-12}$**
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**	**$(k_{MSA}/k_R)\pm2\sigma$**	**$(k_{NO3}\pm2\sigma)/10^{-15}$**	**$\bar{k}_{NO3}\pm2\sigma/10^{-15}$**
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 MSA (σ_{KMSA}) were calculated from the uncertainty of slope of plots (σ_{slope}) and the uncertainty of the reference (σ_{KR}) by using the propagation of uncertainties. [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 MSA 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 supplementary material

[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.

MSA	Oxidant	Exp	[MSA] (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, $k_p = 5 \times 10^{-5}$ 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 $=13.7 \times 10^{-12}$ (estimated using AOPWIN, v1.92). Photolysis rate coefficient estimated for E-4-methylcyclohexanone under our experimental conditions, $k_p = 5 \times 10^{-5}$ 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 square analysis

[e] Experiment using a Teflon gas Bag 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.

MSA	Oxidant	Exp	[MSA] (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	39.4±15.0	40
						41.8±4.6	SPME/GC-TOFMS[d]		
		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	43.3±17.7	
						34.7±4.4	SPME/GC-TOFMS[d]		
		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	62.2±15.0	66
						40.8±2.7	SPME/GC-TOFMS [d]		
		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	36.2±14.6	86
						53.9 [h]	SPME/GC-TOFMS[d]		
		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 Gas Cell of 50 L

[e] Experiment using a Teflon gas Bag of 150 L

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

MSA	Oxidant	Exp	[MSA] (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	43.2±1.8	
						45.2±1.1	SPME/GC-TOFMS[d]		
		2	2.3	8	-	41.7±3.2	SPME/GC-TOFMS[e]		
	Cl[a] + NO	1	14	28	20	36.7±5.0	FTIR	44.2±7.4	40
						49.6±4.5	SPME/GC-TOFMS[d]		
		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	80.7±6.5	91
						71.2±2.6	SPME/GC-TOFMS[d]		
		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	58.0±10.9	99
						45.9±1.6	SPME/GC-TOFMS[d]		
		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 Gas Cell of 50 L

[e] Experiment using a Teflon gas Bag of 150 L

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

[g] Standard deviations 1σ

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

Product	**MSA**			
		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	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 reaction.;

[3] $Total\ Carbon\ (\%) = \sum_1^i \left(\frac{nº\ of\ carbon\ of\ product_i}{nº\ of\ carbon\ of\ MSA} \times molar\ yield_i(\%)\right)$

[4] Without accounting nitrated compounds; [5] From analysis of the experiment number 3 for the reaction of Cl + NO; [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.

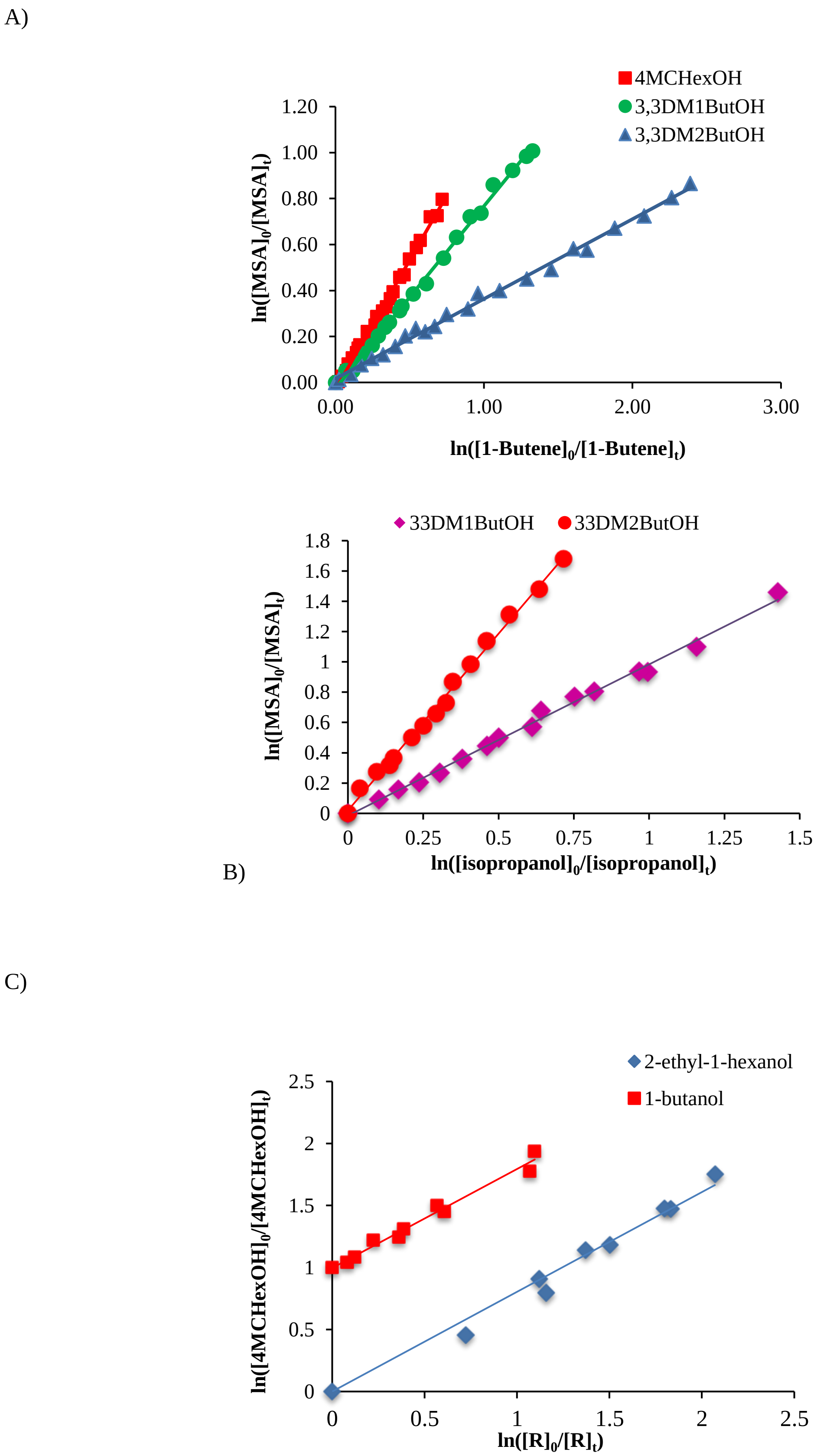

Fig.1: Relative rate plots for the reaction of (A) MSA with chlorine atoms employing 1-butene as a reference compound (B) 3,3-Dimethylbutanols and OH radical with isopropanol as a reference compound and (C) 4MCHexOH and NO_3 with two reference compounds. Data for 1-butanol have been vertically displaced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

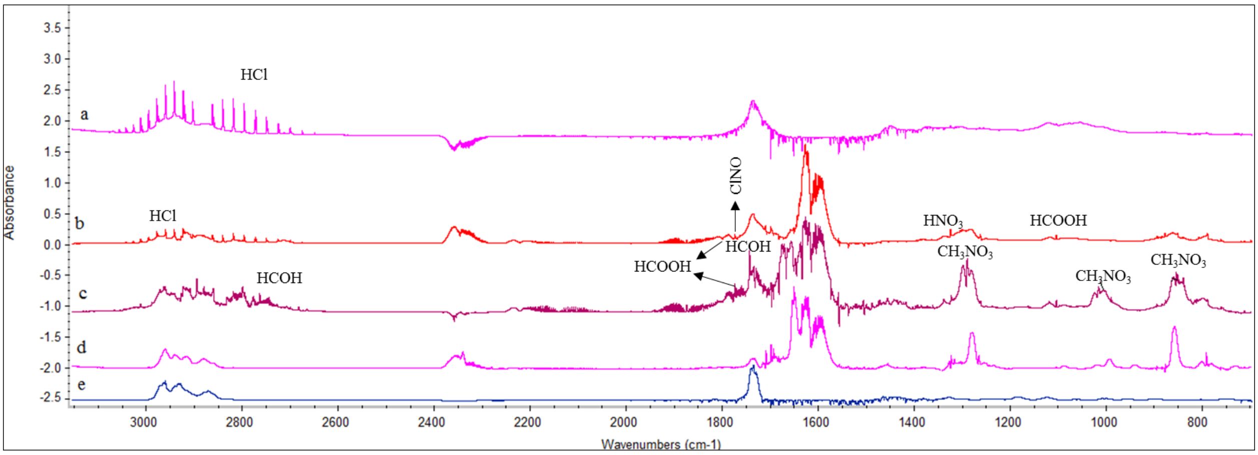

Fig. 2: Product spectra for reaction of 4MCHexOH with: (a) chlorine atoms at 10 min (x 2 to clarify), (b) Cl atoms and NOx at 7 min. (c) OH radical at 40 min and (d) NO_3 radical at 32 min. (e) Spectrum of 4-methylcyclohexanone commercial sample.

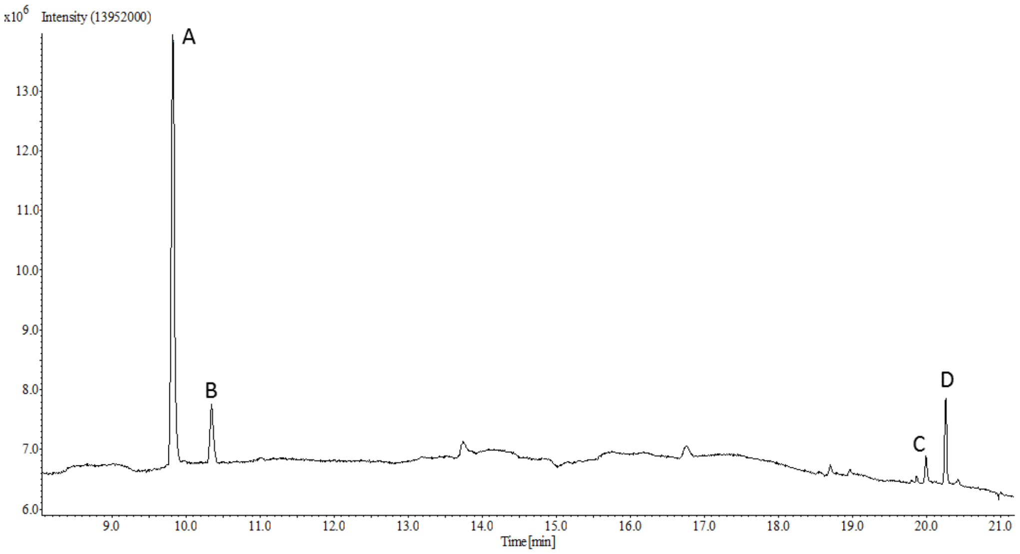

Fig. 3: SPME/GC-TOFMS chromatogram for the reaction of 4MCHexOH with Cl atoms after 15 minutes of reaction. Peak (A) 4MCHexOH. Peak (B) E-4-methylcyclohexanone. Peaks (C) and (D) reaction products.

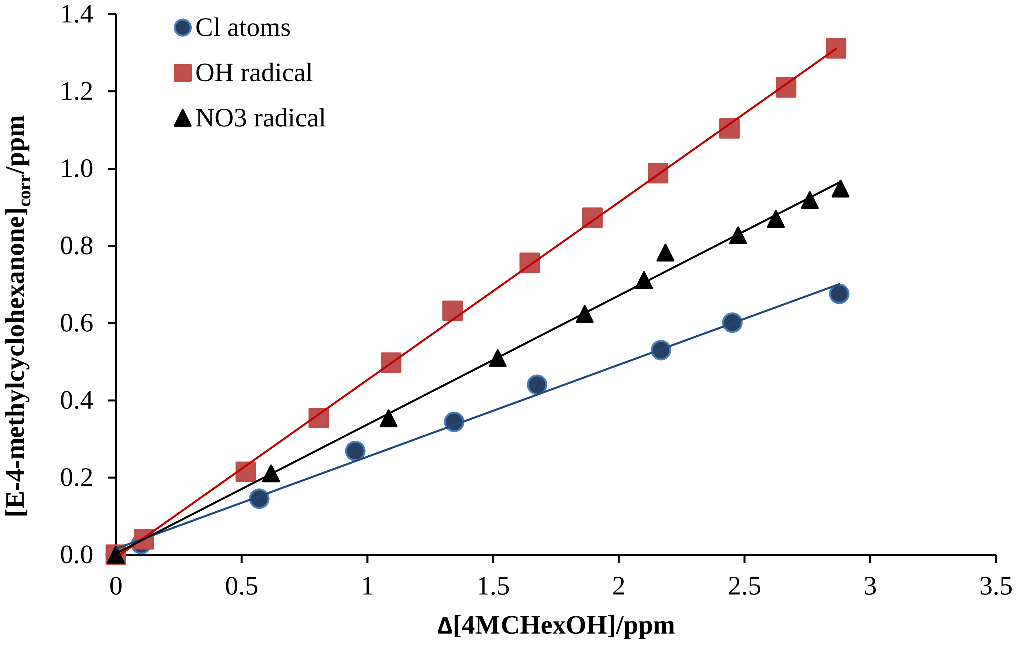

Fig. 4: Plots of corrected concentration of E-4-methylcyclohexanone ([E-4-methylcyclohexanone]$_{corr}$) against 4MCHexOH consumed (Δ[4MCHexOH]) for Cl atoms (in absence of NOx) and OH and NO_3 radical reactions.

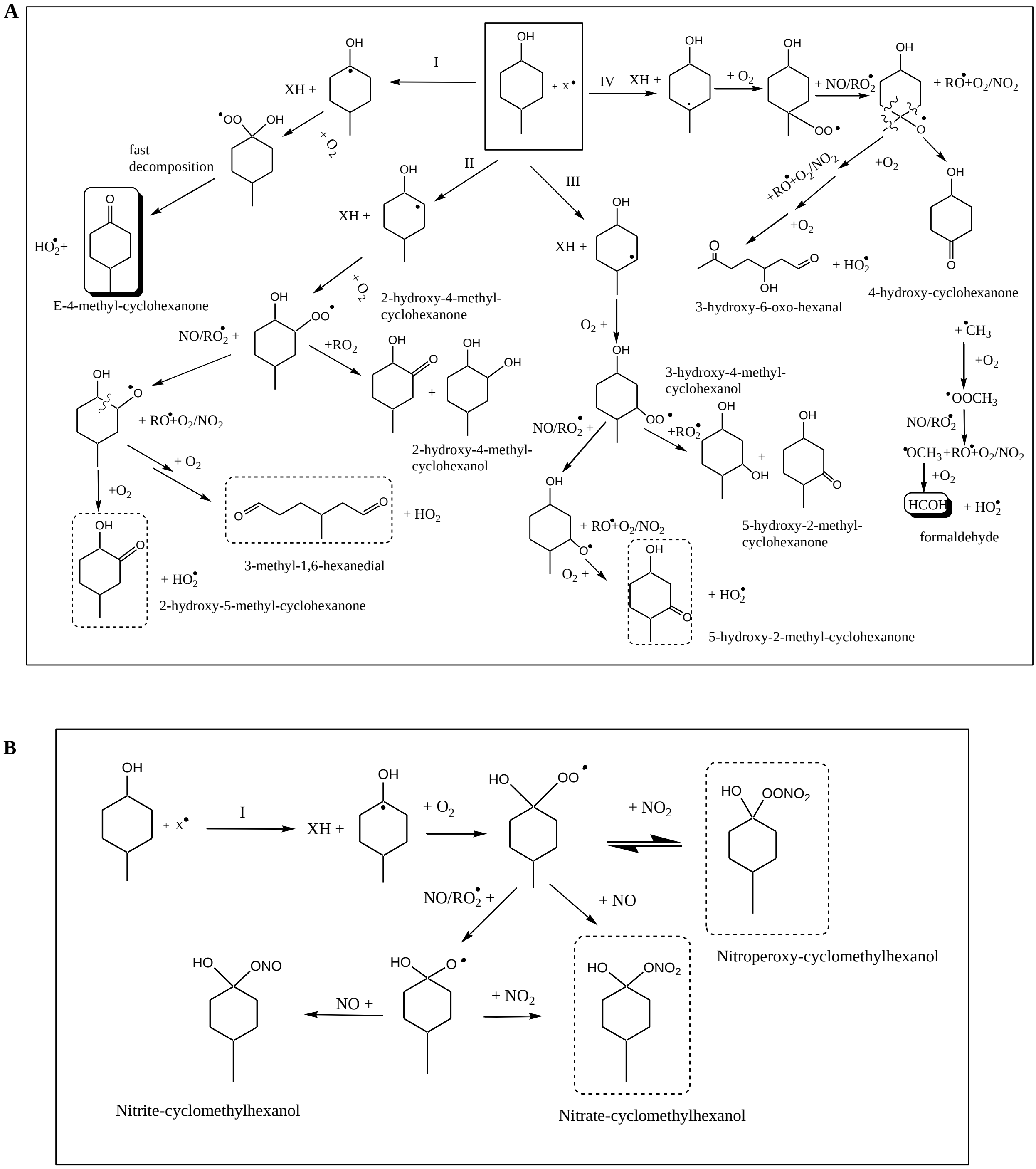

Fig. 5: Reaction mechanism for the degradation of 4MCHexOH with X (Cl atom, OH and NO_3 radicals). (A) Mechanism for the formation of carbonyl compounds, (B) Mechanism for the formation of nitrated compounds. Compounds marked with solid line are positively identified. Compounds marked with shaded lines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

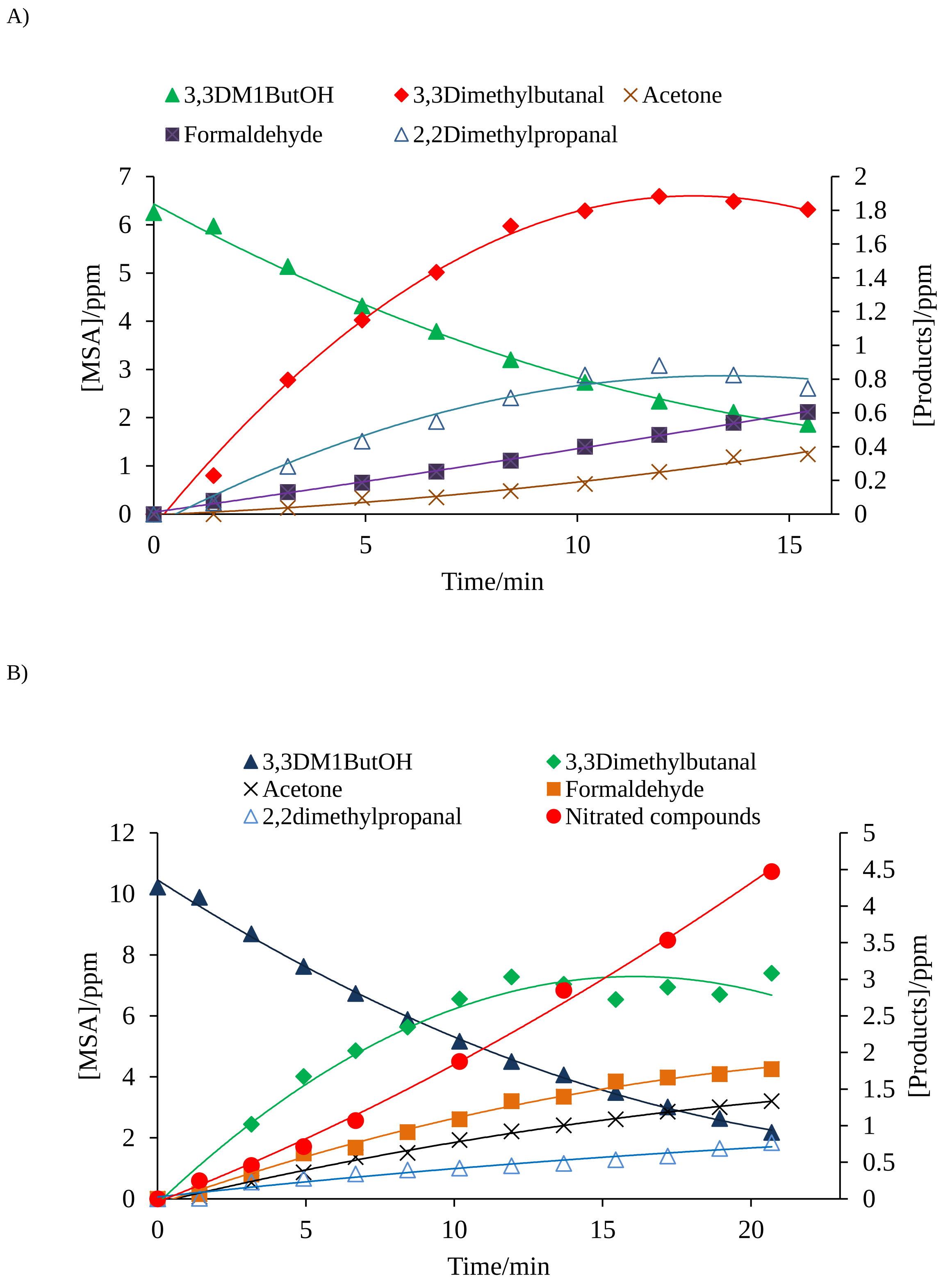

Fig. 6: Concentration-time profiles of MSA (3,3DM1ButOH) and reaction products formed in the reaction of 3,3DM1ButOH with Cl atoms in absence (A) and presence of NO (B).

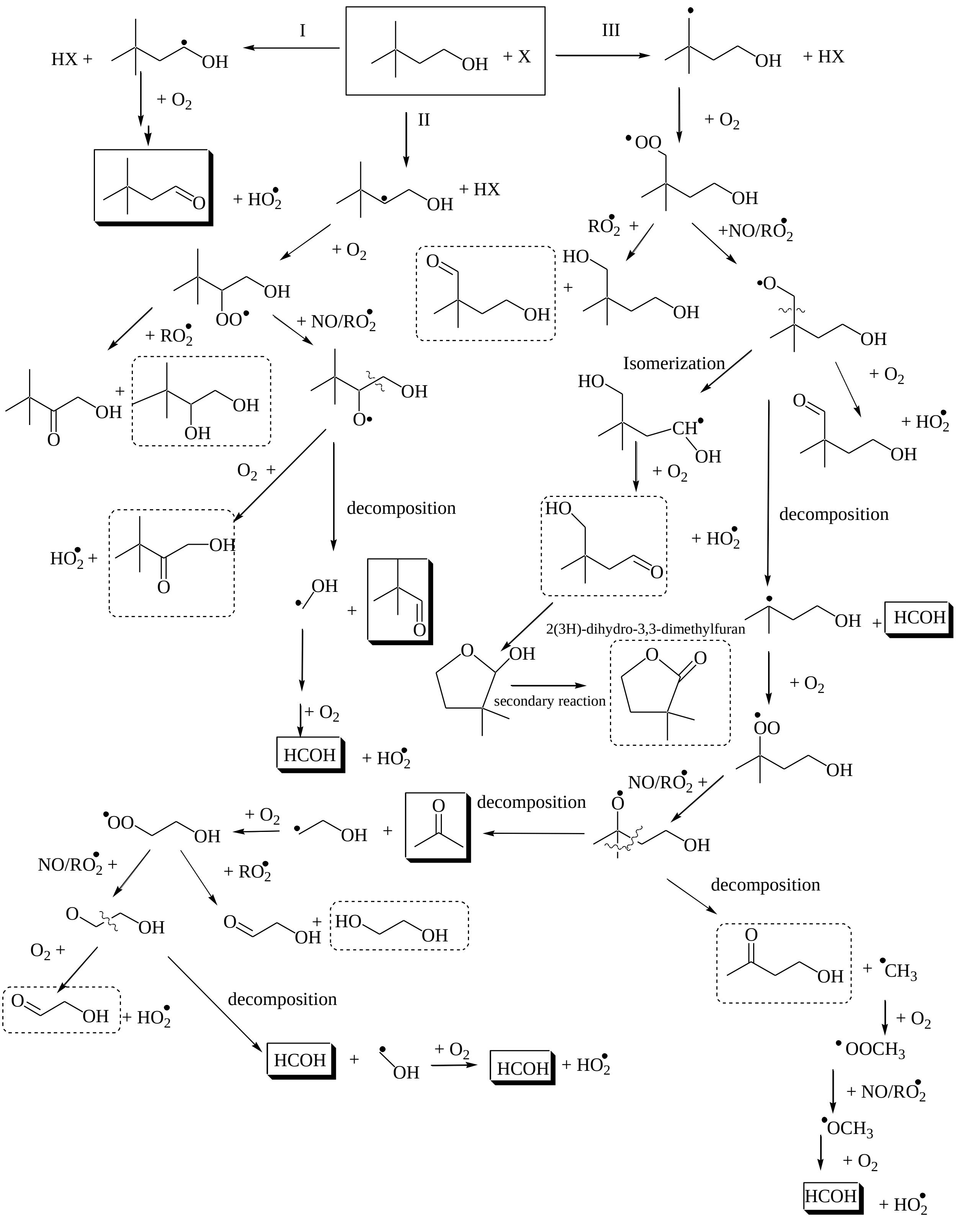

Fig. 7: Reaction mechanism for the degradation of 3,3DM1ButOH with X (Cl atom, OH and NO_3 radical). Mechanism for the formation of carbonyl compounds. Compounds marked with solid line are positively identified. Compounds marked with shaded lines are not positively identified.

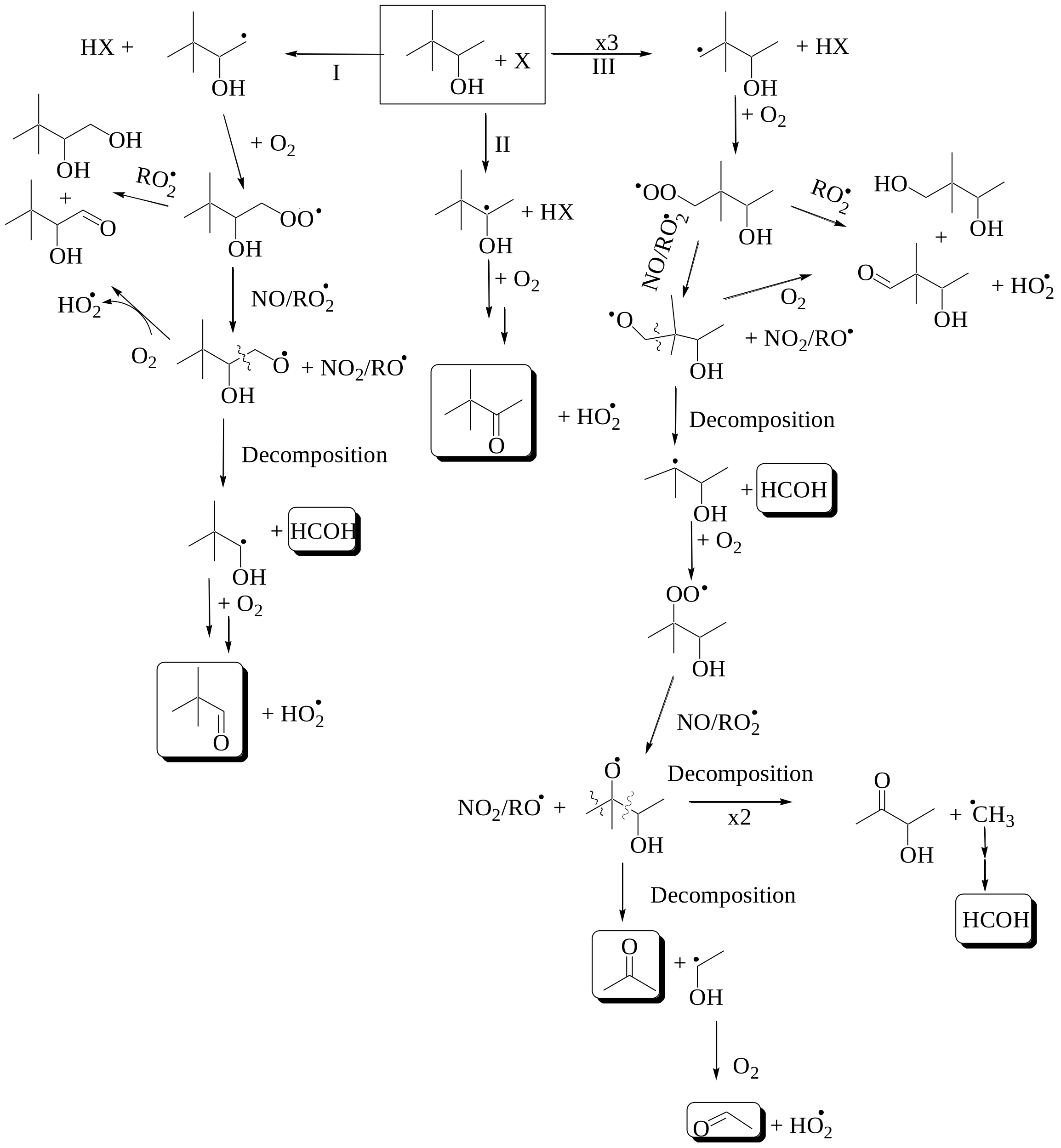

Fig. 8: Reaction mechanism for the degradation of 3,3DM2ButOH with X (Cl atom, OH and NO_3 radical). Mechanism to form carbonyl compounds. Compounds marked with solid line are positively identified. Compounds marked with shaded lines are not positively identified.