



1 **1. Introduction**

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

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

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

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

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

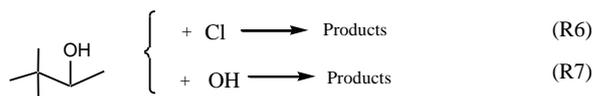
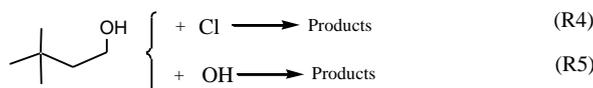
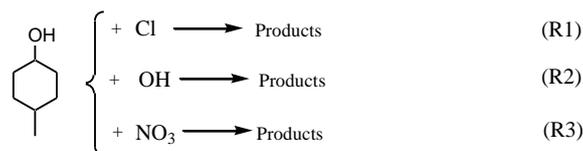


1 are also necessary to better understand the general reactivity of alcohols in the atmosphere since the reactions with
2 this radical are a source of OH during the night-time (Finlayson-Pitts and Pitts, 2000).
3 Although in the last years some studies about reactivity of large alcohols have been made (Andersen et al. 2010;
4 Ballesteros et al., 2007; Calvert et al, 2011; Hurley et al., 2009; Moreno et al., 2012, 2014, Mellouki et al, 2015)
5 the kinetic and mechanistic database is still scarce. In the case of the 3,3-dimethyl-1-butanol and 3,3-dimethyl-2-
6 butanol (derives from 1-butanol, 2-butanol) there is a lack of information regarding the diurnal reactivity (Moreno
7 et al., 2014; Mellouki et al., 2015). Regarding to cyclic alcohols, only data concerning the reactivity of chlorine
8 atoms and OH radicals for cyclohexanol (Bradley et al., 2001; Ceacero-Vega et al., 2012) and OH for
9 cyclopentanol (Wallington et al., 1988) have been reported.
10 Therefore, in the present work, the study of gas phase reactions of some Methyl Saturated Alcohols (MSA): E-4-
11 methylcyclohexanol (4MCHexOH), 3,3-dimethyl-1-butanol (3,3DM1ButOH) and 3,3-dimethyl-2-butanol
12 (3,3DM2ButOH) with the main atmospheric oxidants has been done in order to complete the kinetic and
13 mechanism database, to improve our knowledge of the atmospheric chemistry of alcohols in special saturated
14 alcohols, and to assess a chemical's environmental impact.

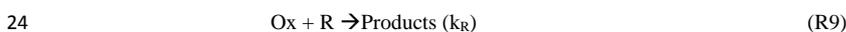
15 2. Experimental Section

16 2.1 Kinetic experiments

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



19
20 Rate coefficients were determined using a relative rate method. This method relies on the assumption that the
21 organic compound (MSA) and the reference compound (R), are removed solely by their reactions with the oxidants
22 (Ox: OH, NO₃ radicals and Cl atoms):



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

27



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

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 . The value of k_{MSA} can therefore be obtained if the rate coefficient k_R of the reference compound is known.

Kinetic measurements were performed at room temperature (~ 298 K) and atmospheric pressure (~ 720 Torr) by employing two experimental set-ups: All kinetic experiments, for the Cl and OH reactions, were performed using a 50 L Pyrex® glass reaction chamber with a White cell that allowed a long pathlength up to 200 m coupled to a FTIR spectrometer (Thermo Nicolet 5700) equipped with a KBr beam splitter and liquid nitrogen-cooled MCT detector, as a detection technique. Typically, for each spectrum, 60 interferograms were co-added over 98 s and approximately 30–40 spectra were recorded per kinetic experiment with a spectral resolution of 1 cm^{-1} . A spectral subtraction procedure was used to derive the concentrations of reactant and reference compounds at time $t=0$ and time t . Chlorine atoms were obtained by photolysis of Cl_2 at a wavelength of 360 nm using 8 actinic lamps. OH radicals were produced by photolysis of Methyl nitrite, CH_3ONO , in the presence of NO in air. CH_3ONO was synthesized in the laboratory as described elsewhere (Taylor et al., 1980).

The reaction of NO_3 with 4MCHexOH was studied using a bigger reactor, a 150 L or 500 L Teflon® in order to minimize the wall deposition and dilution effects of the consecutive additions of N_2O_5 . 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) was used. Samples were collected by exposing a 50/30 mm DVB/CAR/PDMS Solid Phase Micro Extraction fiber (SPME, SUPELCO) for 5 min during the reaction and then thermally desorbed for 15 min at 250°C in the heated GC injection port. A capillary column ($30 \text{ m} \times 0.3 \text{ mm id} \times 1.0 \text{ mm film thickness}$, Tracsil TRB-1701, Teknokroma) was used to separate the compounds. The chromatographic conditions used for the analysis were as follows: injector, 250°C ; interface, 250°C ; oven initial temperature, 40°C for 4 min; ramp, $30^\circ\text{C min}^{-1}$ to 120°C , held for 6 min, second ramp, $30^\circ\text{C min}^{-1}$ to 200°C , held for 3 min. 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 photo degradation 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, 3–5 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 a number of 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



1 The product study was carried out at room temperature (~ 298 K) employing the two detection set-ups mentioned
2 above, FTIR at a pressure of ($\sim 720 \pm 1$) Torr of synthetic air and SPME/GC-TOFMS at atmospheric pressure.
3 During the reaction process in the 50 L Pyrex® glass chamber, the identification of products was made using the
4 FTIR analysis but, at the same time, a sample was taken and analyzed in the SPME/GC-TOFMS system. In
5 addition, independent experiments using SPME/GC-TOFMS technique in a 150/500 L Teflon® reactor were
6 developed. Products analyses were carried out using the same procedure as for the kinetic experiments, without
7 the reference compound, and employing synthetic air as bath gas. In this occasion the heating of the oven was
8 changed slightly in order to get a better separation and to detect the products generated. The temperature ramps of
9 the oven employed in the chromatograph were: 40 °C for 4 min; ramp, 25 °C min⁻¹ to 120 °C, held for 10 min,
10 second ramp, 25 °C min⁻¹ to 200 °C, held for 4 min.

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

15 For the SPME/GC-TOFMS experiments, the NIST webbook (<https://webbook.nist.gov/chemistry/>) and the mass
16 spectra database of the instrument were used to identify the products. Calibrated FTIR spectra and SPME/GC-
17 TOFMS chromatograms of authentic samples were used in those case where the product is commercially available.
18 The yields of the reaction products were estimated from the slopes of plots of the concentration of formed product
19 versus the amounts of MSA ($\Delta[\text{MSA}]$) consumed. To obtain the yield in percentage of carbon, the yield obtained
20 is multiplied by 100 and by the ratio of carbons between the product and the MSA from which it comes.

21 Sometimes, where important loss of reaction product could be taken on by reaction of the oxidant and by photolytic
22 process, the concentration of product was corrected using the formulism of Tuazon et al. (1986) (see S1 in
23 supplementary material). Range concentrations of reactants employed were as follows: 2-14 ppm of MSA, 8-31
24 ppm of Cl₂, 12-57 ppm of NO, 19-66 ppm of methylnitrite and 6-36 ppm of N₂O₅.

25
26 Chemicals used were as follows: 4MCHexOH (97 %, Aldrich), 3,3DM1ButOH and 3,3DM2ButOH (98 %,
27 Aldrich); 1-butene, propene, 2-methyl-2-butanol, isopropanol, 2-methylpropene, 4-methylcyclohexanone and
28 cyclohexene (≥ 99 %, Aldrich), 2-ethyl-1-hexanol (≥ 99 %, Fluka), 1-butanol (99.8 %, Aldrich), 3,3-
29 dimethylbutanal (95 %, Aldrich) and 3,3-dimethyl-2-butanone (98 %, Aldrich), NO (99 %, Praxair), Cl₂ (> 99.8
30 %, Praxair), synthetic Air (Praxair Ultrahigh purity 99.999 %), N₂ (99.999 %, Praxair). For N₂O₅ synthesis, N₂O₄
31 were used (> 99.5 %) from Fluka, P₂O₅ (98 %, such as desiccant) from Fluka and O₃ synthesized by a generator
32 model TRCE-5000, 5 g_{O₃} h⁻¹ OZOGAS.

33

34 **3. Results and discussion**

35

36 **3.1 Kinetic study**

37 Preliminary test experiments indicated that dark heterogeneous reactions and photolytic losses of MSA can be
38 considered negligible ($k \sim 10^{-6}$ s⁻¹). As mentioned above, the kinetic study of Cl atoms and OH radical with the
39 organics was carried out at room temperature (~ 298 K) and at ~ 720 Torr of N₂ gas and synthetic air respectively.



1 Nitrate radical experiments were performed at room temperature and atmospheric pressure using N₂ gas in a 500
2 L Teflon bag and employing the system SPME/GC-TOFMS. A number of injections of the unreacted mixture
3 were carried out in order to determine the associated precision with the sampling method to be used in the error
4 analysis (Brauers and Finlayson-Pitts, 1997). The standard deviations (σ) were as follows: 3.7 % for 4MCHexOH,
5 1.7 % for 1-butanol and 3.5 % for 2-ethyl-1-hexanol. Figure 1 shows examples of the kinetic data plotted according
6 to Eq (1) for the reactions of MSA with different atmospheric oxidants.

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

11 Rate coefficients of reference compounds, for Cl atom reactions (in 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹ units) were: 2-
12 methylpropene (3.40 ± 0.28), 1-butene (3.38 ± 0.48), (Ezzel et al., 2002) and propene (2.23 ± 0.31) (Ceacero-Vega
13 et al., 2009); for OH radical reactions (in 10⁻¹¹ cm³ molecule⁻¹ s⁻¹ units): propene (2.66 ± 0.40), (Atkinson and
14 Aschman, 1989), cyclohexene (6.77 ± 1.69) (Atkinson and Arey, 2003), isopropanol (0.51 ± 0.008) (IUPAC
15 www.iupac-kinetic.ch.cam.ac.uk) and 2-methyl-2-butanol (0.36 ± 0.06) (Jiménez et al., 2005). And for NO₃
16 reactions (in 10⁻¹⁵ cm³ molecule⁻¹ s⁻¹ units): 1-butanol (3.14 ± 0.97) and 2-ethyl-1-hexanol (2.93 ± 0.46) (Gallego-
17 Iniesta et al., 2010). The experimental data are shown in Table 1. The rate coefficients obtained in this work are
18 the first kinetic data reported for these MSA, therefore results obtained can not be compared with literature values.
19

20 As it has been mentioned in introduction section, it is well established that the gas-phase reaction mechanism of
21 saturated organic compounds (alkanes, alcohols, ethers, etc) with the atmospheric oxidants (Cl atoms, OH and
22 NO₃ radicals) are initiated “via” hydrogen atom abstraction from the organic compound to form a stable molecule
23 and an alkyl radical (Finlayson-Pitts and Pitts, 2000; Atkinson and Arey, 2003; Calvert et al., 2011; Ziemann and
24 Atkinson, 2012). The presence of hydroxyl group in saturated alcohols implies two types of hydrogens that can be
25 subtracted, hydrogen bonded to carbon (C-H) of main chain or to an alkyl substituent and hydrogen bonded to
26 oxygen of hydroxyl substituent (-OH). Two literature reviews about reactivity of saturated alcohols (Calvert et al.,
27 2011; Mellouki et al., 2015) conclude that:

28 1- The reactions of aliphatic alcohols with atmospheric oxidants proceed mainly by H atom abstraction from
29 various C-H groups in the alkyl chain being the H atom abstraction from the O-H negligible.

30 2-Rate coefficients for the reactions of Cl, OH and NO₃ are higher than those of the corresponding alkanes due to
31 the activating effect of the OH group. This effect is extended over about 4 carbon atoms (Nelson et al., 1990). As
32 will be discussed later, the activating effect of the OH group is depending on the oxidant.

33 3-The attack percentage of radical to the different sites of alcohol (α , β , γ and δ) depends on the oxidants, structure
34 of saturated alcohol, type, numbers of substituents and temperature. (Moreno et al., 2012, 2014; McGillen et al.,
35 2013, 2016).

36 Taking into account these remarks, the reactivity of the Methyl Saturated Alcohols studied in this work will be
37 analyzed and discussed comparing the rate coefficients of these MSA with: a) the different oxidants, b) the same
38 oxidant with different alcohols and c) with the rate coefficients of their homologous alkanes. The data used to
39 compare are summarized in Table S1 in supplementary material.

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



1 1-The trend in the reactivity of MSA in relation to the different oxidants is the same that the observed for other
2 saturated alcohols: $k_{\text{Cl}} (k \sim 10^{-10}) > k_{\text{OH}} (k \sim 10^{-11}) \gg k_{\text{NO}_3} (k \sim 10^{-15})$, (k in $\text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$ units). This behaviour
3 could be explained for the different size and electronic properties of each oxidant that make the Cl atom the most
4 reactive (value of k in the limit of collision) but also less selective than OH and NO_3 radicals.

5 2- The rate coefficient for the reaction of 4MCHexOH with Cl atoms is similar to the rate coefficient of its
6 homologous alkane (E-1,4-dimethylcyclohexane): $k_{4\text{MCHexOH}} = 37.1 \times 10^{-11} \cong k_{\text{E-1,4-dimethylcyclohexane}} = 36.3 \times 10^{-11}$. In
7 the case of the reaction with OH radical, the rate coefficient of 4MCHexOH is 1.6 times higher than E-1,4-
8 dimethylcyclohexane (see data of Table S1). These results show that the activating effect of hydroxyl group is less
9 important for the Cl reactions due to the high reactivity of Cl atoms. In the case of 3,3-dimethylbutanols, there is
10 not data of rate coefficients of the homologous alkanes for comparison, but in general it is observed a large
11 influence of the structure of the organic compound on the reactivity (SAR Method, Kwok and Atkinson, 1995).
12 This effect has been quantified for each of the functional groups of an organic compound. So, in the case of alcohols
13 the factor of hydroxyl group, is 1.18 for the reaction with Cl, 2.35 for the reactions with OH (Calvert et al., 2011)
14 and 18 for the reactions of the nitrate radical (Kerducci et al., 2014).

15 3-Rate coefficients obtained for these three MSA with the same oxidant are of the same order that the
16 corresponding to other saturated alcohols (See data of Table S1). The activating effect of the length chain in the
17 reactivity is being more marked in the Cl reaction than in the case of OH and NO_3 reactions. Again, this behavior
18 could be explained by the different order of reactivity between the oxidants. For Cl atom, more reactive but less
19 selective, an increase of chain implies more hydrogens available to be subtracted and therefore an increase of the
20 rate coefficient. However, the OH and NO_3 radicals, less reactive and more selective, the attack to subtract the
21 hydrogen will be carried out in a specific place, so an increase of the chain doesn't affect the reactivity
22 significantly.

23 In the reactions of OH and NO_3 radicals, the presence of activating substituents or the formation of a more stable
24 radical after the H-abstraction could have a major effect in the reactivity than in the case of Cl atom reaction. This
25 last assumption could also explain the minor rate coefficient observed for the Cl reaction with secondary alcohols
26 (2-propanol, 2-butanol, 2-pentanol, 3-methyl-2-butanol and 3,3-dimethyl-2-butanol) instead of primary alcohols
27 (1-propanol, 1-butanol, 1-pentanol, 3-methyl-1-butanol and 3,3-dimethyl-1-butanol) (see Table S1).

28 All that could imply a different mechanism in the hydrogen abstraction process for Cl atoms versus OH and NO_3
29 radicals. Nelson et al. (1990) and Smith and Ravishankara (2002) indicate the possible formation of an
30 intermediate adduct between the OH radical and the oxygen of the hydroxyl group via hydrogen bond that will
31 imply a specific orientation. Theoretical studies found in bibliography show this different hydrogen-abstraction
32 process in the reaction of saturated alcohols with Cl atoms (Garzon et al., 2006) and OH (Moc and Simmie, 2010).
33 These differences in the mechanism for each oxidant should be observed in the analysis of the reaction products
34 implying different yields and products distributions.

35

36 3.1.1 Estimation of rate coefficients

37

38 In order to estimate the rate coefficient of the reactions of organic compounds with the atmospheric oxidants,
39 multitude of methods have been proposed (Vereecken et al. 2018). The most popular and used is the SAR method



1 develop initially by Kwok and Atkinson (1995) to estimate the rate coefficients at room temperature for gas phase
2 reactions of OH radical. This method has been updated for OH reactions (Jenkin et al., 2018) and extended to NO₃
3 (Kerducci et al., 2010, 2014) and Cl (Calvert et al., 2011; Poutsma 2013) reactions. The EPA (United States
4 Environmental Protection Agency) has developed the EPI Suite™-Estimation Program Interface that allows to
5 estimate the rate coefficient for the reaction of OH radical and organic compounds using the AOPWIN v1.92
6 program. In this work the rate coefficients of MSA with the three oxidants have been estimated using the SAR
7 method and are shown in Table 2.

8 The values of estimated rate coefficients agree with experimental data with ratios k_{exp}/k_{SAR} between 0.8 and 1.27,
9 except for the case of 3,3DM1ButOH and NO₃ radical with a k_{exp}/k_{SAR} of 3.29. In general, the SAR method applied
10 to alcohols predicts better rate coefficients for Cl atoms and OH radical than for NO₃ radical, especially for primary
11 alcohols. It is important to note that the kinetic database for the NO₃ reactions is more limited than for Cl and OH
12 reactions, so the estimated rate coefficient for NO₃ radical should be treated with caution (Calver et al., 2011).

13 It is known that organic compounds which reacts in the same way with different atmospheric oxidants, present a
14 correlation between their rate coefficients. In this sense, along the years, different correlations have been proposed
15 that allow to estimate the unknown rate coefficient when the other one is known (Wayne, 1991, 2000; Atkinson,
16 1994; Calvert et al., 2011; Gallego-Iniesta et al., 2014). Correlations $\log k_{Cl} - \log k_{OH}$ and $\log k_{NO_3} - \log k_{OH}$ have been
17 built for a set of alcohols, ethers and saturated alcohols by Calvert et al., (2011) obtaining the following
18 relationships:

$$19 \quad \log(k_{Cl}/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}) = 0.634 \times \log(k_{OH}/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}) - 2.71 \quad (r^2=0.72) \quad (2)$$

$$20 \quad \log(k_{NO_3}/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}) = 1.11 \times \log(k_{OH}/\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}) - 2.42 \quad (r^2=0.66) \quad (3)$$

21 These equations have been used to estimate the rate coefficients of the reactions of MSA with Cl and nitrate radical
22 using the experimental rate coefficients measured in this work for OH reactions. The results obtained are (k in cm^3
23 $\text{molecule}^{-1} \text{s}^{-1}$ units): $k_{Cl-3,3DM1ButOH} = 14.3 \times 10^{-11}$; $k_{Cl-3,3DM2ButOH} = 21.4 \times 10^{-11}$; $k_{Cl-4MCHexOH} = 31.2 \times 10^{-11}$; k_{NO_3-}
24 $3,3DM1ButOH} = 1.22 \times 10^{-15}$; $k_{NO_3-3,3DM2ButOH} = 2.48 \times 10^{-15}$ and $k_{NO_3-4MCHexOH} = 4.81 \times 10^{-15}$. This estimation method
25 obtains slightly better results than SAR for NO₃ reactions. The better prediction for the NO₃ rate coefficients than
26 for those of Cl could be due to the fact that the mechanism for Cl atom reactions is different than for OH radical
27 reaction. Assumption that must be satisfied to apply the correlation. It is important to indicate that in the case of
28 Cl reactions, other effects as thermochemistry and the polar effect, must be considered to estimate rate coefficients
29 for hydrogen abstraction reactions (Poutsma, 2013).

30

31 3.2 Product and Mechanistic Study

32

33 A product study of 4MCHexOH, 3,3DM1ButOH and 3,3DM2ButOH with chlorine atoms in absence/presence of
34 NO_x, hydroxyl and nitrate radicals has been performed by employing the two experimental set-ups mentioned
35 above (FTIR and SPME/CG-TOFMS). IR absorption bands of HCl, CO₂, CO, HNO₃, N₂O, NO₂, HCOOH, HCOH,
36 ClNO, ClNO₂ and CH₃NO₃ were observed in the FTIR experiments. Bands that are due to the decomposition of
37 the precursors employed (Cl₂, CH₃NO₂ and N₂O₅) and in some cases due to heterogeneous reactions with the walls
38 of the gas cell. The formation of O₃ and N₂O₅ have also been observed at large reaction time for reactions of MSA
39 and Cl atoms in presence of NO, due to the high concentration of the NO₂ in the medium of reaction. Quantitative



1 analysis was carried out by linear subtraction of a spectrum's absorption bands and peak areas of GC
2 chromatograms with the use of calibrated spectra and reference chromatograms.
3 The experimental conditions and yields of the main products formed in the reactions of MSA and analyzed by
4 FTIR and SPME/GC-TOFMS techniques are given in Tables 3-6. Yields could be affected to large errors
5 associated with the SPME sampling method and due to the presence of interfering IR band absorptions, mainly
6 associated with precursors of OH and NO₃ radicals or by nitrated compounds formed.

8 3.2.1 - 4MCHexOH

9
10 E-4-methylcyclohexanone was identified in the reaction with Cl, Cl+NO, OH + NO and NO₃ + NO₂. An example
11 of the product spectra obtained in the FTIR system is shown in Fig. 2. Formation of the E-4-methylcyclohexanone
12 was confirmed by introducing a sample of the commercial product (spectrum (e)). A set of experiments using the
13 SPME/GC-TOFMS system were also carried out for the reaction of 4MCHexOH with Cl atoms and OH and NO₃
14 radicals. An example of the chromatogram obtained for the reaction of 4MCHexOH with chlorine atoms is shown
15 of Fig. 3. In all the studied reactions, formation of a product peak at 10.35 min was observed. This peak (B) on
16 Fig. 3 was assigned to E-4-methylcyclohexanone and confirmed by comparing with the retention time and MS
17 spectrum of a commercial sample. In the reactions with chlorine atoms (absence/presence of NO_x) and OH radical
18 two additional peaks at 19.80 min (C) and 20.25 min (D) were observed.

19 The time-concentration profiles of 4MCHexOH and E-4-methylcyclohexanone obtained by FTIR for the reaction
20 with chlorine atoms in the presence of NO_x is shown on Fig. S1. The concentrations of E-4-methylcyclohexanone,
21 corrected according to Eq (S1), (S2) and (S3), were plotted versus the amounts of 4MCHexOH consumed in order
22 to obtain the yield of 4-methylcyclohexanone from the slope. An example of the obtained plots is shown in Fig.
23 4. Yields, Y (%), of E-4-methylcyclohexanone obtained in all experiments are listed in Table 3. Based on the
24 average yield of E-4-methylcyclohexanone, the carbon balance is below to 50 % for reactions with Cl and OH
25 radical and ~ 60 % for NO₃.

26 Residuals spectra after subtraction of E-4-methylcyclohexanone show IR absorption bands compatible with the
27 presence of hydroxy carbonyl compounds (~1750, 1720, 1060 cm⁻¹) and nitrated organic compounds (RONO₂ ~
28 1260, 1264 and 862 cm⁻¹, and/or ROONO₂ ~ 1720, 1300 and 760 cm⁻¹) (See residual spectra, Fig. S2 in
29 supplementary material). The amount of nitrated compounds was estimated using the average integrated absorption
30 coefficient of 1.2x10⁻¹⁷ cm molecule⁻¹ of similar compounds corresponding to the IR band 1260-1305 cm⁻¹ (Tuazon
31 and Atkinson,1990). The calculated yields of RONO₂ were 20 % and 60 % for Cl + NO and NO₃ reactions
32 respectively. A yield of 10 % of nitrated compounds was estimated for the reaction with OH radical. This lower
33 yield could be due to fact that the NO_x, present in the reaction medium, reacts faster with the CH₃O• (formed in
34 the reaction of CH₃ONO with NO) than others alcoxyradicals. Table 6 shows a summary of the average yields of
35 reaction products quantified for 4MCHexOH.

36 Considering the products detected here and the detected in the study of Bradley et al., (2001) relative to
37 cyclohexanol with OH radical reactions, a degradation mechanism for 4MCHexOH with the atmospheric oxidants
38 has been proposed. Figure 5A shows the paths to explain the formation of carbonyl or hydroxy carbonyl



1 compounds and Figure 5B shows an example path to explain the formation of nitrated organic compounds
2 (ROONO₂ and RONO₂). Similar compounds could be formed by routes II-IV. The abstraction of Hydrogen atoms
3 in α -position with respect to alcohols group (channel I) followed by the addition of oxygen, formation of a peroxy
4 radical and fast decomposition of this radical explains the formation of E-4-methylcyclohexanone. Based on the
5 yield obtained for E-4-methylcyclohexanone for each oxidant (See Table 6), this channel represents ~ 25-30 %,
6 ~40 % and ~60 % of reaction mechanism of 4McHexOH with Cl and Cl+NO, OH and NO₃ reaction, respectively.
7 Percentages are two times higher than SAR method prediction in the case of Cl atoms reactions and 1.3 times
8 higher for OH and NO₃ reactions. It should be noted that these data should be taken with caution, since they could
9 imply many sources of error.

10 Apart from E-4-methylcyclohexanone, other carbonyl and hydroxy carbonyl compounds could be formed by
11 routes II, III, and IV. The presence of this kind of compounds have been observed in the reactions with Cl and OH.
12 According to the EI MS spectra (Fig. S3, supplementary material) of peaks (C) and (D) shown in Fig. 3, an
13 assignation to 2-hydroxy-5-methyl-cyclohexanone and 5-hydroxy-2-methyl-cyclohexanone or 3-methyl-1,6-
14 hexanedial respectively has been proposed. However, according to the atmospheric reactivity (Finlayson and Pitts,
15 2000; Calvert et al., 2011; Ziemann and Atkinson, 2012) and the study of Bradley et al., (2001), the compound
16 that would be expected is 3-methyl-1,6-hexanedial, which comes from the decomposition of the alkoxy radical
17 formed in route II. However, confirmation was not possible since these compounds are not commercially available.
18 The detection of HCOH about 9 % in the reaction with Cl atoms indicates that the elimination of the methyl group
19 in route IV is minor.

20 In the case of nitrate radical only E-4-methylcyclohexanone was detected as carbonyl compound, suggesting that
21 the route I may be the dominant pathway for this radical. The large difference between the yields of E-4-
22 methylcyclohexanone obtained using the SPME/GC-TOFMS system (~75 %) or the FTIR (35 %) could be due to
23 the influence of the volume of reactor (150 or 500 liters in the SPME/GC-TOFMS compared to 50 L of the FTIR),
24 which favors the formation of carbonyl compounds instead of nitrates in the case of using a large volume reactor.
25 This fact is more pronounced in the case of reactions with nitrate radical since, due to the precursor used, the
26 reaction occurs in the presence of high concentrations of NO₂ favoring the addition of NO₂ to peroxy or alkoxy
27 radicals (See Figure 5B). Taking into account, the yields of E-4-methylcyclohexanone and the nitrated compounds
28 for the NO₃ reaction using FTIR, a total carbon balance of 100% is obtained (See Table 6).

29

30 **3.2.2 -3,3DM1ButOH**

31

32 Following the same procedure as above, 3,3-dimethylbutanal was identified as the main reaction product in the
33 reaction of 3,3DM1ButOH with the three atmospheric oxidants. Figure S4A shows the FTIR spectra obtained for
34 the reactions of 3,3DM1ButOH with Cl, Cl + NO, OH and NO₃ after subtraction.

35 Residual FTIR spectra after subtraction of 3,3-dimethylbutanal (Fig. S4B), the SPME/GC-TOFMS
36 chromatograms (Fig. S5) and EI MS spectra (Fig. S6), show that other reaction products as carbonyl, hydroxy
37 carbonyl and nitrated compounds are formed. These compounds could be HCOH, 2,2-dimethylpropanal,
38 glycolaldehyde, acetone, peroxy-3,3-dimethyl-butyryl nitrate (P33DMBN) (CH₃)₃CCH₂C(O)OONO₂. These
39 compounds can be formed as primary products (see Fig. 6 below) or secondary products from degradation of 3,3-



1 dimethylbutanal (See Fig. S7). The SPME/GC-TOFMS chromatograms show common peaks for the three
2 oxidants, but the number of peaks and its distribution are very different, especially for OH reactions. In the case
3 of SPME/GC-TOFMS system a set of experiment using Field Ionization was carried out in order to help us to
4 establish the identification of reaction products.

5 Time-concentration profiles of 3,3DM1ButOH, 3,3-dimethylbutanal and those reaction products positively
6 identified by FTIR analysis were made in order to establish if the profiles correspond with a primary or secondary
7 reaction products. An example of the reactions with chlorine atoms in the absence and presence of NO_x is shown
8 on Fig. 6, observing that in the absence of NO the profiles of acetone and formaldehyde show a typical profile of
9 secondary reactions. This behaviour is only clearly observed in the profile of nitrated compounds in the reaction
10 of Cl atoms in the presence of NO (Fig. 6B).

11 Commercial sample of 3,3-dimethylbutanal was used to estimate yields in both experimental systems. These yields
12 are shown in the Table 4. The yields of acetone and HCOH were calculated using a FTIR reference spectrum of
13 commercial sample and FTIR reference spectra from Eurochamp database ([https://data.eurochamp.org/data-
14 access/spectra/](https://data.eurochamp.org/data-access/spectra/)), respectively. A FTIR reference spectrum of 2-methylpropanal (from this same database) has been
15 used to estimate the yield of 2,2-dimethylpropanal.

16 The amounts of 3,3-dimethylbutanal formed were corrected by its reaction with Cl atoms, and OH and NO₃ radicals
17 as is described previously using the rate coefficients available in bibliography or for reactions of structurally
18 compounds similar (see footnote Table 4). Estimated yields of formaldehyde, acetone, 2,2-dimethylpropanal and
19 nitrated compounds are summarized in Table 6 together with an average yield of 3,3-dimethylbutanal. The higher
20 yield of nitrated compounds in the reaction of 3,3DM1ButOH with nitrate radical could indicate secondary
21 products (See Fig. S7). A total of carbon yield (nitrated compounds have not been accounted) of ~70 %, ~85 %
22 and ~40 % have been justified for Cl (absence and presence of NO), OH and NO₃ reaction respectively, but must
23 be noted that there are reaction products that could not possibly be quantified as carbonyl or hydroxy carbonyl
24 compounds in the Cl atoms reactions and primary nitrated compounds in the Cl + NO and NO₃ radical reactions.

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

31 Estimated yields of 3,3-dimethylbutanal (formed by H-Abstraction in α position of 3,3DM1BuOH) for Cl and OH
32 reaction (~40-43) %, ~57 %) are very similar to the one predicted by the SAR method (40 % and 66 %
33 respectively). In the case of NO₃ radical a large difference between both yields are observed (33 % estimated in
34 this work, 85 % predicted by SAR method). This discrepancy could be explained by the fact that the SAR method
35 (Kerducci et al., 2014) underestimates the attack of NO₃ in β -position, because it does not consider the possible
36 effect of the alcohol group jointed to -CH₂. That is, the SAR method considers the effect of -CH₂ and perhaps must



1 also consider the factor of $-\text{CH}_2\text{OH}$. This could also explain the large difference observed between the estimated
2 and measured rate coefficient as was shown in Table 2. On the other hand, as discussed above, the volume of the
3 reactor can also have influence to formation of 3,3-dimethylbutanal.

4 According with the yields of the products quantified and/or observed in the SPME/GC-TOFMS chromatograms,
5 it can be concluded that for OH radical reaction, the route I (attack in α position) seems to be the main reaction
6 route. For Cl atoms the three routes can occur although the I and III (attack in δ position, especially evident in
7 presence of NO) seem to be the major routes. The major yield of HCOH, acetone and 2,2-dimethylpropanal in the
8 reactions of Cl atoms in presence of NO versus Cl atoms reactions in absence of NO could indicate that in absence
9 of NO the self peroxy radical reaction “via” molecular channel (formation of carbonyl and dihydroxy organic
10 compounds) is more favored than “via” radical channel, with formation of two alkoxy radicals. For NO_3 radical,
11 routes I and II (attack in β position) with formation of nitrated compounds apart from 3,3-dimethylbutanal seem
12 to be the unique routes.

13 3.2.3 -3,3DM2ButOH

14 The analysis of FTIR spectra obtained for the reactions of 3,3DM2ButOH with Cl atoms, in presence and absence
15 of NO, OH radical and NO_3 radical shows the formation of 3,3-dimethyl-2-butanone as a main product (see Fig.
16 S8). Others compounds such as HCOH, acetone, 2,2-dimethylpropanal and Peroxy Acetyl Nitrate (PAN), have
17 also been observed. The residual FTIR spectra after subtraction of all known IR bands again shows the presence
18 of carbonyl compounds (IR bands absorption in the range of $1820\text{-}1700\text{ cm}^{-1}$); hydroxy compounds ($1060\text{-}1040$
19 cm^{-1}) in the reaction of Cl atoms in absence of NO and also nitrated compounds (RONO_2 ; 1650 , $1305\text{-}1260$, 890
20 cm^{-1}) in the reaction of Cl + NO and NO_3 radical (Fig. S8C). The presence in the residual FTIR spectra of a IR
21 absorption band around 1800 cm^{-1} in the reaction of Cl atoms at large reaction times could be due to the formation
22 of chlorine compounds by reaction of 3,3dimethyl-2-butanone with Cl_2 (Ren et al., 2018) or the formation of cyclic
23 compounds as hydrofurans. The SPME/GC-TOFMS chromatograms and MS spectra (Fig. S9 and S10) confirm
24 other reaction products apart from 3,3-dimethyl-2-butanone in the case of Cl, Cl + NO and NO_3 reactions. Only
25 one peak is observed in chromatograms obtained for the OH reactions.

26 Acetone, HCOH, 2,2-dimethylpropanal, nitrated compounds and acetaldehyde have also been quantified. Plots of
27 concentration versus time show, typical profiles of secondary reactions for HCOH, acetone and nitrated
28 compounds in the reactions of Cl with NO (See Fig. S11). These compounds could also be formed by degradation
29 of 3,3dimethyl-2-butanone (See Fig. S12). The estimated yields of 3,3-dimethyl-2-butanone for all individual
30 experiments are given in Table 5, where the measured concentrations have again been corrected for secondary
31 reactions. Table 6 summarizes the yields of all quantified products.

32 A total carbon yields of $\sim 60\%$, 112% , 95% and 58% have been accounted for Cl (absence and presence of NO),
33 OH and NO_3 reaction, respectively (See Table 6). It is important to note that in the case of the reaction of Cl atoms
34 without NO where the total carbon yield is lower than 100% there are many reaction products that could not be
35 quantified, as carbonyl and/or hydroxy carbonyl compounds. In the reaction of NO_3 radical, due to our



1 experimental conditions, an important amount of primary nitrated compounds is expected to be formed (See Fig.
2 S8C).

3 A mechanism of hydrogen abstraction in different positions of the carbon chain has been proposed for the reaction
4 of 3,3DM2ButOH with Cl, OH and NO₃ reactions. The mechanism is shown in Figure 8. Table S3, in
5 supplementary material, shows a summary of the reaction products proposed in this mechanism observed or
6 tentatively identified in the reactions of 3,3DM2ButOH with the atmospheric oxidants.

7 Yields of 3,3-dimethyl-2-butanone obtained in this work imply a percentage of attack of the oxidant in β position
8 (route I of mechanism) of: 43 % and 44 %, in the case of chlorine atom; 81 % for OH radical and 58 % for NO₃
9 radical. Percentages are very similar to that predicted by SAR method except for NO₃ radical. High NO₂
10 concentration present in the reaction would highly favor the formation of nitrated compounds versus 3,3-dimethyl-
11 2-butanone. The main reaction products observed in the reaction of Cl atoms in presence of NO (3,3-dimethyl-2-
12 butanone, HCOH, 2,2-dimethylpropanal, acetone, acetaldehyde) confirm that the Cl atoms could attack in other
13 sites with an important percentage. Based on the estimated yield of acetone, the attack in δ position with abstraction
14 of hydrogen of methyl groups (route III) could be ~58 %, and based on the estimated yield for 2,2-
15 dimethylpropanal, the route (I) could account with a 10 %. These data agree with the SAR predictions for Cl atom
16 reactions. On the other hand, the major yields of acetone, HCOH, 2,2-dimethylpropanal and acetaldehyde in the
17 reaction of Cl atoms in presence of NO than in absence of NO could indicate that in presence of NO the peroxy
18 self-reactions (RO₂) “via” molecular channel is negligible. The lower yield (17 %) estimated by acetaldehyde
19 versus 58% of its coproduct (acetone) is due to its fast degradation by Cl atoms reaction with formation of Peroxy
20 acetyl nitrates as it has been observed in the FTIR experiments (See Fig. S8B).

21 4. Atmospheric Implications

22 The pollutants in the atmosphere, could create serious environmental problems such a photochemical smog, acid
23 rain and degradation of the ozone layer (Finlayson-Pitts and Pitts, 2000). So, it is important to evaluate the
24 parameters that help us to know the impact of the presence of these compounds in the atmosphere. These
25 parameters are, the time that such compounds remains in the atmosphere, the Global Warming Potential (GWP)
26 and their degradation mechanisms in order to estimate the impact of products formed.

27 The first important parameter of the environmental impact of an Oxygenated Volatile Organic Compounds in the
28 atmosphere, is the global lifetime, τ_{global} , which considers all the degradation processes which could suffer these
29 compounds in the Troposphere. This parameter can be obtained from the sum of the individual sink processes such
30 as reactions initiated by OH and NO₃ radicals, Cl atoms, and O₃ molecules; photolysis and dry and wet deposition,
31 Eq (4):

$$32 \tau_{global} = \left[\frac{1}{\tau_{OH}} + \frac{1}{\tau_{Cl}} + \frac{1}{\tau_{NO_3}} + \frac{1}{\tau_{O_3}} + \frac{1}{\tau_{photolysis}} + \frac{1}{\tau_{other\ processes}} \right]^{-1} \quad (4)$$

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

$$35 \tau = \frac{1}{k_{Ox}[Ox]} \quad (5)$$



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

$$9 \quad \tau_{wet} = \frac{H_{atm}}{v_{pm}RTk_H} \quad (6)$$

10 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
11 average precipitation rate for Ciudad Real (Spain) (402 mm/year) (www.aemet.es), R is the gases constant and T
12 is the temperature considered as constant and equal to 298 K. In bibliography there is only data of the constant of
13 Henry for 3,3DM2ButOH (5.6×10^{-1} mol m^{-3} Pa $^{-1}$) (Sander, 2015). Comparing the available data for similar
14 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
15 and 3,3DM1ButOH respectively.

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

21 The global lifetime of the three alcohols is of the order of ~ 1-2 days, indicating that these compounds will probably
22 be degraded near their sources. These global lifetimes also indicate that MSA have not a significant contribution
23 to radiative forcing of climate change (Mellouki et al., 2015), which is supported through the estimation of their
24 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}
25 for 4MCHexOH, 3,3DM1ButOH and 3,3DM2ButOH respectively, which are very low. So, these compounds
26 will only have an important impact in the troposphere at local or regional level.

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

37 **5. Conclusions**

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



1 -The kinetic and product study confirms that the atmospheric degradation mechanism for methyl saturated
2 alcohols and possibly for the rest of unstudied saturated alcohols, proceeds mainly by abstraction of the hydrogen
3 atom bonded to carbon instead hydrogen atoms bonded to oxygen atom of the alcohol group.

4 -Chlorine atoms subtract any type of hydrogen from saturated alcohols with a high percentage, compared to the
5 hydroxyl radical and the nitrate radical. OH and NO₃ radicals subtract mainly the hydrogen in the α position, if
6 the saturated alcohols are secondary. For primary alcohols the hydrogen in α position is subtracted almost
7 exclusively for the OH radical and α and β position to 50 % in the case of the NO₃ radical, extending the inductive
8 effect to α and β position. Therefore, for the reaction of NO₃ radical, it is necessary to update the SAR method
9 developed by Kerducci et al., (2010, 2014) to take into account the effect of the OH group in β position, (-
10 CH₂OH) and not only the effect in α position (-OH).

11 -Theoretical ab-initio studies should be done in order to obtain more information about how the type of radical
12 determine the distribution of reaction products specially in reactions that occurs by an initial hydrogen
13 abstraction, that is the case of primary methyl saturated alcohols.

14 -The atmospheric conditions determine the reaction mechanism and therefore the reaction products obtained in
15 the degradation of methyl saturated alcohols. So, in polluted environments with high concentrations of NO_x, the
16 peroxyradicals (RO₂·) reacts mainly with NO to form the alkoxy radical instead of other peroxyradical. In these
17 conditions, nitrated organic compounds (RONO₂) are formed apart from polyfunctional organic compounds.
18 Also, when the concentration of NO₂ is higher than NO concentration, ozone is formed. In clean atmosphere, as
19 in the case of the experiments of Cl atoms in absence of NO, the reaction products are different because of
20 peroxyradicals (RO₂·) react mainly “via” self-reaction molecular channel instead to “via” self-reaction radical
21 channel.

22 -The uncounted polyfunctional could explain the low carbon balance obtained in Cl or NO₃ reaction. However,
23 the carbon balance must be taken with caution since the calculated yields have a high degree of uncertainty.

24 -Calculated lifetimes for methylsaturated alcohols (the order of ~1 day) imply that these compounds are pollutants
25 at local-regional scale, but it is also important to indicate that MSA are sources of stable nitrated compounds
26 (ROONO₂), depending on environment conditions, that can travel to large distance from their sources
27 contributing to form ozone in clean areas, for example in forest or rural areas.

28 -The main products coming from the degradation of the methyl saturated alcohols, aldehydes and ketones,
29 develop a very important secondary chemistry with formation of products of special relevance such as the PAN
30 observed in the degradation of 3,3-dimethyl-2-butanol. Also, more experiments should be done using other
31 detection techniques, in order to evaluate the formation of SOA because it is well known that polyfunctional
32 organic compounds are important SOA precursors.

33 -From the environmental point of view, this work shows that the degradation of methyl saturated alcohols is an
34 important source of pollutants in the atmosphere with greater or lesser impact depending on the environmental
35 conditions and the quantities of saturated alcohols present in the atmosphere. Therefore, the use of saturated



1 alcohols as additives in the production of biofuels should be controlled, avoiding that a bad handling involves
2 high concentrations of these alcohols in the atmosphere.

3 -Rate coefficients and reaction products measured in this work are the first available data, so this work contributes
4 to a better understanding of atmospheric chemistry of oxygenated compounds expanding the kinetic and
5 mechanistic data base and additionally, contributes to develop or to improve prediction models that help us to
6 avoid or mitigate the effects of climate change or air quality.

7 **6. Supplementary material.**

8 Attached in a separated file.

9 **7. Author contribution**

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

15 **8. Competing interests**

16 The authors declare that they have no conflict of interest.

17 **9. Acknowledgment**

18 The authors would like to thank the financial support provided by Junta de Comunidades de Castilla-La Mancha
19 (Projects SBPLY/17/180501/000522).

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1 **Table 1.** Rate coefficients for the reactions of a series of MSA with Cl atoms and OH and NO₃ radicals at 298 K
 2 and ~ 720 Torr of pressure. Rate coefficients, k, in cm³ molecule⁻¹ s⁻¹.

Reaction	Reference	(k _{Cl} ±2σ)/10 ⁻¹⁰	k _{Cl} ±2σ /10 ⁻¹⁰	$\bar{k}_{Cl} \pm 2\sigma / 10^{-10}$
3,3DM1ButOH + Cl	1-butene	2.89 ± 0.45	2.72 ± 0.44	2.70 ± 0.55
		2.68 ± 0.43		
		2.58 ± 0.43		
	Propene	2.63 ± 0.34	2.68 ± 0.35	
		2.70 ± 0.35		
		2.71 ± 0.35		
3,3DM2ButOH + Cl	1-butene	1.42 ± 0.31	1.32 ± 0.30	1.21 ± 0.37
		1.17 ± 0.29		
		1.38 ± 0.31		
	Propene	1.08 ± 0.22	1.15 ± 0.23	
		1.12 ± 0.22		
		1.26 ± 0.24		
4MCHexOH + Cl	2-methylpropene	3.69 ± 0.31	3.66 ± 0.31	3.71 ± 0.53
		3.95 ± 0.31		
		3.35 ± 0.32		
	1-butene	3.86 ± 0.52	3.84 ± 0.52	
		3.78 ± 0.52		
		3.90 ± 0.53		
Reaction	Reference	(k _{OH} ±2σ)/10 ⁻¹²	k _{OH} ±2σ /10 ⁻¹²	$\bar{k}_{OH} \pm 2\sigma / 10^{-12}$
3,3DM1BuOH + OH	Isopropanol	5.09 ± 0.21	5.53 ± 0.36	5.57 ± 0.66
		5.78 ± 0.47		
		5.72 ± 0.40		
	2-methyl-2-butanol	5.85 ± 0.82	5.80 ± 0.82	
		5.71 ± 0.81		
		5.86 ± 0.83		
3,3DM2BuOH + OH	Isopropanol	11.90 ± 0.46	10.77 ± 0.44	10.51 ± 0.81
		10.46 ± 0.44		
		9.95 ± 0.42		
	2-methyl-2-butanol	8.70 ± 0.98	9.18 ± 1.00	
		10.64 ± 1.08		
		8.21 ± 0.95		
4MCHexOH + OH	Propene	17.1 ± 3.2	19.2 ± 3.5	19.1 ± 6.5
		20.2 ± 3.6		
		20.4 ± 3.5		
	Cyclohexene	18.2 ± 8.8	18.2 ± 8.8	
		18.4 ± 8.8		
		18.0 ± 8.8		
Reaction	Reference	(k _{NO3} ±2σ)/10 ⁻¹⁵	k _{NO3} ±2σ /10 ⁻¹⁵	$\bar{k}_{NO3} \pm 2\sigma / 10^{-15}$
4MCHexOH + NO ₃	1-butanol	3.39 ± 1.11	3.86 ± 1.25	2.92 ± 1.38
		5.70 ± 1.82		
		2.51 ± 0.81		
	2-ethyl-1-hexanol	2.08 ± 0.72	2.51 ± 0.83	
		2.93 ± 0.96		
		2.51 ± 0.82		



1 The uncertainties for rate coefficients of MSA were calculated from the uncertainty of slope of plots and the
2 uncertainty of the reference by using the propagation of uncertainties. The average value of the rate coefficient
3 obtained with different reference compounds and its associated error were obtained by weighted average. 2σ
4 statistical errors were obtained from the regression analysis (σ_{slope}) and the quoted error in the value of the rate
5 coefficient for the reference compound (σ_{kR}).

6



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

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

4 ^aEstimated using method described by Calvert et al., 2011

5 ^bData obtained in this work

6 ^cEstimated using AOPWIN v1.92

7 ^dEstimated using method described by Kerducci et al., 2010, 2014

8 ^eData obtained by Moreno et al., 2014

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

MSA	Oxidants	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		
		5	7	10	-	33.4±0.6	FTIR		
	NO ₃ ^c	1	3	6	-	56.8±11.4	SPME/GC- TOFMS ^e	58.0±23.5	75
		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		

3 ^a Rate coefficient k (in $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ unit) used to correct the concentration of E-4-methylcyclohexanone by
 4 loss with the reaction of Cl atoms was of 11.2×10^{-11} (data of 2-methylcyclohexanone and Cl atoms (Herath et al.,
 5 2018)). Photolysis rate constant estimated for E-4-methylcyclohexanone under our experimental conditions. $k_p = 5$
 6 $\times 10^{-5} \text{s}^{-1}$

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

10 ^c Rate coefficient k (in $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ unit) used to correct the concentration of E-4-methylcyclohexanone by
 11 loss with the reaction of NO₃ radical was of 2.28×10^{-16} (estimated using SAR method, Kerducci et al., 2014)

12 ^d Indicated errors are the associated error to the slope of plots obtained in the least square analysis

13 ^e Experiment using a Teflon gas Bag of 150 or 500 L

14 ^f Standard deviations 1σ

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

MSA	Oxidant	Exp	[MSA] (ppm)	[Precursor] (ppm)	[NO] (ppm)	Carbonyl compound Yield (%)	Technique	Average ^g (%)	SAR Yield (%)
3,3DM1ButOH	Cl ^a	1	11	24	-	40.3±0.2 41.8±4.6	FTIR 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 34.7±4.4	FTIR SPME/GC- TOFMS ^d	43.3±17.7	40
		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 40.8±2.7	FTIR 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		
		1	11	36	-	29.2±0.5 53.9 ^h	FTIR SPME/GC- TOFMS ^d		
	2	11	32	-	26.5±1.6	FTIR			

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

6 ^b Rate coefficient k (in $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ unit) used to correct the concentration of 3,3-dimethylbutanal by loss
 7 with the reaction of OH radical was of 2.73×10^{-11} (Aschmann et al., 2010). Photolysis rate constant estimated for
 8 3,3-dimethylbutanal under our experimental conditions. $k_p = 1 \times 10^{-4} \text{s}^{-1}$

9 ^c Rate coefficient k (in $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ unit) used to correct the concentration of 3,3-dimethylbutanal by loss
 10 with the reaction of NO₃ radical was of 1.27×10^{-14} (D'Anna, 2001).

11 ^d Experiment using a FTIR Gas Cell of 50 L

12 ^e Experiment using a Teflon gas Bag of 150 or 500 L

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

14 ^g Standard deviations 1σ

15 ^h Yield estimated using only one data

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

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

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

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

9 ^cNo corrected

10 ^dExperiment using a FTIR Gas Cell of 50 L

11 ^eExperiment using a Teflon gas Bag of 150 or 500 L

12 ^fStandard deviations 1σ

13 ^gIndicated errors are the associated error to the slope of plots obtained in the least square analysis

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

Product	MSA			
	4MCHexOH			
	Cl	Cl + NO	OH	NO ₃
E-4-methylcyclohexanone¹	25.2 ± 1.9	29.5 ± 0.7	40.2 ± 5.4	58.0 ± 23.5
HCOH²	9	-	-	-
Nitrated compounds	-	20	10	60
Total Carbon	34	50	50	~100
	3,3DM1ButOH			
	Cl	Cl + NO	OH	NO ₃
3,3-dimethylbutanal¹	39.4 ± 15.0	43.3 ± 17.7	62.2 ± 15.0	36.2 ± 14.6
HCOH²	10	22	-	-
2,2-dimethylpropanal²	22	8	23	-
Acetone²	5	17	-	-
Nitrated compounds	-	40 ⁴	35 ⁵	200 ⁶
Total Carbon³	67	68	85	36
	3,3DM2ButOH			
	Cl	Cl + NO	OH	NO ₃
3,3-dimethyl-2-butanone¹	43.2 ± 1.8	44.2 ± 7.4	80.7 ± 6.5	58.0 ± 10.9
HCOH²	10	64	-	-
2,2-dimethylpropanal²	14	10	14	-
Acetone²	3	58	-	-
Acetaldehyde²	-	17	-	-
Nitrated compounds	-	30	20	120
Total Carbon³	~60	112	94	58

3 ¹Average Tables 3-5; ²Yield obtained in earlier step of reaction.; ³Without accounting nitrated compounds;
 4 ⁴From analysis of the experiment number 3 for the reaction of Cl + NO; ⁵From average of experiments number
 5 2, 3 and 4 for the reaction with OH; ⁶From analysis of the experiments number 1 and 2 for reaction with NO₃.

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

	τ_{OH} (days)	τ_{Cl}^a (days)	τ_{Cl}^b (days)	τ_{NO_3} (days)	τ_{wet} (years)	τ_{global}^a (days)
4MCHexOH	0.61	31.20	0.24	7.93	~2.1	0.55
3,3DM1ButOH	2.08	42.87	0.33	13 ^c	~15.8	1.72
3,3DM2ButOH	1.10	95.65	0.74	6.73 ^c	11.3	0.94

2 ^aDetermined with the 24 hours average of chlorine atoms.

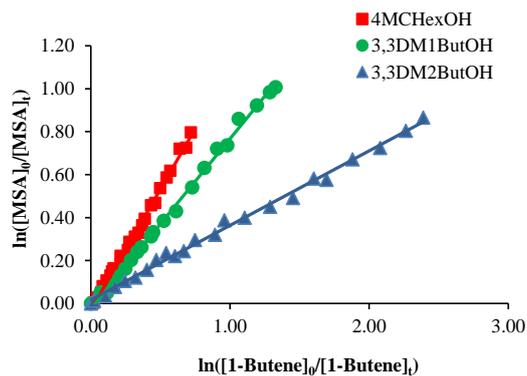
3 ^bDetermined with the peak concentration of chlorine atoms.

4 ^cDetermined using the rate coefficient obtained by Moreno A. et al., 2014.

5

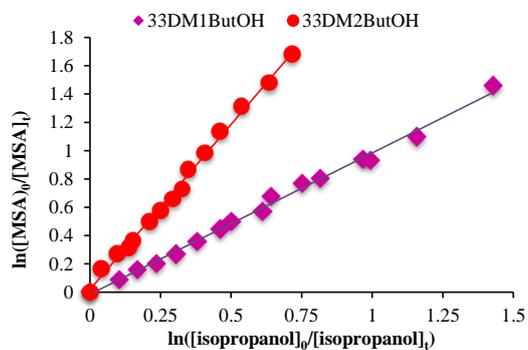


1 A)



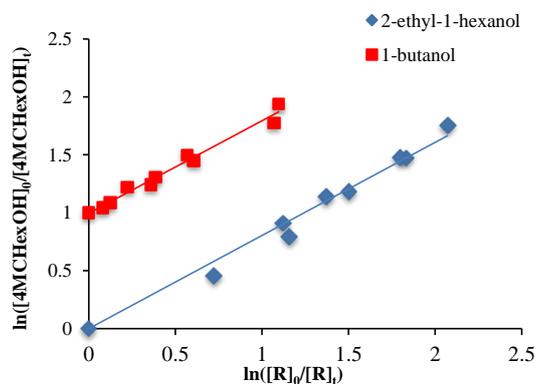
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3 B)



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5 C)

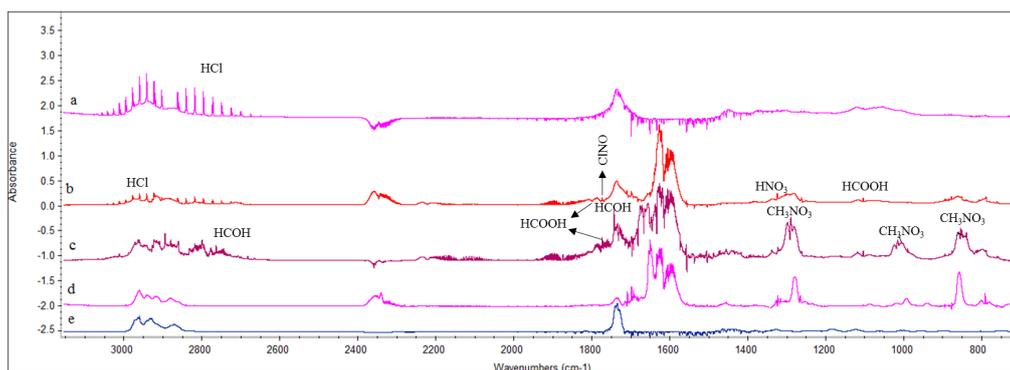


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7 Fig.1: Relative rate plots for the reaction of (A) MSA with chlorine atoms employing 1-butene as a reference
8 compound (B) 3,3-Dimethylbutanols and OH radical with isopropanol as a reference compound and (C)
9 4MCHexOH and NO₃ with two reference compounds. Data for 1-butanol have been vertically displaced for clarity.

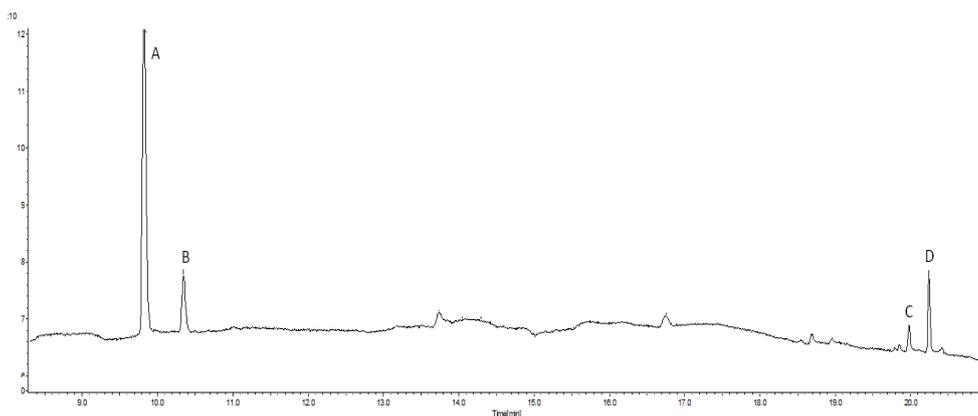


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Fig. 2: Product spectra for reaction of 4MCHexOH with: (a) chlorine atoms at 10 min (x 2 to clarify), (b) chlorine atoms and NO_x at 7 min. (c) OH at 40 min and (d) NO₃ at 32 min. (e) Spectrum of 4-methylcyclohexanona commercial sample.

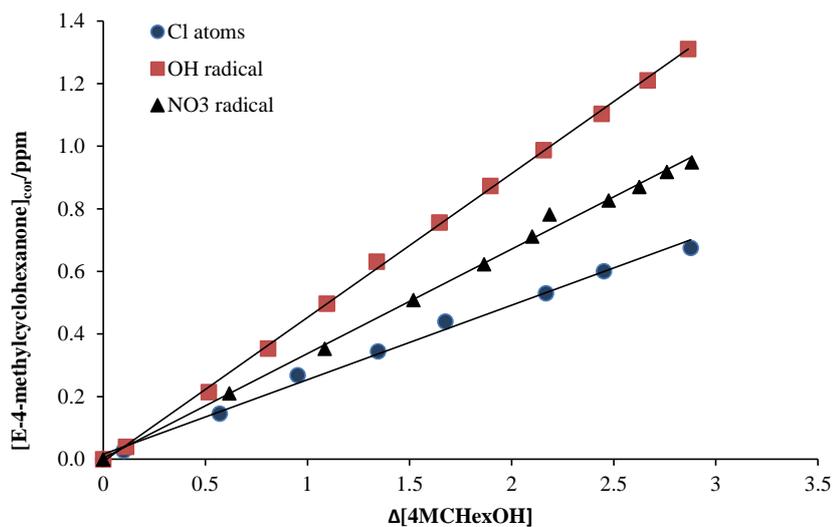


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Fig. 3: SPME/GC-TOFMS chromatogram for the reaction of 4MCHexOH with chlorine atoms after 15 minutes of reaction. Peak (A) 4MCHexOH. Peak (B) E-4-methylcyclohexanone.



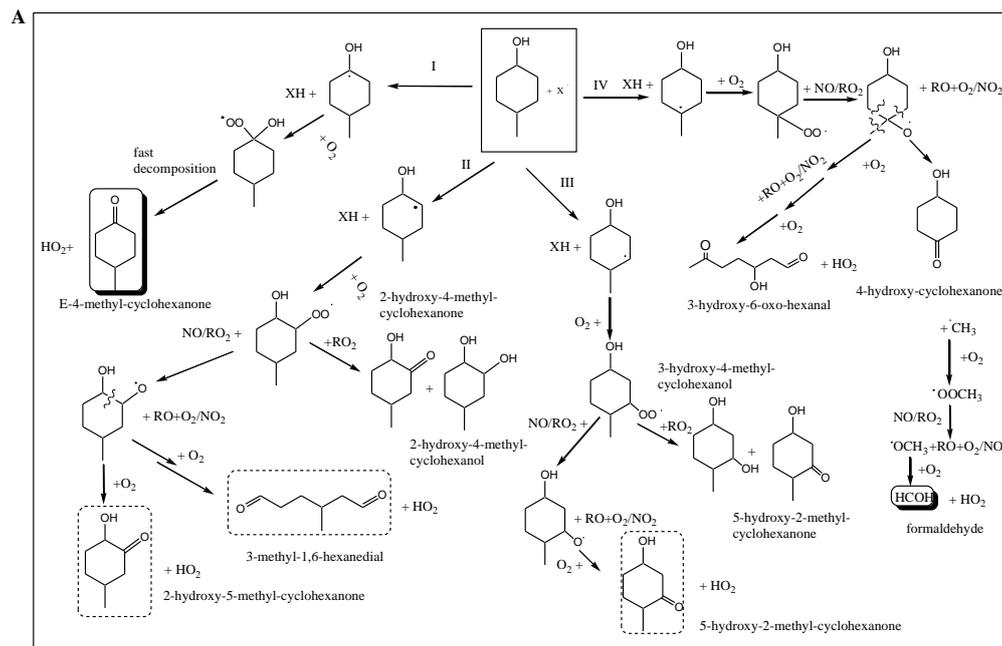
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4 Fig. 4: Plots of corrected concentrations of E-4-methylcyclohexanone against 4MCHexOH consumed for Cl atoms
5 (in absence of NO_x) and OH and NO₃ radical reactions.
6

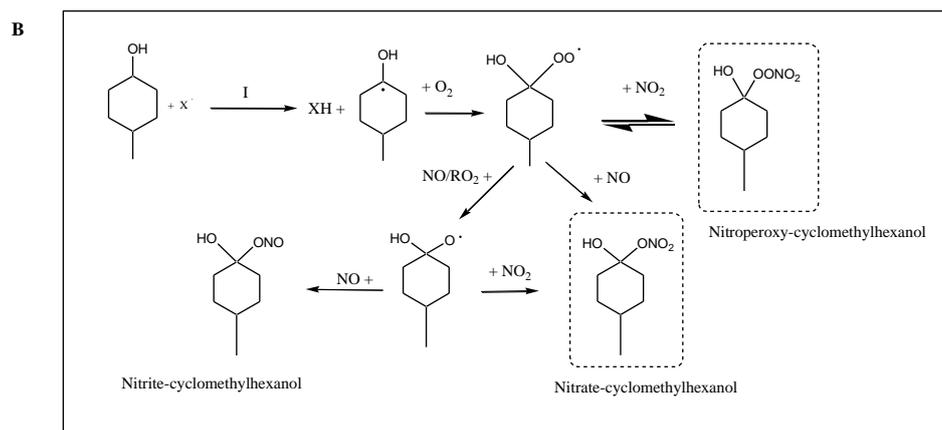


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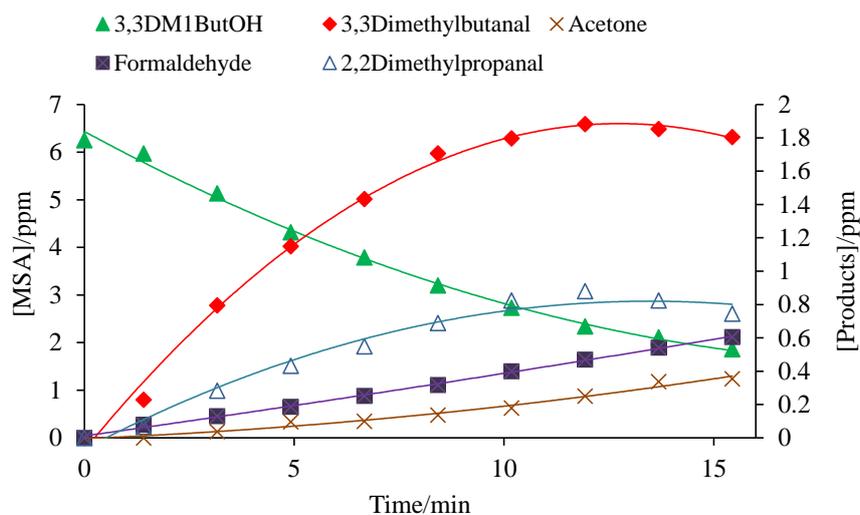


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5 Fig. 5: Reaction mechanism for the degradation of 4MCHexOH with X (Cl atom, OH and NO₃ radicals). (A)
 6 Mechanism for the formation of carbonyl compounds, (B) Mechanism for the formation of nitrated compounds.
 7 Compounds marked with solid line are positively identified. Compounds marked with shaded lines are not
 8 positively identified.

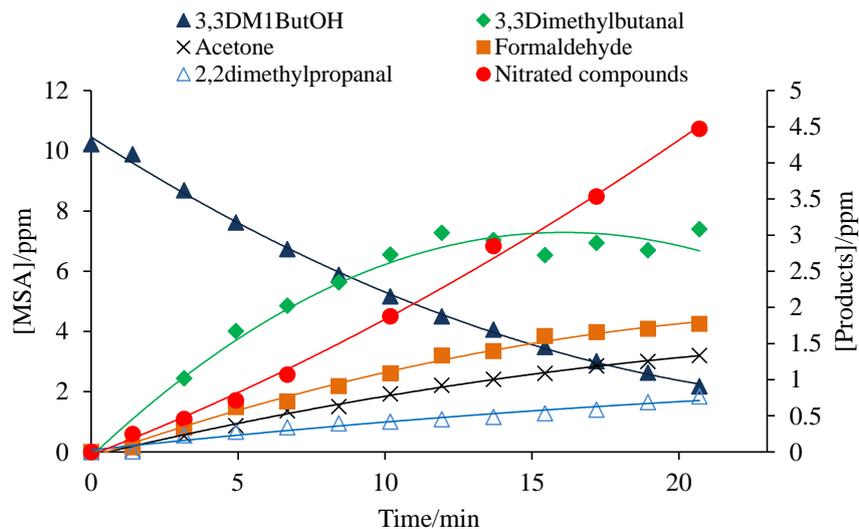


1 A)



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3 B)



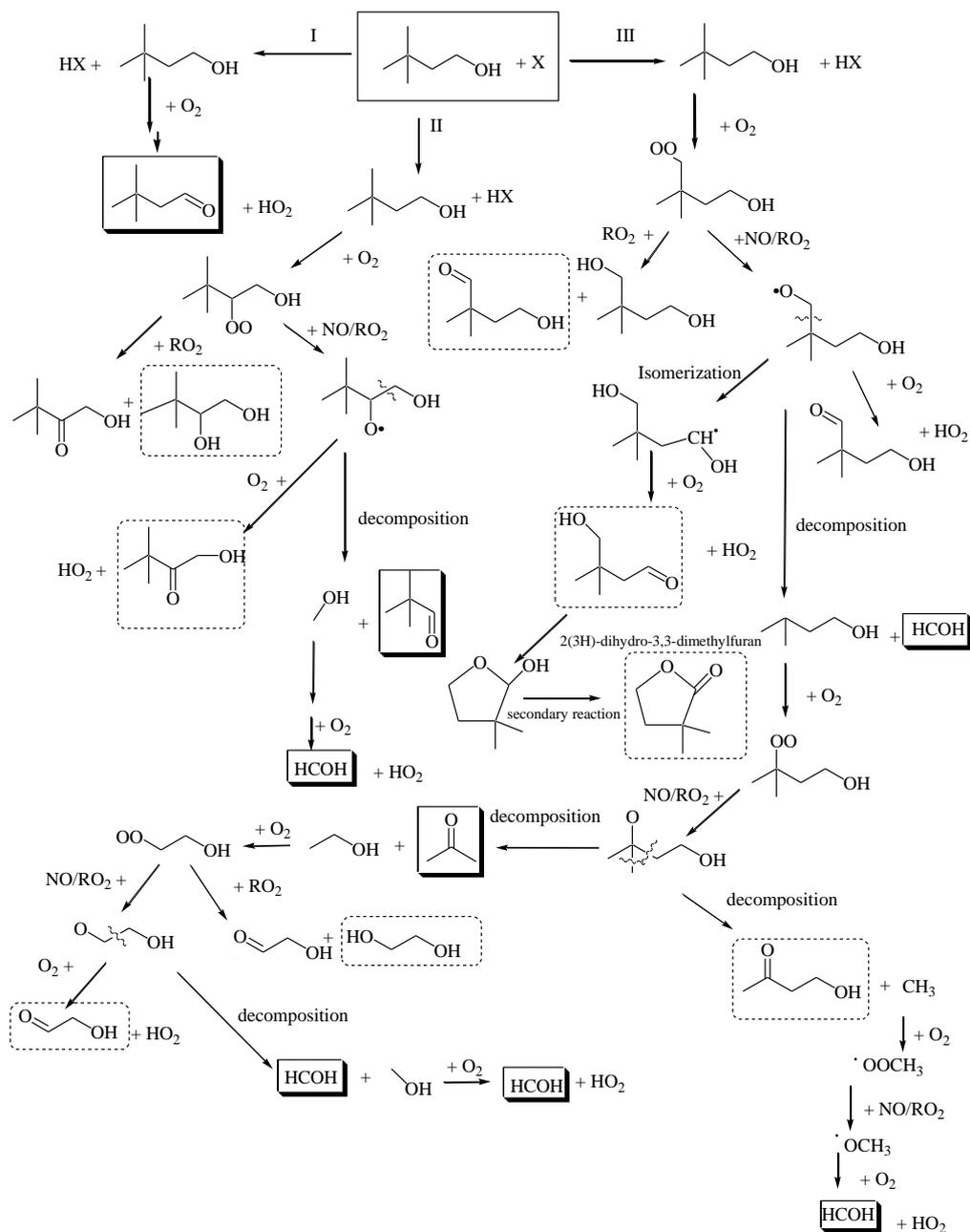
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5 Fig. 6: Concentration-time profiles of MSA and Products for 3,3DM1ButOH with Cl atoms in absence (A) and
6 presence of NO (B).

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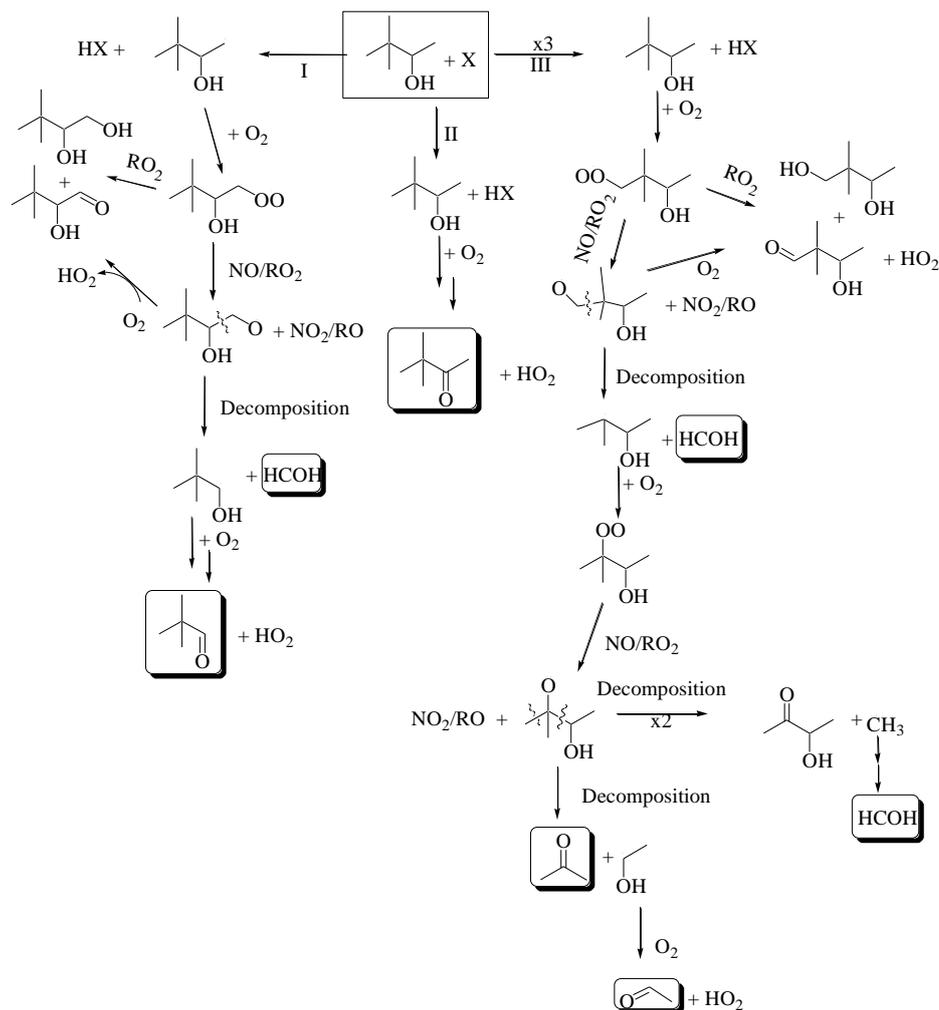
3 Fig. 7: Reaction mechanism for the degradation of 3,3DM1ButOH with X (Cl atom, OH and NO₃ radical).
 4 Mechanism for the formation of carbonyl compounds. Compounds marked with solid line are positively identified.
 5 Compounds marked with shaded lines are not positively identified.

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3 Fig. 8: Reaction mechanism for the degradation of 3,3DM2ButOH with X (Cl atom, OH and NO₃ radical).
 4 Mechanism to form carbonyl compounds. Compounds marked with solid line are positively identified. Compounds
 5 marked with shaded lines are not positively identified.

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