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*Supplement of*

## **Atmospheric fate of a series of saturated alcohols: kinetic and mechanistic study**

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## Supplementary material

### S1. Tuazon formalism

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



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

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

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

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

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

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

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

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

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

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

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

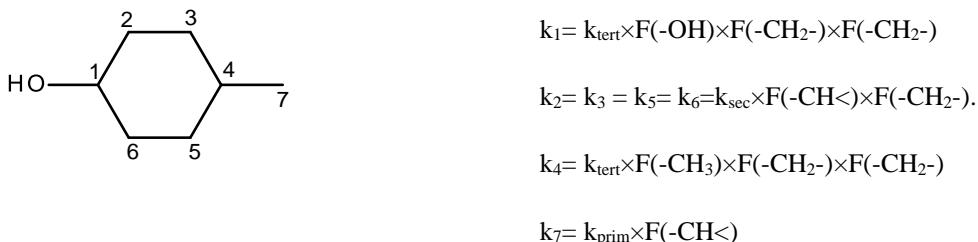
## S2. Structure-Activity Relationship (SAR) method

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

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

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

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



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

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

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

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

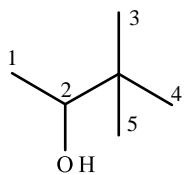


$$k_{3,3\text{DM1ButOH+Cl}} = 2.10 \times 10^{-10} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$$

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

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

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



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

$$k_2 = k_{\text{tert}} \times F(>C<) \times F(-CH_3) \times F(-OH)$$

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

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

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

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

## Tables

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

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

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

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

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

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

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

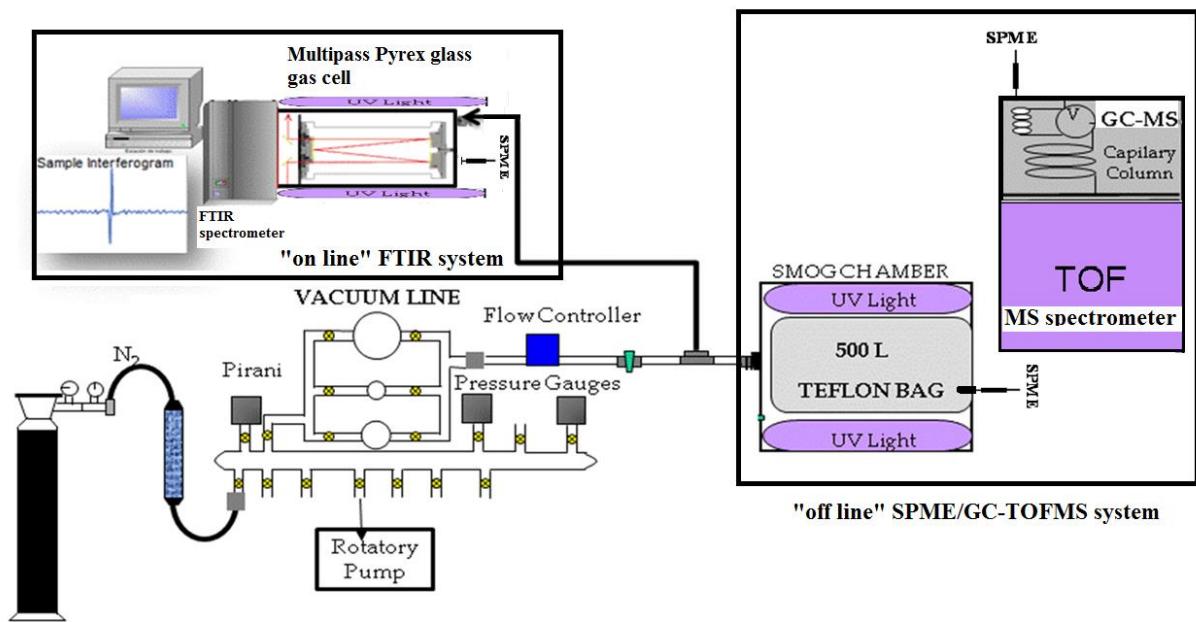
The compounds with X have been positively identified with reference FTIR or MS spectrum. Those that have / have been probably identified through the analysis of the IR bands of the residual spectra and Mass Spectra using as a source of ionization Electron Ionization (EI) and Field Ionization (FI) source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

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

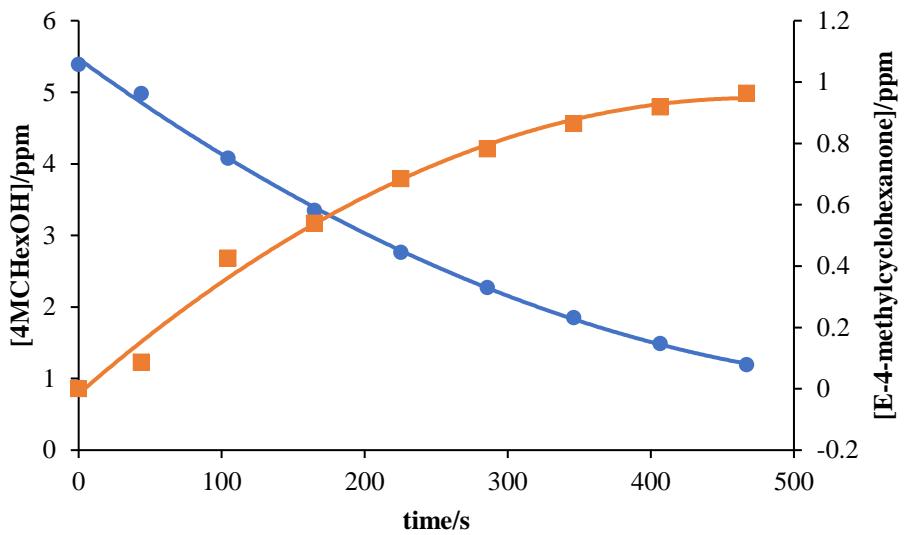
Product propose in the mechanism	FTIR				GC-MS				Retention time (min)
	Cl	Cl + NO	O H	NO <sub>3</sub>	Cl	Cl + NO	OH	NO <sub>3</sub>	
<b>Route I</b>									
3,3-dimethyl-1,2-butanediol	-	-	-	-	-	-	-	-	-
3,3-dimethyl-2-hydroxybutanal	-	-	-	-	-	-	-	-	-
Formaldehyde	X	X	X*	-	-	-	-	-	-
2,2-dimethylpropanal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

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

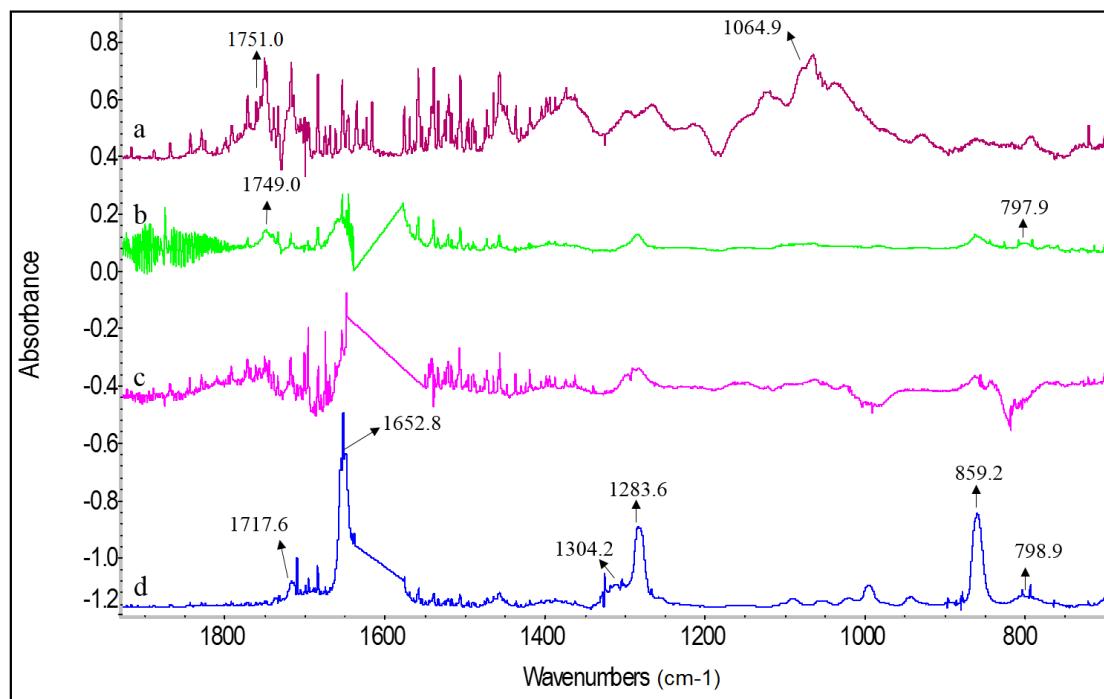
X\* Formaldehyde is a product, but it is also formed by decomposition of the precursor in the reaction with OH radical, and it is not possible to differentiate which comes from the reaction or from the decomposition process.



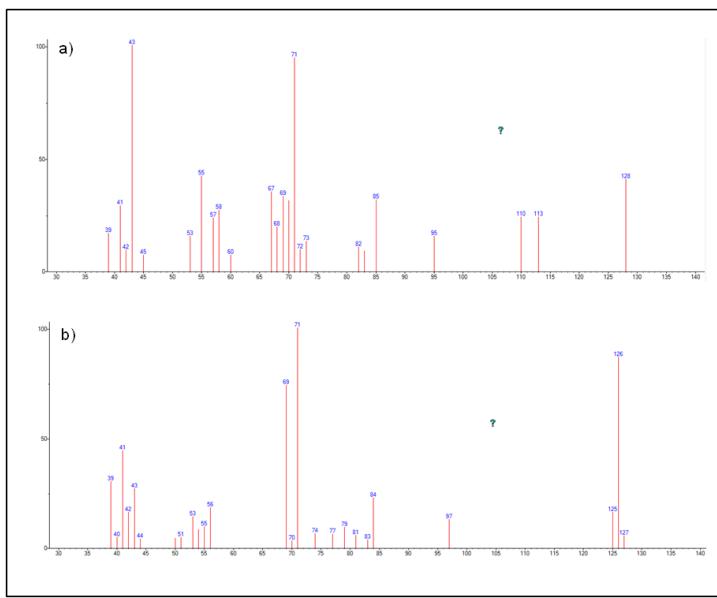
**Fig.S1** Schematic diagram of experimental system: FTIR and SPME/GC-TOFMS.



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

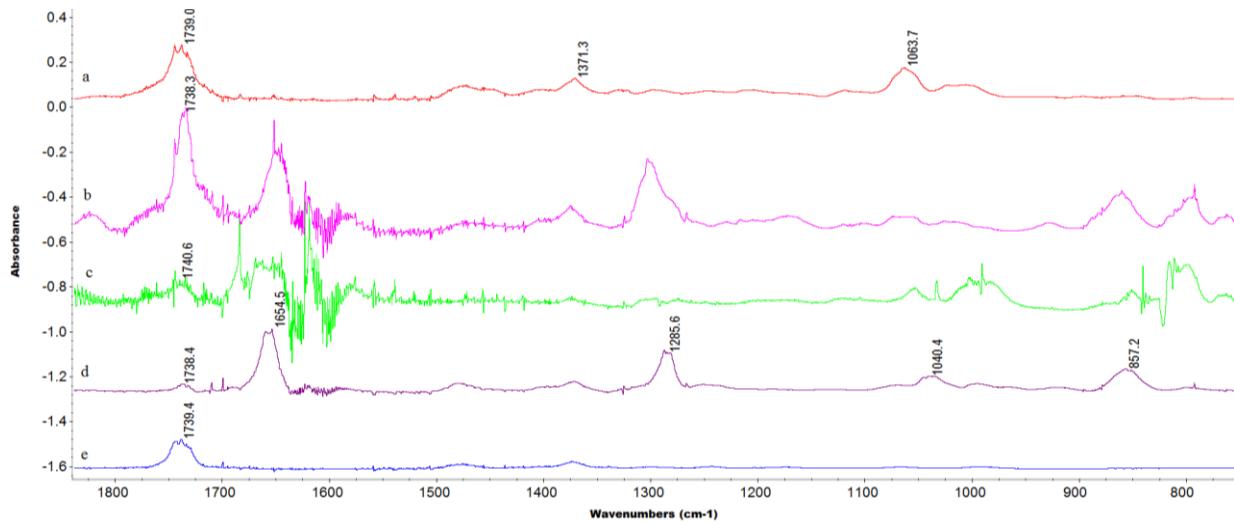


**Fig. S3.** Residual FTIR spectra obtained in the reaction of 4MCHexOH with (a) Cl atoms, (b) OH radicals, (c) Cl atoms in the presence of NO, and (d) NO<sub>3</sub> radicals. The gap in the range of 1650-1590 cm<sup>-1</sup> corresponds to NO<sub>2</sub> absorption.

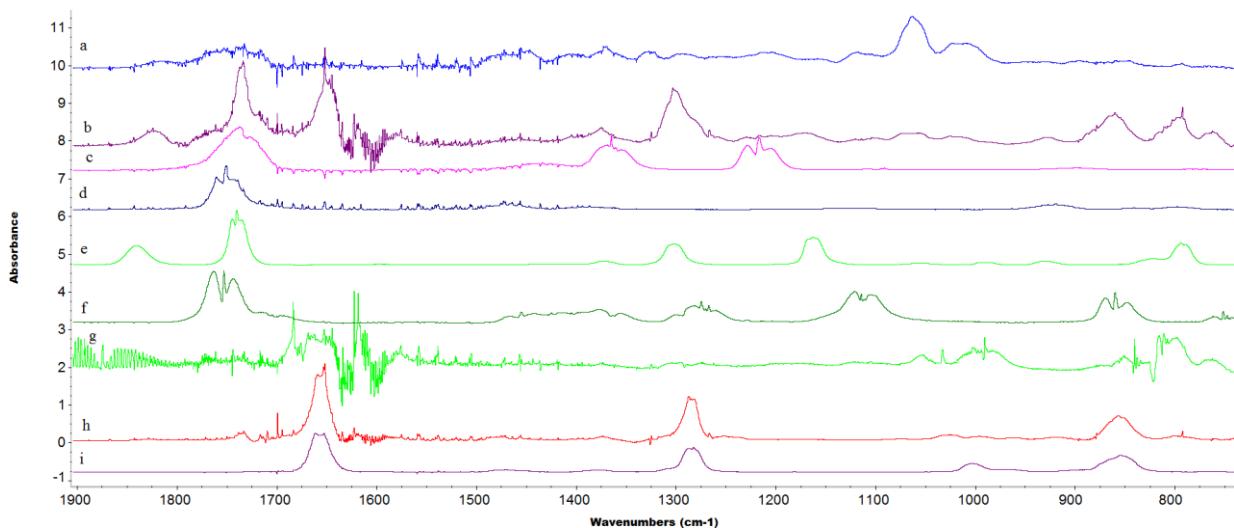


**Fig. S4.** EI MS spectra of peak C (a) and D (b) observed at 20 and 23 min of retention time in the reaction of 4MCHexOH with Cl atoms. Tentatively assigned to 2-hydroxy-5-methyl cyclohexanone, 5-hydroxy-2-methyl-cyclohexanone and or 3-methyl-1,6-hexanodial.

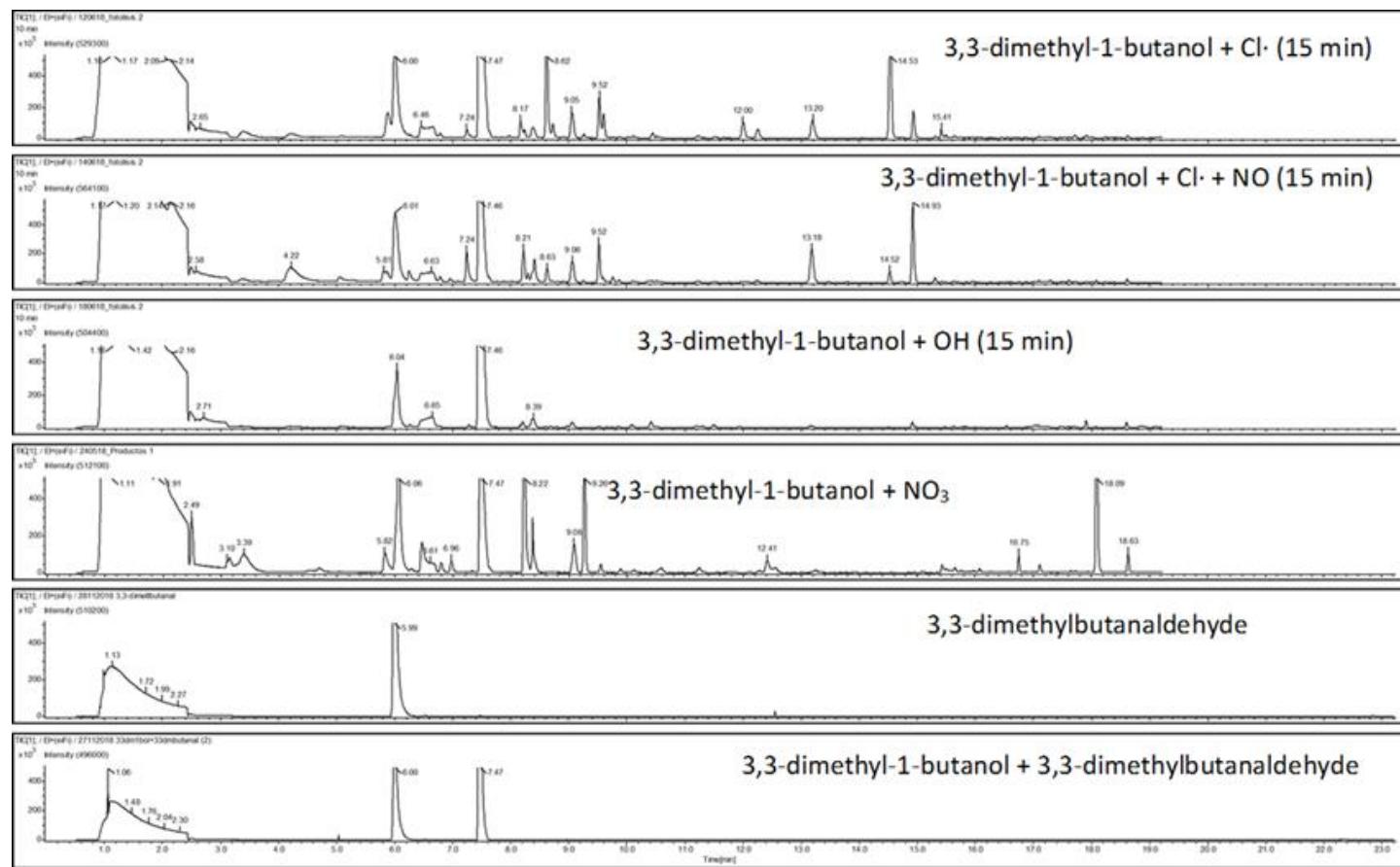
A



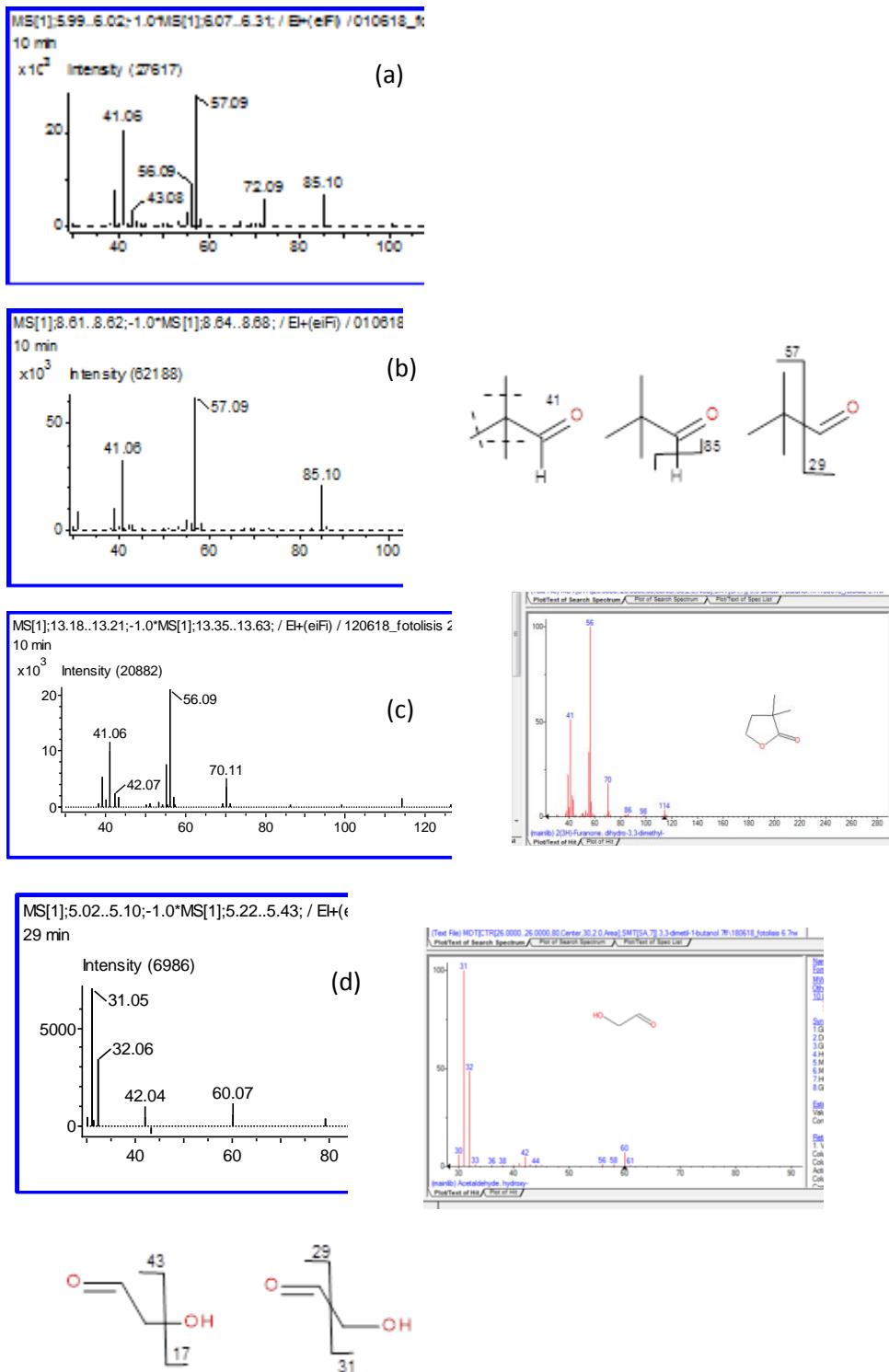
B



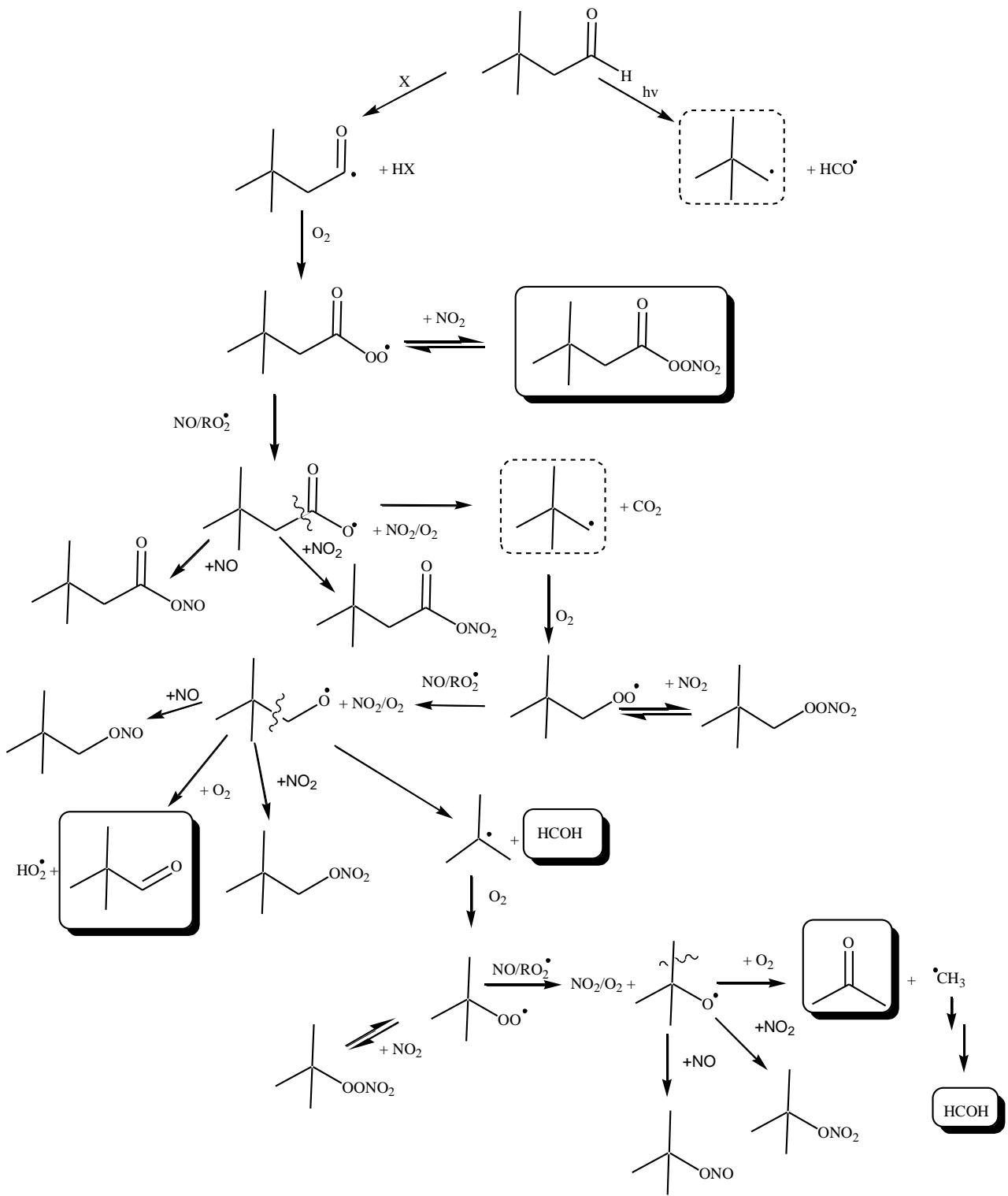
**Fig. S5.** **A)** Residual FTIR spectra obtained in the reaction of 3,3DM1ButOH with (a) Cl atoms, (b) Cl atoms in the presence of NO, (c) OH radicals and (d) NO<sub>3</sub> radicals. The IR absorption bands subtracted were:3,3DM1ButOH, HCl, CINO<sub>2</sub>, CINO, HCOH, HCOOH, HONO, NO<sub>2</sub>, NO, N<sub>2</sub>O and peroxy nitric acid (for Cl in the absence and presence of NO); N<sub>2</sub>O<sub>5</sub>, HNO<sub>3</sub>, NO<sub>2</sub> (for NO<sub>3</sub> reactions) and HCOH, HCOOH, HNO, NO<sub>2</sub>, CH<sub>3</sub>ONO and CH<sub>3</sub>ONO<sub>2</sub> (for OH reactions). (e) FTIR reference spectrum of 3,3-dimethylbutanal. **B)** Residual FTIR spectra: (a) Cl atoms, (b) Cl atoms in the presence of NO, (g) OH radicals and (h) NO<sub>3</sub> radicals without 3,3-dimethylbutanal. Reference spectra (c) acetone from a commercial sample; (d) 2-methylpropanal; (e) PAN; (f) glycolaldehyde; and (i) isobutylnitrate from Eurochamp 2020 database.



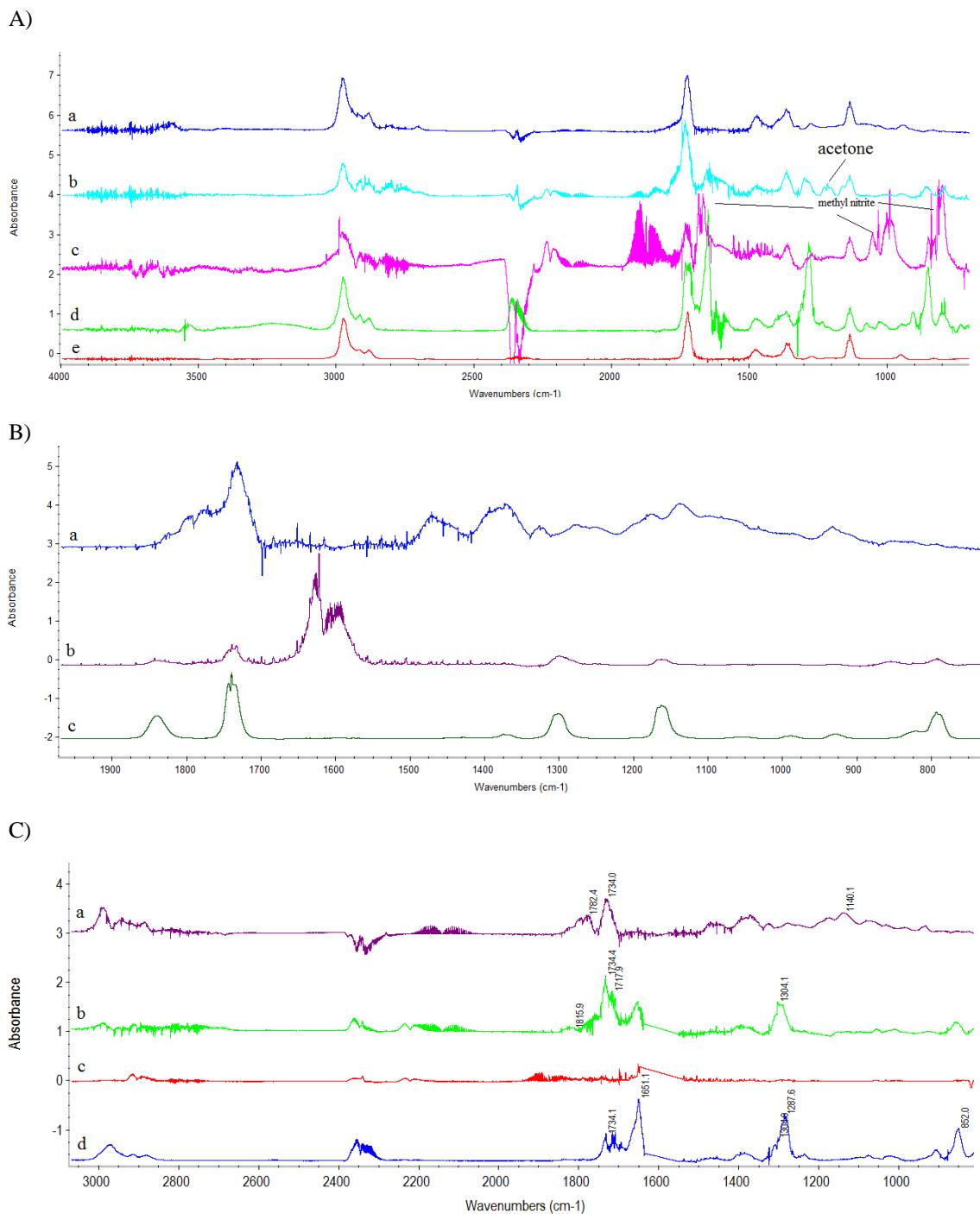
**Fig. S6.** SPME/GC-TOFMS chromatograms obtained for the reaction of of 3,3DM1ButOH with Cl atoms , Cl atoms in the presence of NO, OH radicals and NO<sub>3</sub> radicals (30 min) and reference chromatograms of 3,3DM1ButOH and 3,3-dimethylbutanaldehyde.



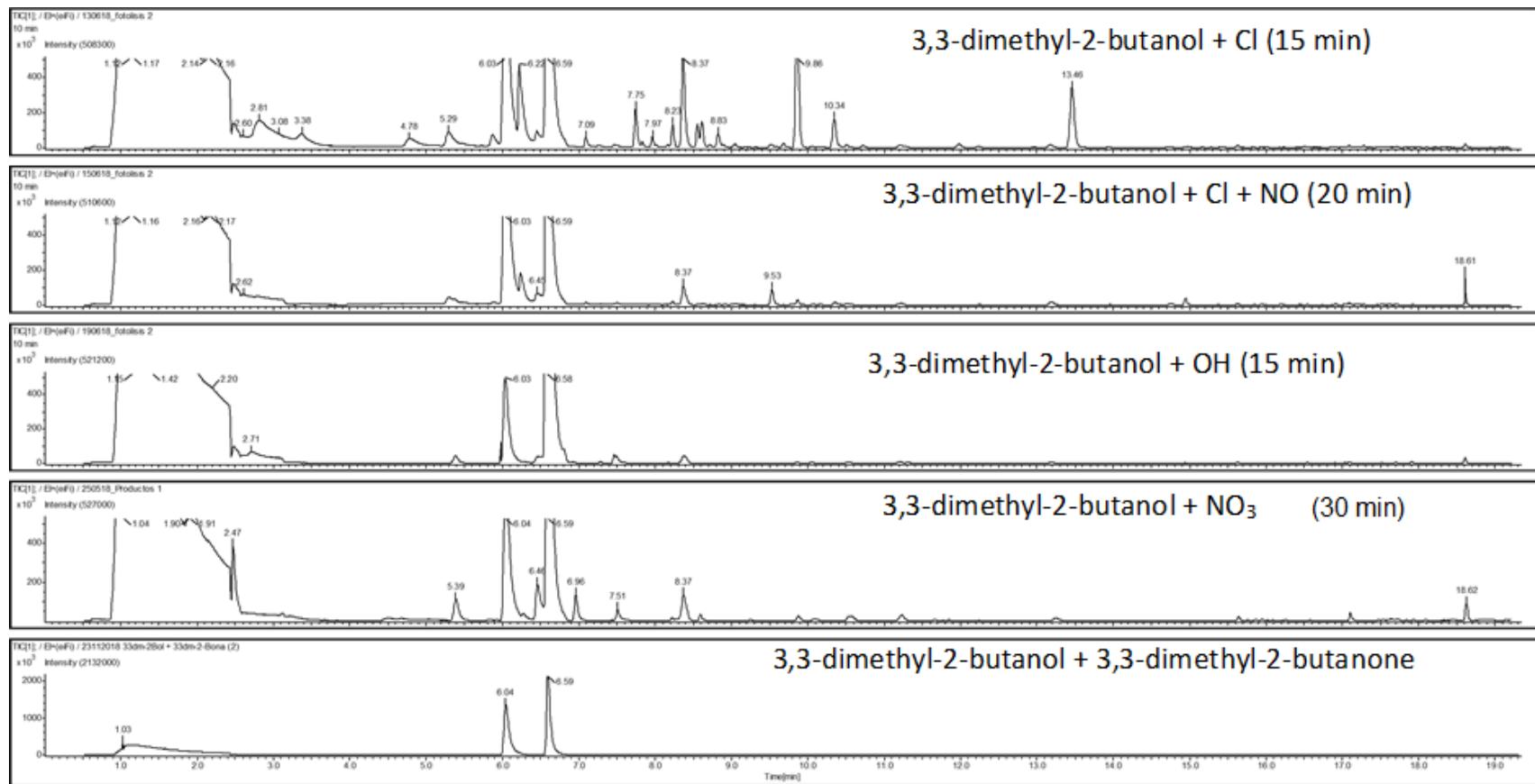
**Fig. S7.** EIMS spectra of the peaks of chromatograms shown in Fig. S6 obtained for the reaction of of 3,3DM1ButOH with Cl atoms, Cl atoms in the presence of NO, OH radicals and NO<sub>3</sub> radicals. (a) t<sub>R</sub>= 6.00 min; (b) t<sub>R</sub>= 8.61 min; (c) t<sub>R</sub>= 13.17 min; (d) t<sub>R</sub>= 5.05 min).



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

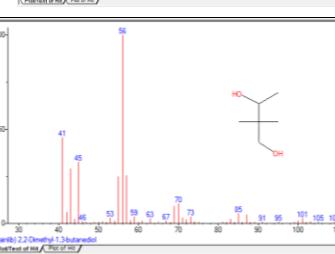
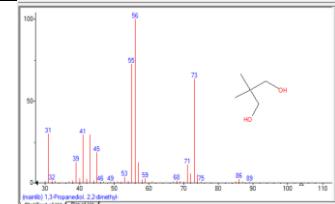
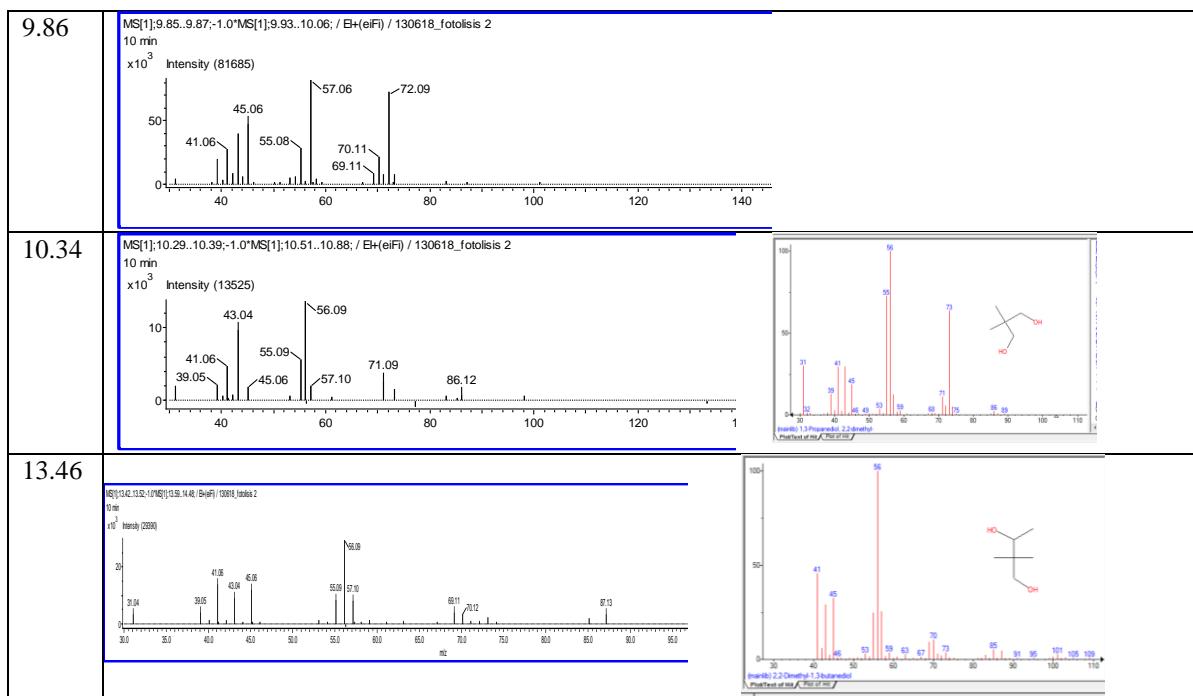


**Fig. S9.** A) FTIR spectra obtained in the reaction of 3,3DM2ButOH with (a) Cl atoms, (b) Cl atoms in the presence of NO, (c) OH radials and (d) NO<sub>3</sub> radicals at 5 minutes of reaction. (e) FTIR reference spectrum of 3,3-dimethyl-2-butanone. B) FTIR spectra obtained in the reaction of 3,3-dimethyl-2-butanol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



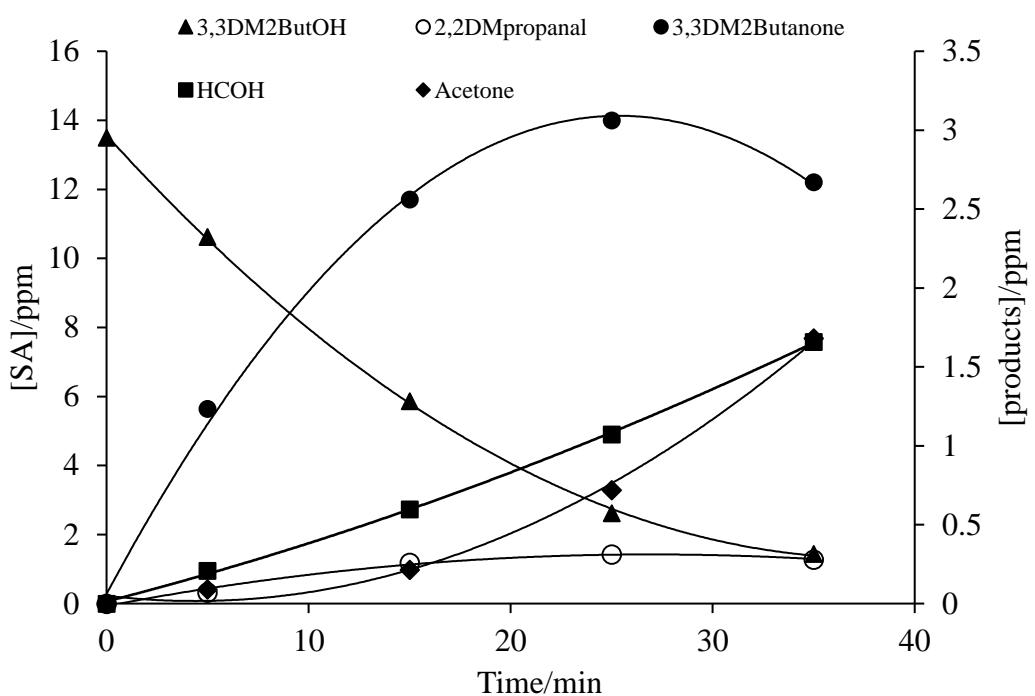
**Fig. S10.** SPME/GC-TOFMS chromatograms obtained for the reaction of 3,3DM2ButOH with Cl atoms, Cl atoms in the presence of NO, OH and NO<sub>3</sub> radicals and reference chromatograms of 3,3DM2ButOH and 3,3-dimethyl-2-butanone.

$t_R$ (min)	EI MS
2.16	<p>MS[1];2.10..2.22;-1.0*MS[1];2.43..2.93; / El+(eIF) / 130618_fotolisis 2 10 min</p> <p style="text-align: center;">Acetone</p>
5.39 ?	<p>MS[1];5.3..5.4;-1.0*MS[1];5.4..5.5; / El+(eIF) / 250518_Productos 1 10 min</p> <p style="text-align: center;">2,2-dimethylpropanal</p> <p>Propanal, 2,2-dimethyl- MASS SPECTRUM</p> <p>NIST Chemistry WebBook (<a href="https://webbook.nist.gov/chemistry">https://webbook.nist.gov/chemistry</a>)</p>
6.03	<p>MS[1];6.01..6.08;-1.0*MS[1];6.14..6.58; / El+(eIF) / 150618_fotolisis 2 10 min</p> <p style="text-align: center;">3,3-dimethyl-2-butanone</p>
6.22	<p>MS[1];6.20..6.24;-1.0*MS[1];6.29..6.58; / El-</p> <p>10 min</p> <p style="text-align: center;">Acetic Acid (SI 80%)</p>
6.46	SPME
6.96	<p>MS[1];6.94..6.98;-1.0*MS[1];7.04..7.33; / El+(eIF) / 250518_Productos 1 10 min</p> <p style="text-align: center;">Nitrated compound</p>
7.75	<p>MS[1];7.73..7.76;-1.0*MS[1];7.79..7.92; / El+(eIF) / 130618_fotolisis 2 10 min</p>
8.37	<p>MS[1];8.38;-1.0*MS[1];8.38..8.45; / El+(eIF) / 130618_fotolisis 2 10 min</p>

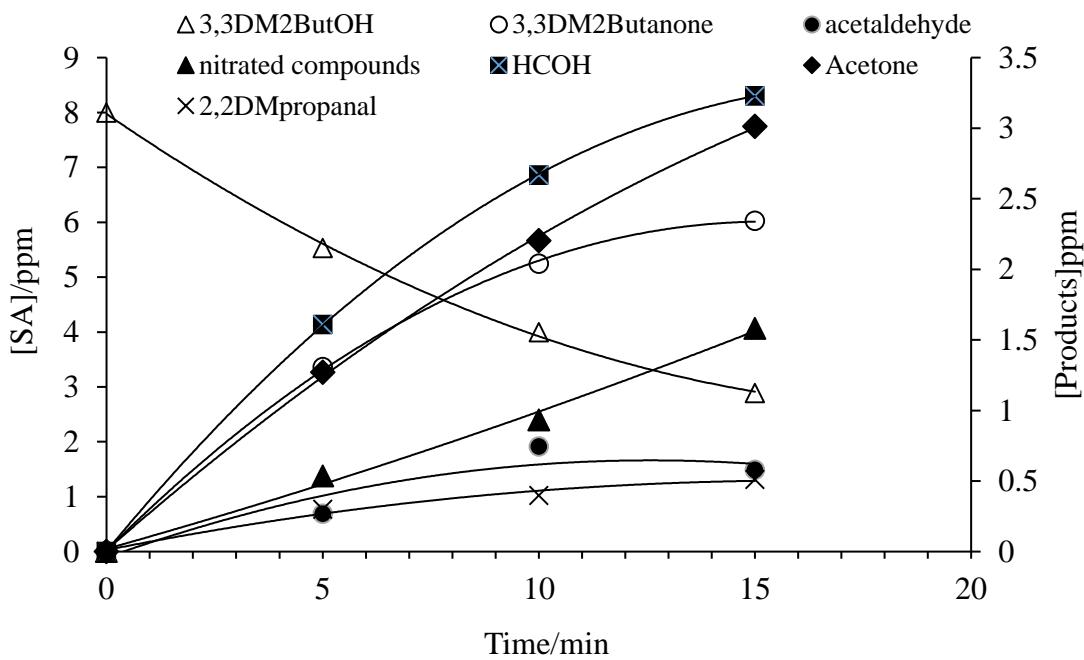


**Fig. S11.** EIMS spectra of the peaks of chromatograms shown in Fig. S10 obtained for the reaction of 3,3DM2ButOH with Cl atoms Cl atoms in the presence of NO, OH and NO<sub>3</sub> radicals,

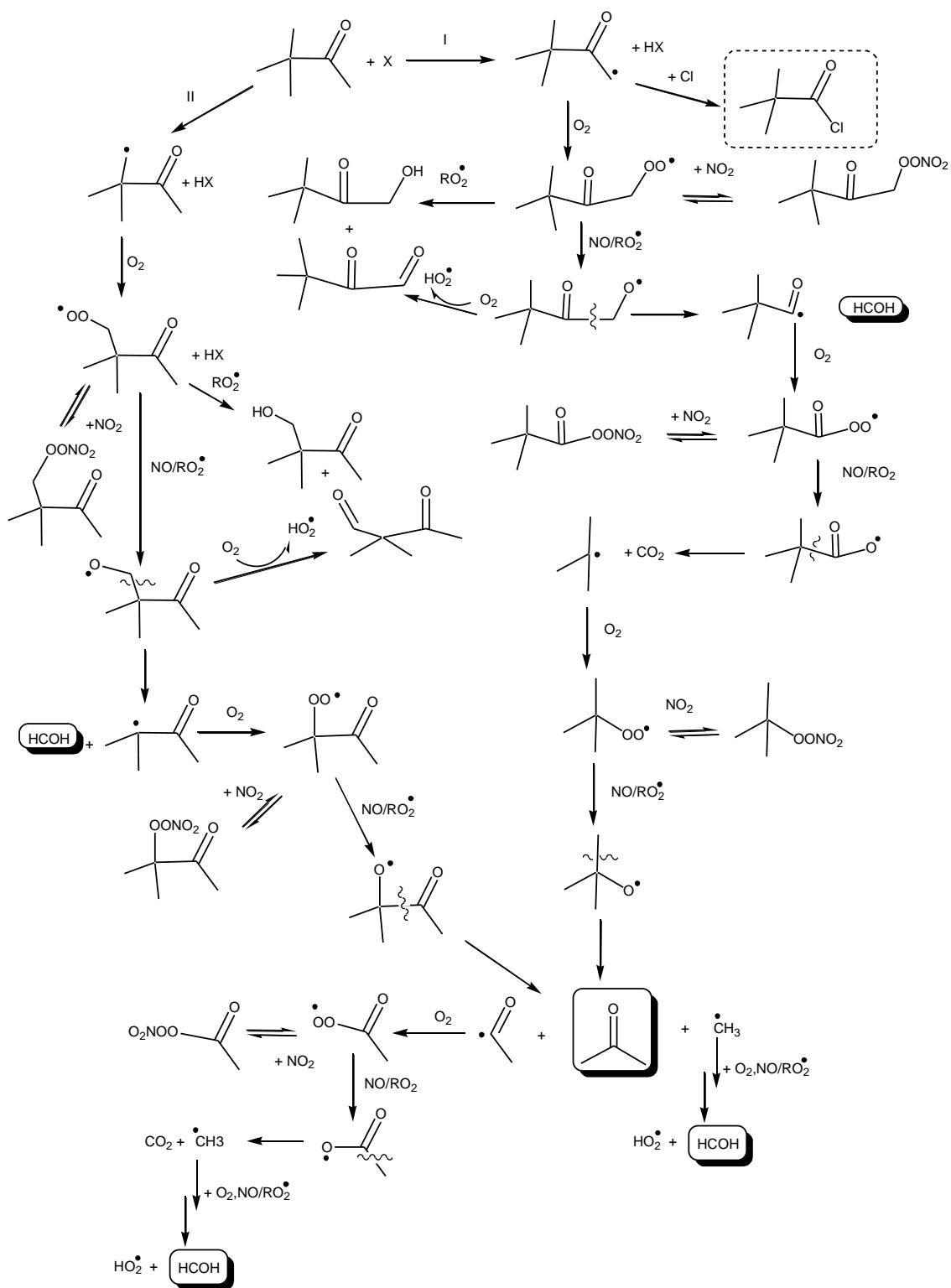
A)



(B)



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



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

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