Supplementary material

S1. Tuazon formalism

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

MSA + Ox $\rightarrow \Sigma$ Y product1 (k_S) (RS1)
Product1 + Ox $\rightarrow$ Product2 (k_p) (RS2)
Product1 + hν $\rightarrow$ Product3 (k_1) (RS3)

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

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

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

From Eq (S1) it is possible to calculate the concentration of oxidant in the system.
Using the relationship obtained by Tuazon et al. (1986) the corrected concentration of the reaction products can be calculated as follows:

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

Where $[\mathrm{MSA}]_{t1}$, $[\mathrm{product1}]_{t1}$ and $[\mathrm{MSA}]_{t2}$, $[\mathrm{product1}]_{t2}$ are the observed concentrations of the methyl saturated alcohol and the products at times t_1 and t_2 respectively, and $Y_{t1\text{-}t2}$ is the yield of formation of the individual products on the period of time (t_1 - t_2).

By means of equations (S1) and (S2), $Y_{t1\text{-}t2}$ can be calculated. The concentration of the reaction products, corrected for the reaction with radical and other processes of loss is given by:

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

Where $[\mathrm{product1}]^{\mathrm{corr}}{}_{t1}$ and $[\mathrm{product1}]^{\mathrm{corr}}{}_{t2}$ are the concentrations of the product1 corrected at times t_1 and t_2 respectively:

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

Tables

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

Compound	$k_{Cl}\times10^{11}$	$k_{OH}\times10^{12}$	$k_{NO3}\times10^{15}$
Alkanes			
Methane	0.01	0.0064	<0.001[f]
Ethane	5.70[a]	0.24[f]	<0.01[f]
Propane	12.7[a]	1.09[f]	<0.07[f]
Butane	19.4[a]	2.36[f]	0.046[f]
Pentane	25.0[a]	3.80[f]	0.087[f]
Hexane	30.5[a]	5.20[f]	0.110[f]
Heptane	36.5[a]	6.76[f]	0.150[f]
Octane	40.9[a]	8.11[kf]	0.190[f]
Nonane	46[b]		0.220[b]
Decane	52.7[b]		0.260[b]
2-Methylpropane	13.0[a]	2.12[f]	0.106[f]
2-Methylbutane	19.6[a]	3.60[f]	0.162[f]
2-Methylpentane	25.8[a]	5.2[f]	0.180[f]
3-Methylpentane	26.9[b]	5.2[f]	0.220[f]
2-Methylhexane	31.2[a]	6.72[e]	-
2,3-Dimethylbutane	20[a]	5.78[f]	0.44[f]
2,2-Dimethylbutane	-	22.3[f]	-
2,2,4-trimethylpentane	22.5[a]	3.34[f]	0.09[f]
Cyclopentane	32.6[c]	4.97[f]	-
Cyclohexane	33[d]	6.97[f]	0.14[f]
Methylcyclohexane	35.1[e]	9.5[e]	-
Trans-1,4-dimethylcyclohexane	36.3[e]	12.1[e]	-
Ethylcyclohexane	38.8[e]	11.8[e]	-
Saturated Alcohols			
Methanol	5.5	0.9	0.13
Ethanol	10	3.2	<2
1-propanol	16	5.8	<2.1
2-propanol	8.7	5.1	1.4
1-butanol	22	8.5	1.87[g]
2-butanol	12[h]	8.7	2.51[q]
1-pentanol	24[i]	11[i]	-
2-pentanol	22[i]	11.8[i]	-
3-pentanol	20[i]	13[i]	-
1-hexanol	31[i]	13[i]	-
2-hexanol	-	12[i]	-

1-heptanol	37[i]	13[i]	-
4-heptanol	-	-	<6.2
1-octanol	42[i]	13[i]	-
2-methyl-1-propanol	20.6[j]	11.4[j]	-
2-methyl-2-propanol	3.26[k]	1.07[k]	-
2-ethyl-1-hexanol	18.8[l]	11.3[l]	-
2-methyl-1-butanol	-	-	2.32[g]
2-methyl-2-butanol	7[h]	3.64[n]	1.57[q]
3-methyl-1-butanol	25[i]	14[i]	2.09[g]
3-methyl-2-butanol	11.7[h]	12.5[o]	3.06[q]
2-methyl-2-pentanol	-	7.1[i]	-
4-methyl-2-pentanol	-	17[i]	-
2,2-dimethyl-1-propanol	-	5.5[i]	-
3,3-dimethyl-1-butanol	**27.0**	**5.57**	1.78[g]
3,3-dimethyl-2-butanol	**12.1**	**10.51**	3.44[g]
2,3-dimethyl-2-butanol	10.3[h]	9.1[n]	3.64[q]
2,4-dimethyl-2-pentanol	-	11[i]	-
3,5-dimethyl-3-hexanol	-	13[i]	-
cyclopentanol	-	10.7[k]	-
cyclohexanol	32.1[m]	19.0[p]	-
4MCHexOH	**37.1**	**19.1**	**2.92**

Data obtained from IUPAC Subcommittee on Gas Kinetics Data Evaluation and the following references: [a]Hooshiyar and Niki, 1995; [b]Calvert et al., 2015; [c]Wallington et al., 1989; [d]Calvert et al., 2008; [e]Began et al., 2018; [f]Atkinson, 2003; [g]Moreno et al., 2014; [h]Ballesteros et al., 2007; [i]Calvert et al., 2011; [j]Andersen et al., 2010; [k]Wallington et al., 1988; [l]Gallego-Iniesta et al., 2010; [m]Ceacero-Vega et al., 2012; [n]Jiménez et al., 2005; [o]Mellouki et al., 2004; [p]Bradley et al., 2001; [q]Moreno 2012.

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

Reaction Product of reaction mechanism	**FTIR**				**GC-MS**				
	Cl	Cl + NO	OH	NO_3	Cl	Cl + NO	OH	NO_3	t_R/min
Route I									
3,3-dimethylbutanal	X	X	X	X	X	X	X	X	6.00
Route II									
1-hidroxy-3,3-dimethyl-2-butanone	-	-	-	-	-	-	-	-	-
3,3-dimetil-1,2-butanodiol	-	-	-	-	-	-	-	-	-
2,2-dimethylpropanal	X	X	X	-	/	-	-	-	8.61?
Formaldehyde	X	X	X*	-		-	-	-	-
Route III									
4-hidroxy-2,2-dimethylbutanal	-	-	-	-	-	-	-	-	-
2,2-dimethyl-1,4-butanodiol	-	-	-	-	-	-	-	-	-
4-hidroxy-3,3-dimethylbutanal	-	-	-	-	-	-	-	-	-
Cyclic alcohols	-	-	-	-	-	-	-	-	-
Cyclic carbonyls (2(3H)dihydro,3,3-dimethylfuran)	-	-	-	-	/	/	/	/	13.17
4-hidroxy-2-butanone	-	-	-	-	-	-	-	-	-
Acetone	X	X	-	-	-	/	-	-	2.14
Glycolaldehyde	-	/	-	-	-	/	/	/	5.05
1,2-etanodiol	-	-	-	-	-	-	-	-	-
Formaldehyde	X	X	X*	-	-	-	-	-	-

The compounds with X have been positively identified with reference FTIR or MS spectrum. Those that have been probably identified through the analysis of the IR bands of the residual spectra and Mass Spectra using as a source of ionization Electronic Impact (EI) and Field Ionization (FI) source 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 mechanims	**FTIR**				**GC-MS**				
	Cl	**Cl + NO**	**OH**	**NO_3**	**Cl**	**Cl + NO**	**OH**	**NO_3**	**Retention time (min)**
Route I									
3,3-dimethyl-1,2-butanediol	-	-	-	-	-	-	-	-	-
3,3-dimethyl-2-hydroxybutanal	-	-	-	-	-	-	-	-	-
Formaldehyde	X	X	X*		-	-	-	-	-
2,2-dimethylpropanal	X	X	X	-	-	-	/	/	5.39
Route II									
3,3-dimethyl-2-butanone	X	X	X	X	X	X	X	X	6.04
Route III									
2,2-dimethyl-1,3-butanediol	-	-	-	-	/	-	-	-	13.46
2,2-dimethyl-3-hydroxybutanal	-	-	-	-	-	-	-	-	-
Formaldehyde	X	X	X*	-	-	-		-	-
3-hydroxybutanone (Acetoin)	-	-	-	-	-	-	-	-	-
Acetone	X	X	-	-	/	/	-	-	2.16
Acetaldehyde	-	X	-	-	-	-	-	-	-

The compounds with X have been positively identified in denoted equipment. Those that have / have been probably identified through the analysis of the IR bands of the residual spectra and the analysis of the mass spectra using as a source of ionization by electronic impact 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.

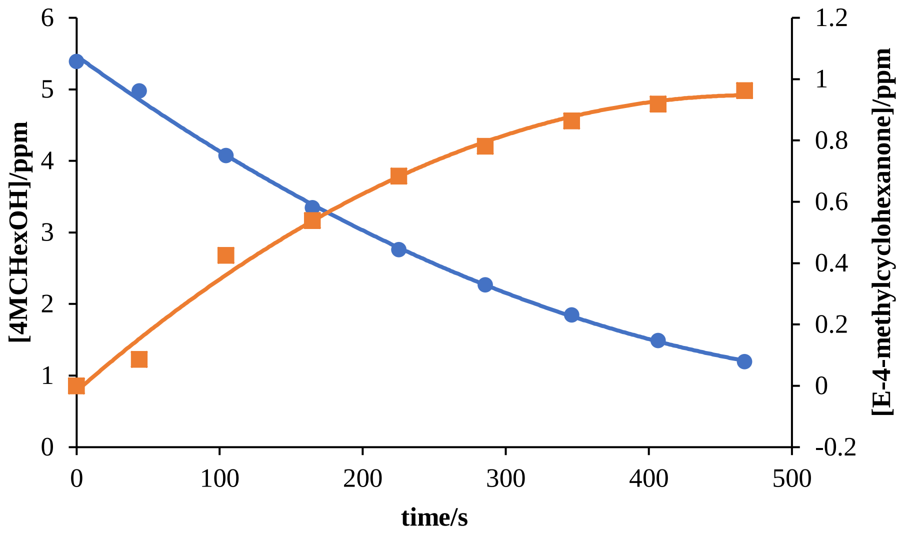


Fig. S1. Time-concentration profiles of 4MCHexOH • and 4-methylcyclohexanone ■, for the reaction of with chlorine atoms in the presence of NOx obtained by FTIR.

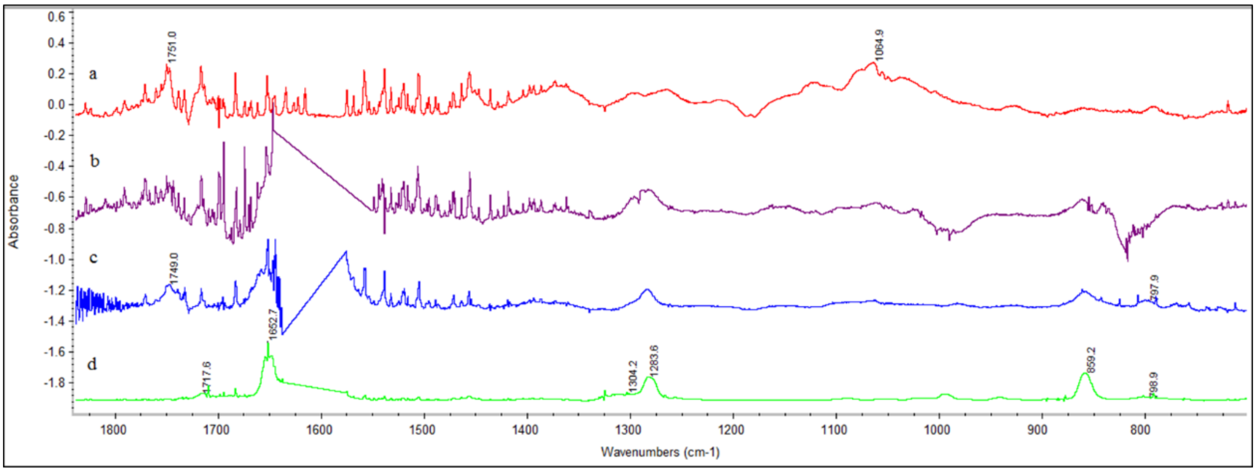


Fig. S2. Residual FTIR spectra obtained in the reaction of 4MCHexOH with Cl (a), Cl + NO (c), HO (b) and NO_3 (d). The gap in the range of 1650-1590 cm^{-1} corresponds to NO_2 absorption.

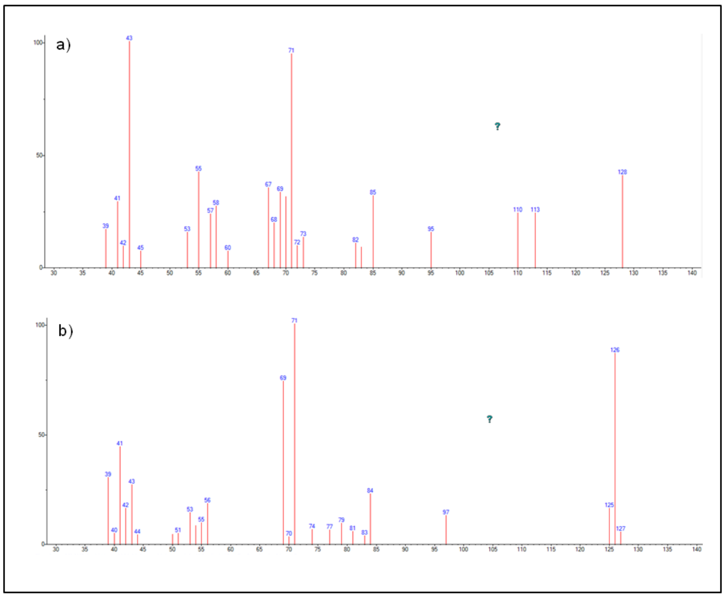


Fig. S3. EI MS spectra of peak C (a) and D (b) observed at 20 and 23 min of retention time in the reaction of 4-methylcylcohexanol with chlorine atoms. Tentatively assigned to 2-hydroxy-5-methyl cyclohexanone, 5-hydroxy-2-methyl-cyclohexanone and or 3-methyl-1,6-hexanedial.

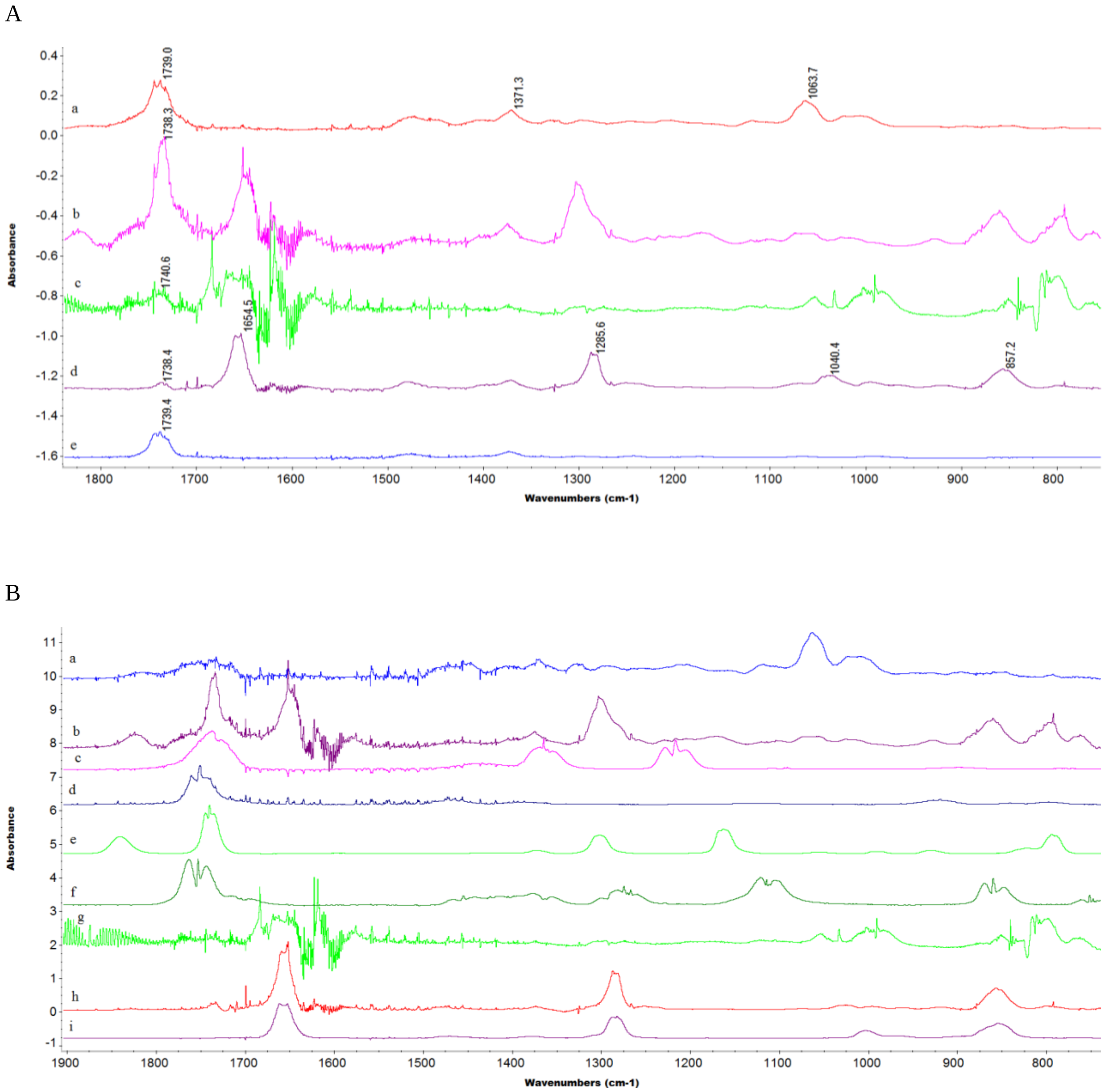


Fig. S4. A) Residual FTIR spectra obtained in the reaction of 3,3DM1ButOH with Cl (a), Cl + NO (b), OH (c) NO_3 (d). The IR absorption bands subtracted were:3,3DM1ButOH, HCl, $ClNO_2$, ClNO, HCOH, HCOOH, HONO, NO_2, NO, N_2O and peroxy nitric acid (for Cl and Cl + NO reactions); N_2O_5, HNO_3, NO_2 (for NO_3 reactions) and HCOH, HCOOH, HNO, NO_2, methyl nitrite and methylnitrate (for OH reactions). (e) FTIR reference spectrum of 3,3-dimethylbutanal**. B)** Residual FTIR spectra: Cl (a), Cl + NO (b), HO (g) and NO_3 (h) without 3,3-dimethylbutanal. Reference spectra of acetone (c) from a commercial sample; 2-methylpropanal (d); PAN (e); Glycolaldehyde (f); and isobutylnitrate (i) from Eurochamp 2020 database.

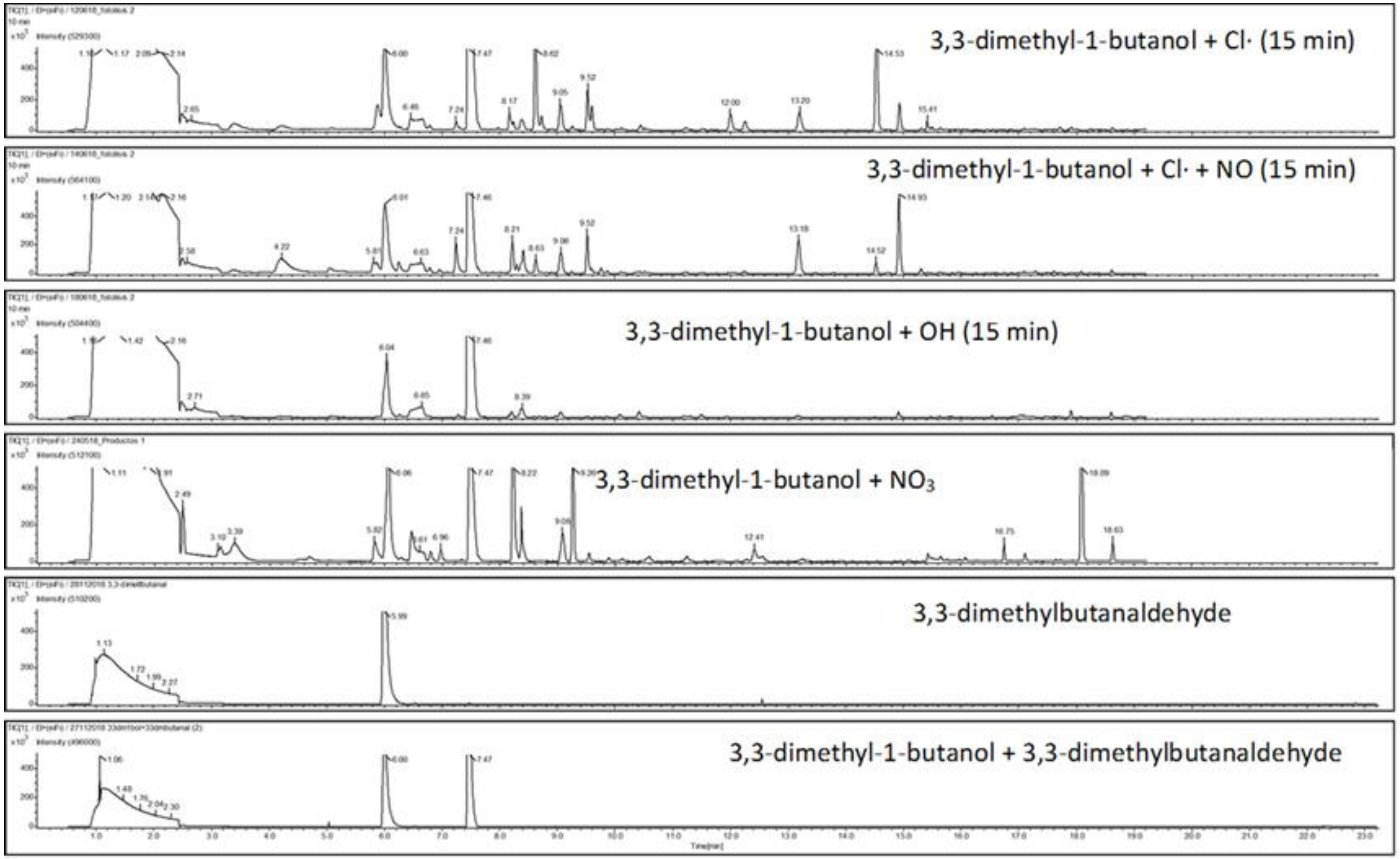


Fig. S5. SPME/GC-TOFMS chromatograms obtained for the reaction of of 3,3-dimethyl-1-butanol with Cl, Cl + NO, HO and NO$_3$ (30 min).

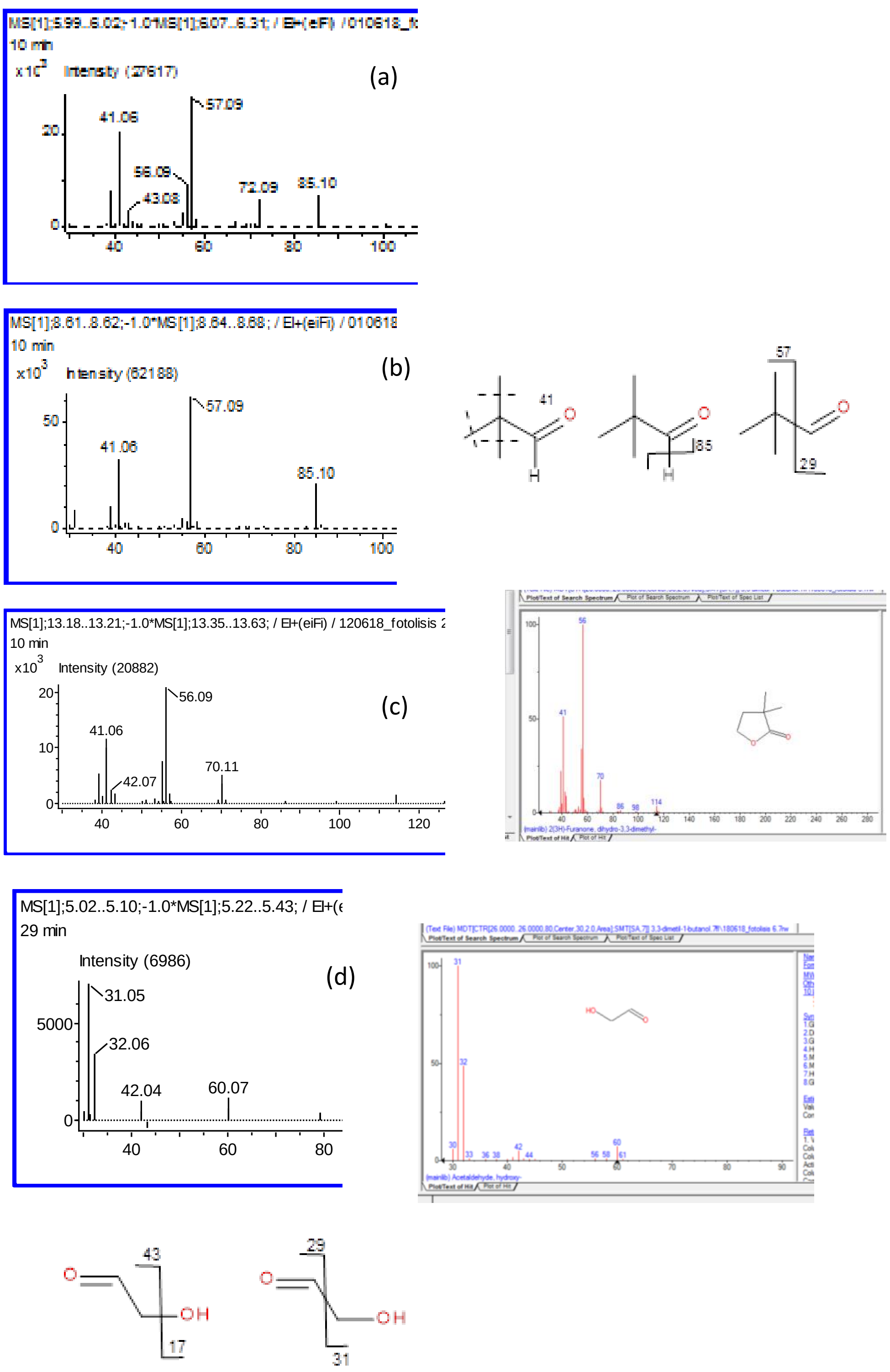


Fig. S6. EI MS spectra obtained for the reaction of of 3,3-dimethyl-1-butanol with Cl, Cl + NO, HO and NO_3. (a) t_R= 6.00 min; (b) t_R= 8.61 min; (c) t_R= 13.17 min; (d) t_R= 5.05 min).

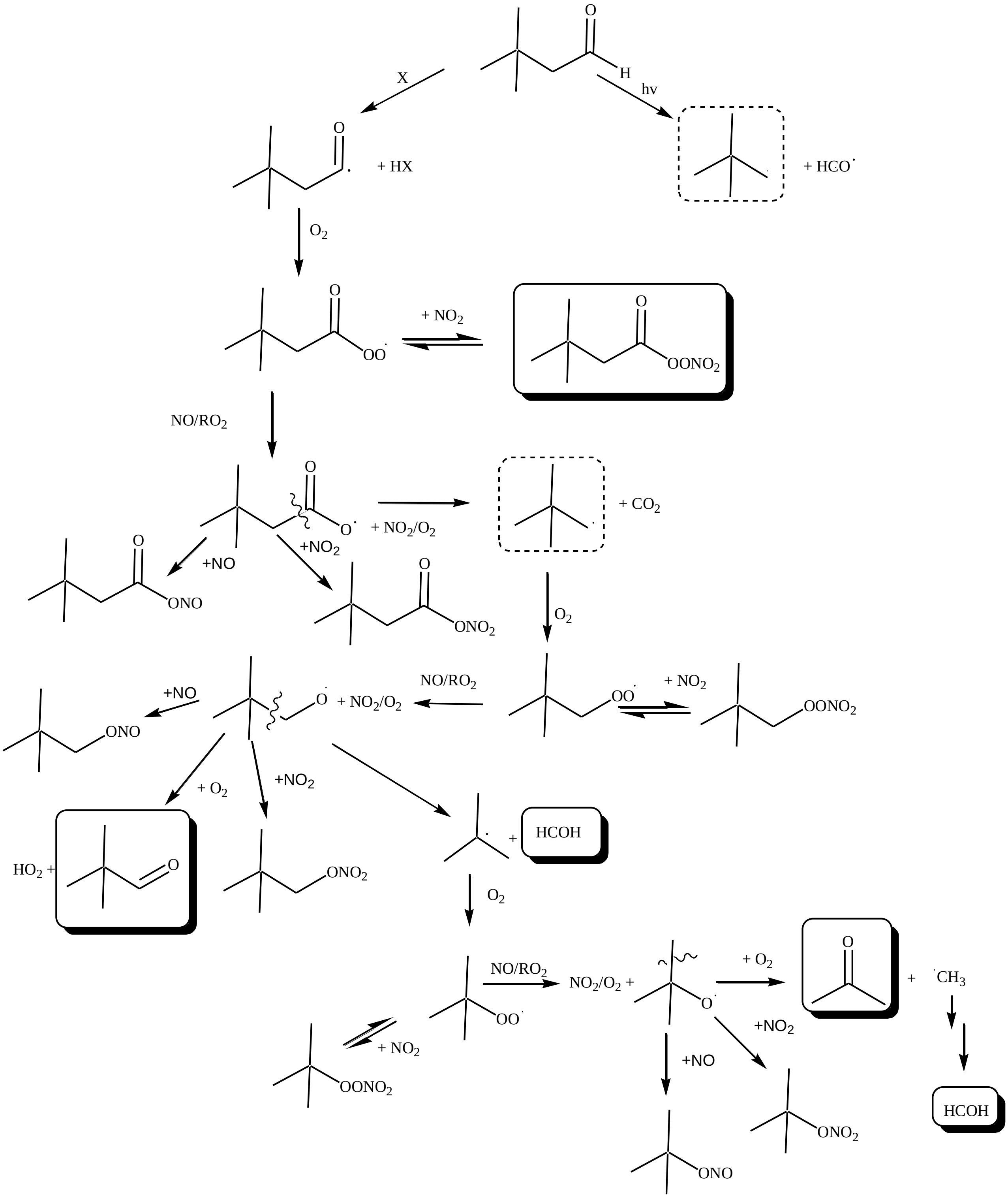


Fig. S7. Reaction mechanism for degradation of 3,3-dimethylbutanal with the atmospheric oxidants in presence of NOx. H-Atom Abstraction from the -COH Group in 3,3-Dimethylbutanal. Aschamnn et al., 2010.

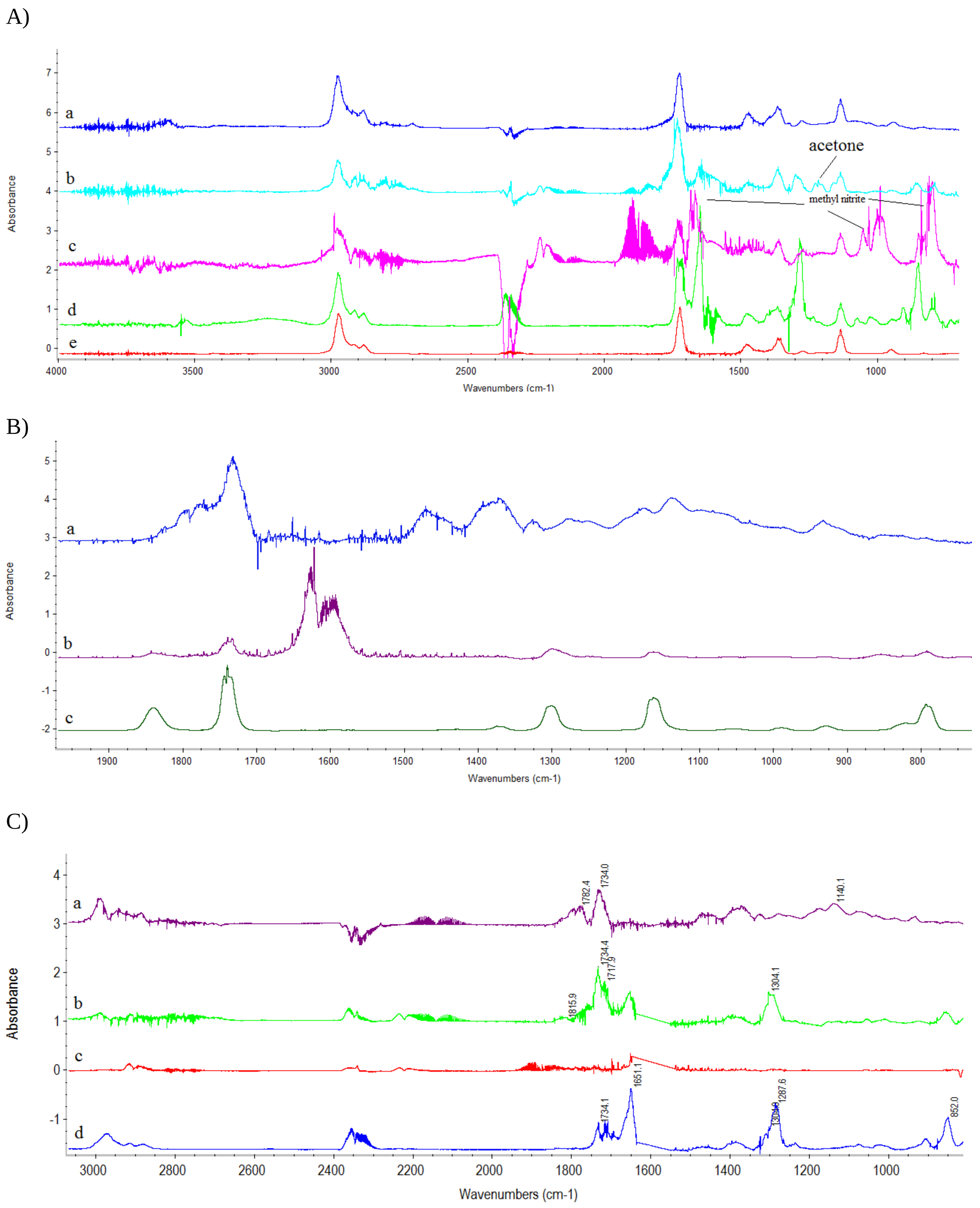
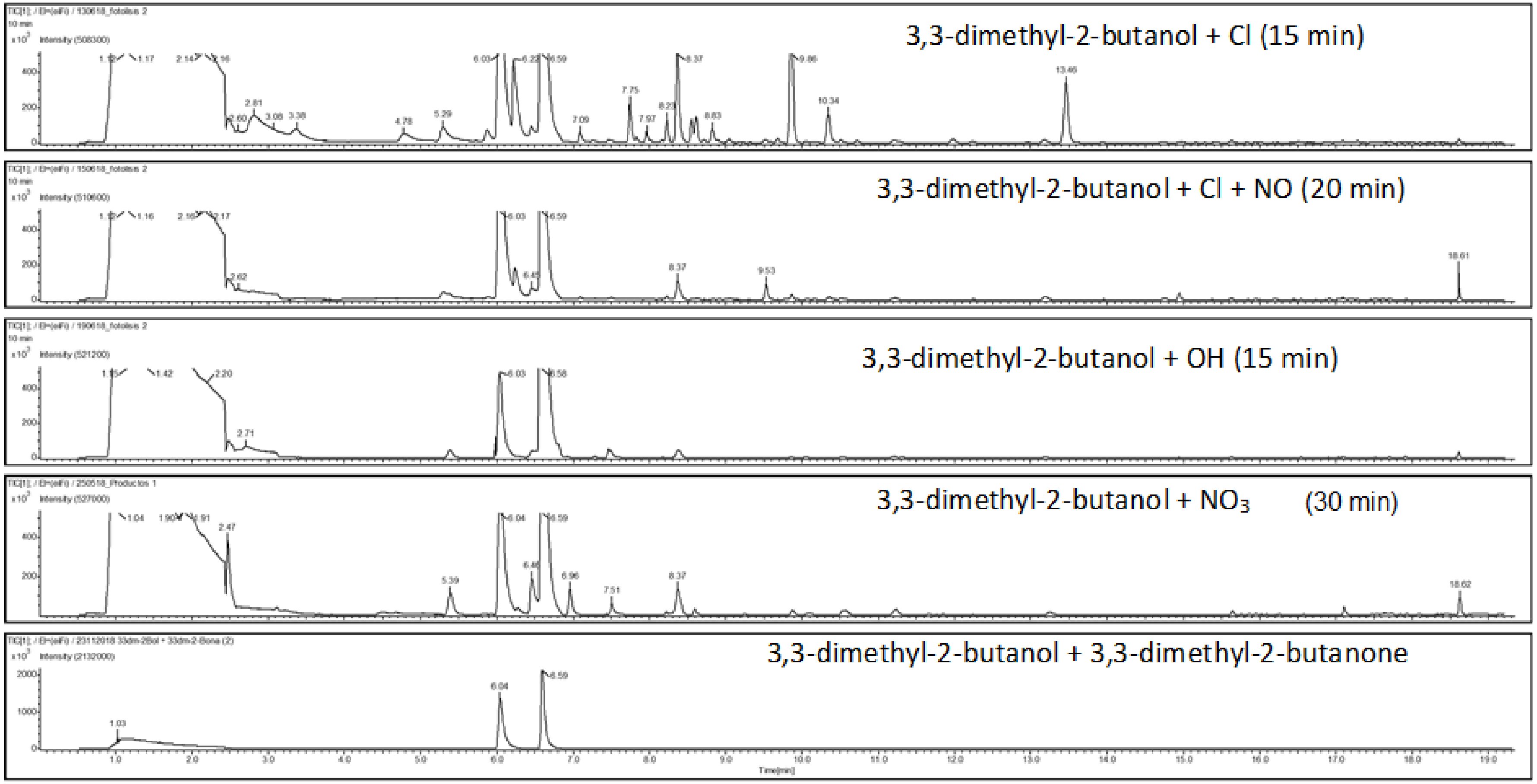


Fig. S8. A) FTIR spectra obtained in the reaction of 3,3DM2ButOH with Cl (a), Cl + NO (b), OH (c) NO_3 (d) at 5 minutes of reactions. (e) FTIR reference spectrum of 3,3-dimethyl-2-butanona. B) FTIR spectra obtained in the reaction of 3,3-dimethyl-2-butanol with Cl (a), Cl + NO (b), 25 minutes and 35 minutes of reactions respectively. (c) PAN spectrum. C) Residual FTIR spectra after subtraction of all known bands. Cl (a), Cl + NO (b), HO (c) and NO_3 (d).



3,3-dimethyl-2-butanol + Cl (15 min)

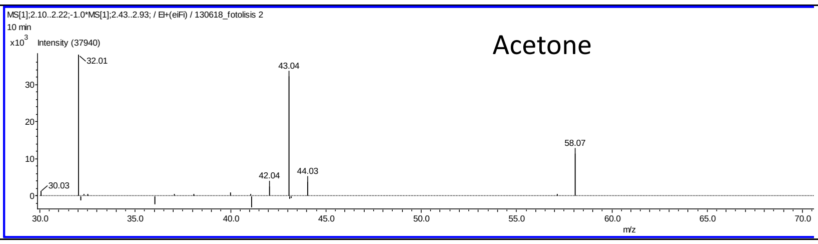
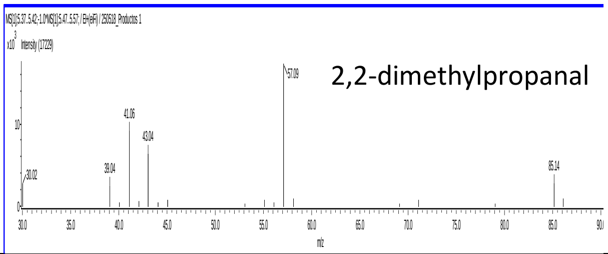
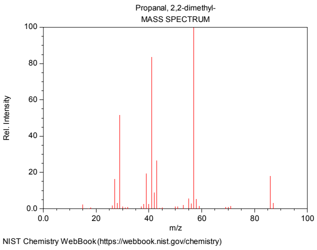
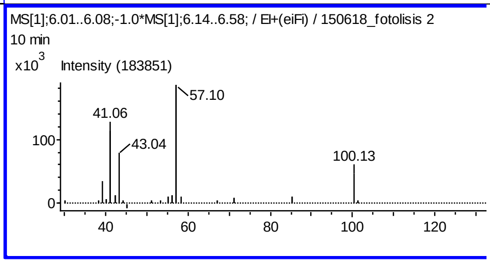
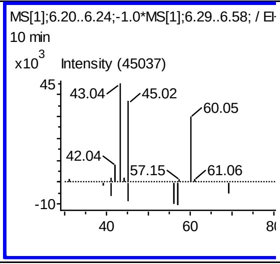
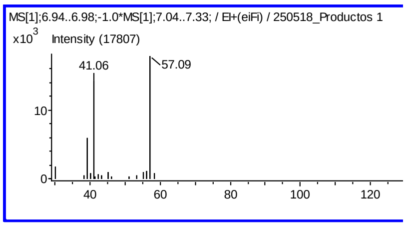
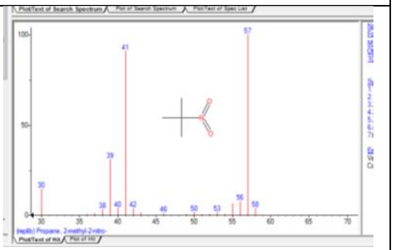
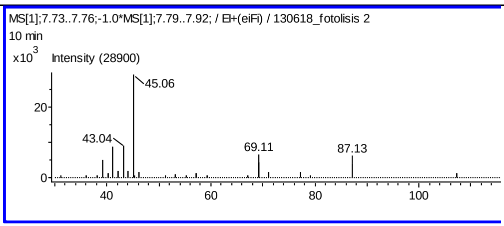
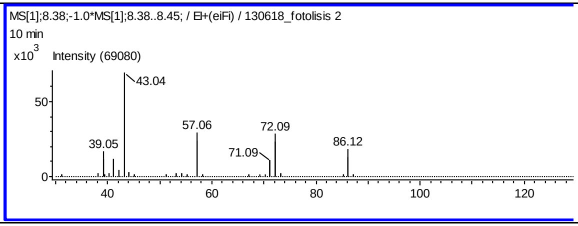
3,3-dimethyl-2-butanol + Cl + NO (20 min)

3,3-dimethyl-2-butanol + OH (15 min)

3,3-dimethyl-2-butanol + NO_3 (30 min)

3,3-dimethyl-2-butanol + 3,3-dimethyl-2-butanone

Fig. S9. SPME/GC-TOFMS chromatograms obtained for the reaction of of 3,3-dimethyl-2-butanol with Cl, Cl + NO, HO and NO_3.

t_R (min)	EI MS
2.16	 Acetone
5.39 ?	 2,2-dimethylpropanal 
6.03	 3,3-dimethyl-2-butanone
6.22	 Acetic Acid (SI 80%)
6.46	SPME
6.96	 Nitrated compound 
7.75	
8.37	

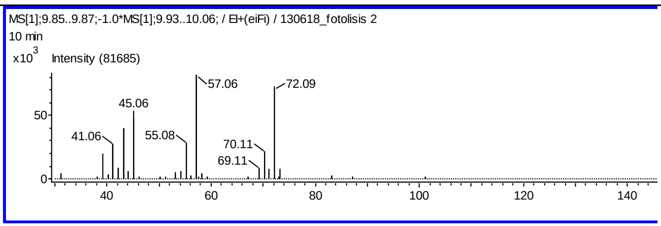
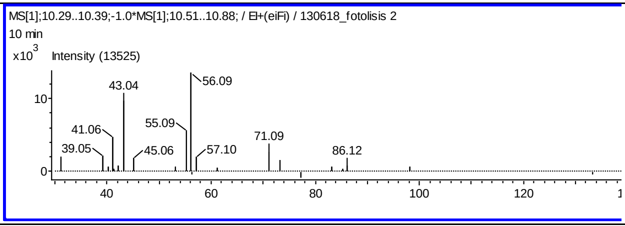
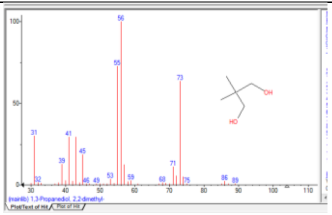
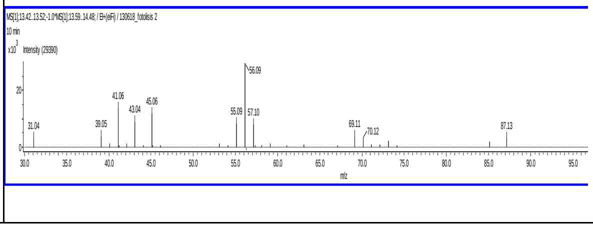
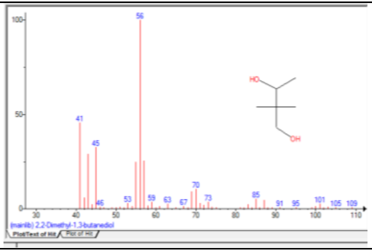
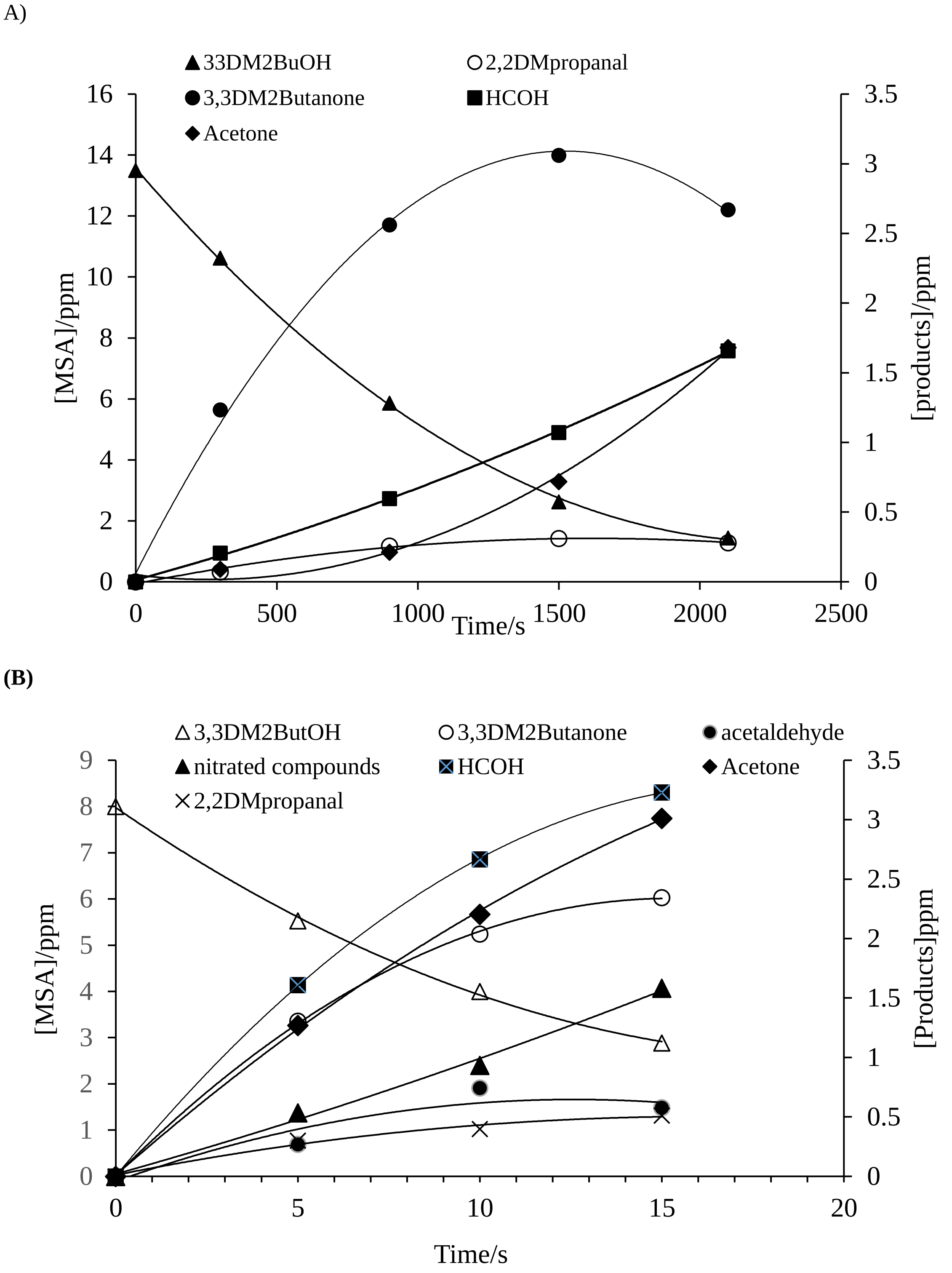
9.86	
10.34	 
13.46	 

Fig. S10. EI MS spectra obtained for the reaction of of 3,3DM2ButOH with Cl, Cl + NO, HO and NO_3.



Fig, S11. Concentration-time profiles obtained for the reaction of 3,3DM2ButOH with Cl atoms in absence (A) and presence of NO (B).

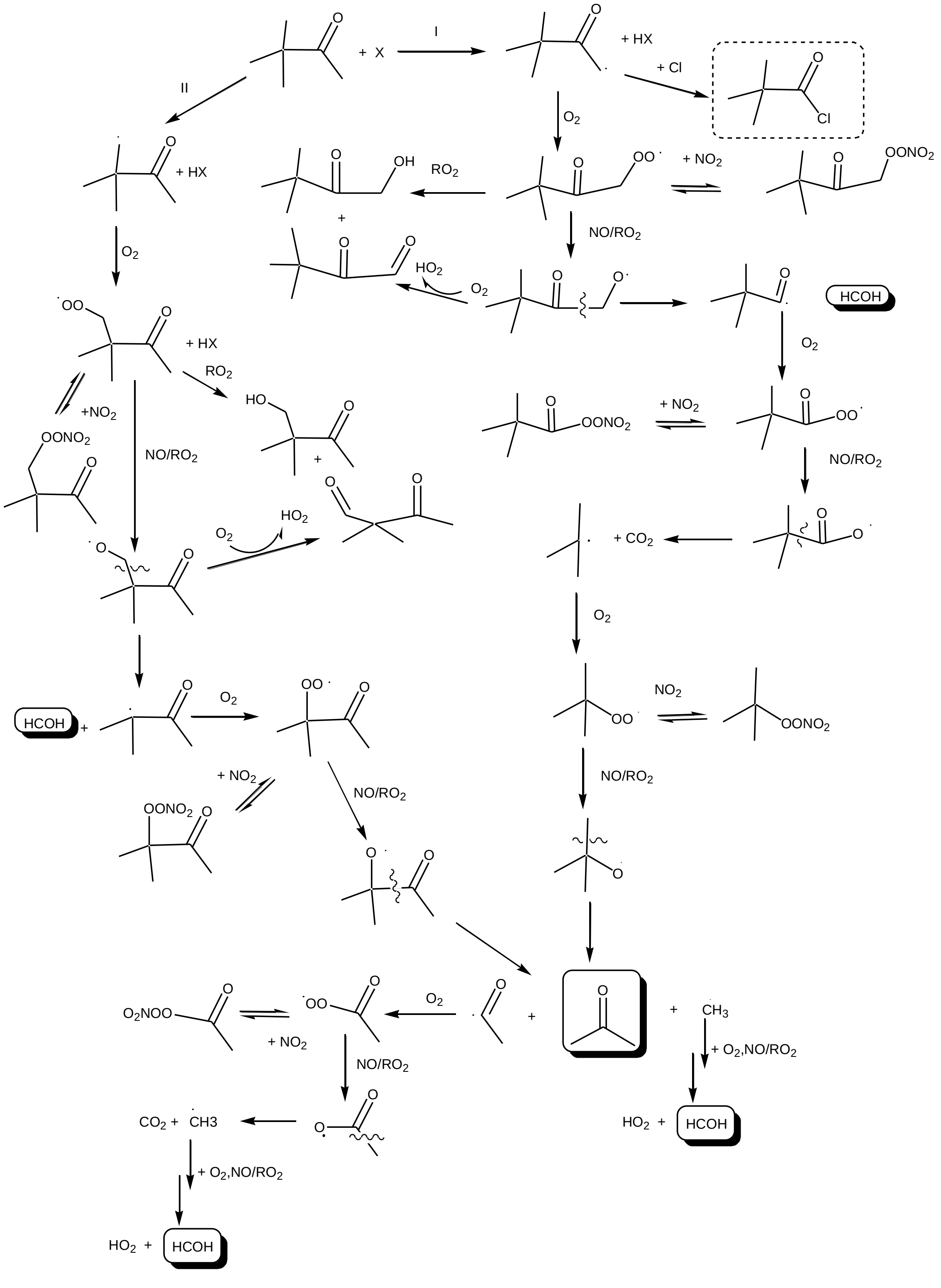


Fig. S12. Reaction mechanism for degradation of 3,3-dimethyl-2-butanone with the atmospheric oxidants in presence of NOx.

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