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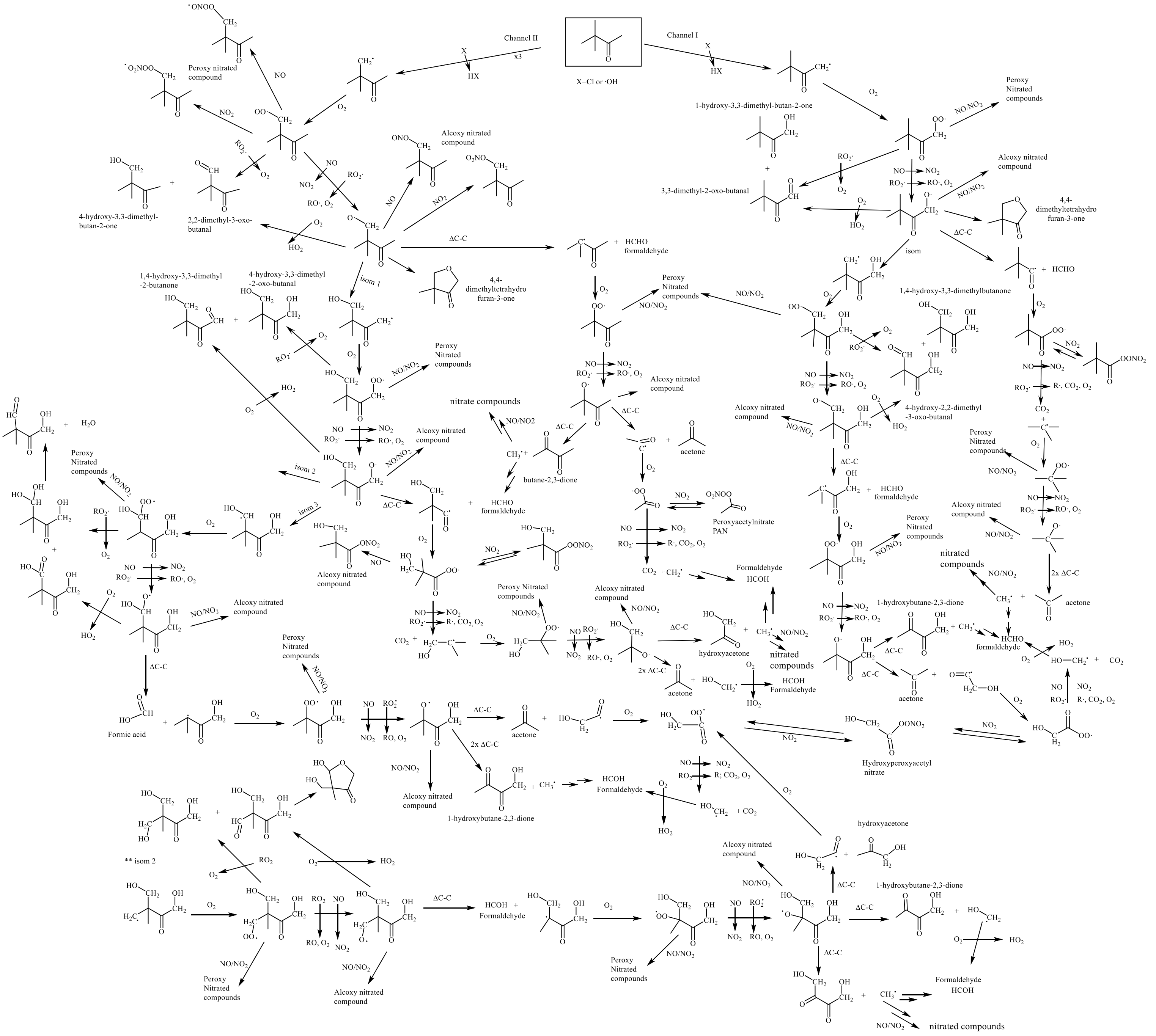
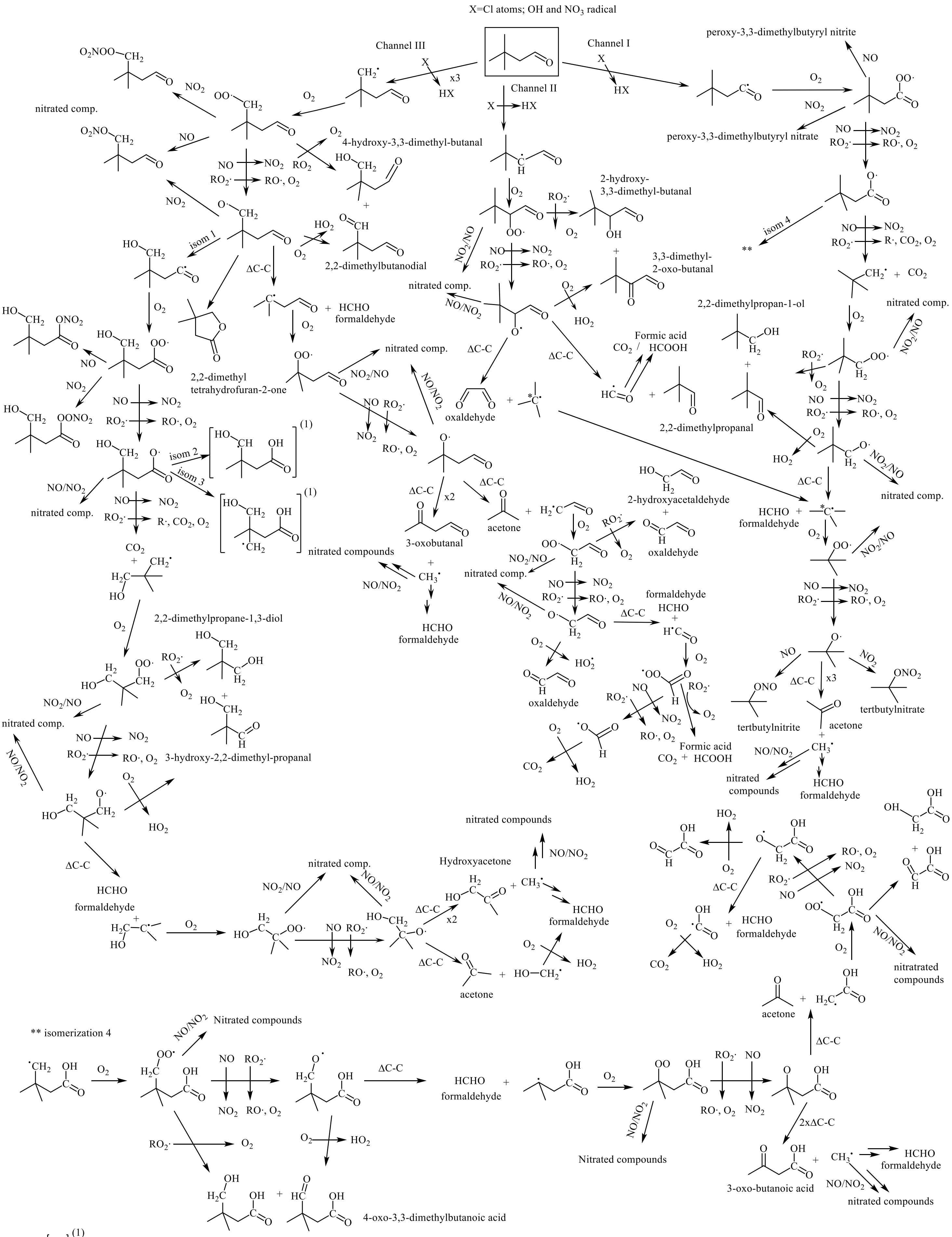


Scheme 1S: General Mechanism for the reactions of 33DMbutanone with Cl atom and OH radical.



[ ](1) -Alcoky radical that continues reacting according to the general principles of tropospheric reactivity

Scheme 2S. General Mechanism for the reactions of 33DMbutanal with the main atmospheric oxidants.

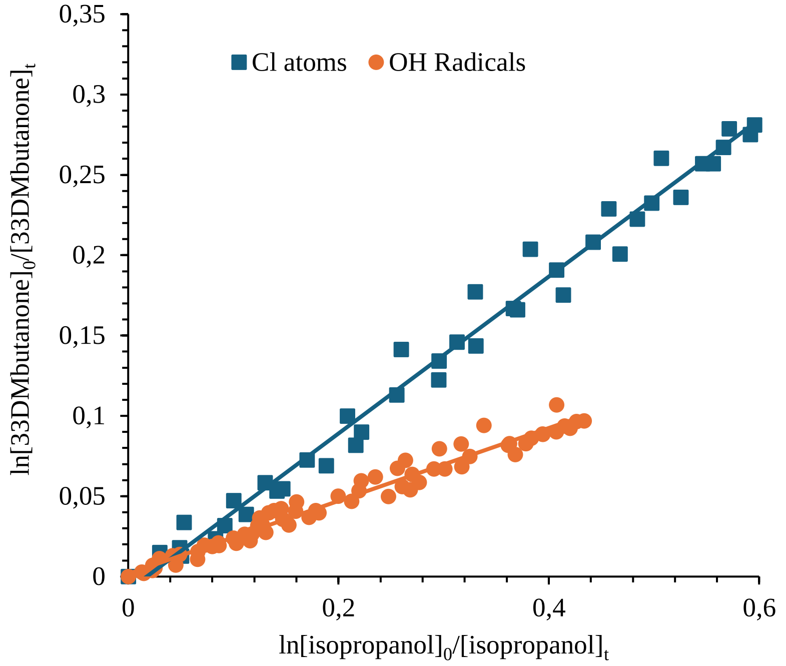


Figure 1S. Plot of Eq (I) for the reaction of 33DMbutanone with Cl atoms and OH using isopropanol as reference compound.

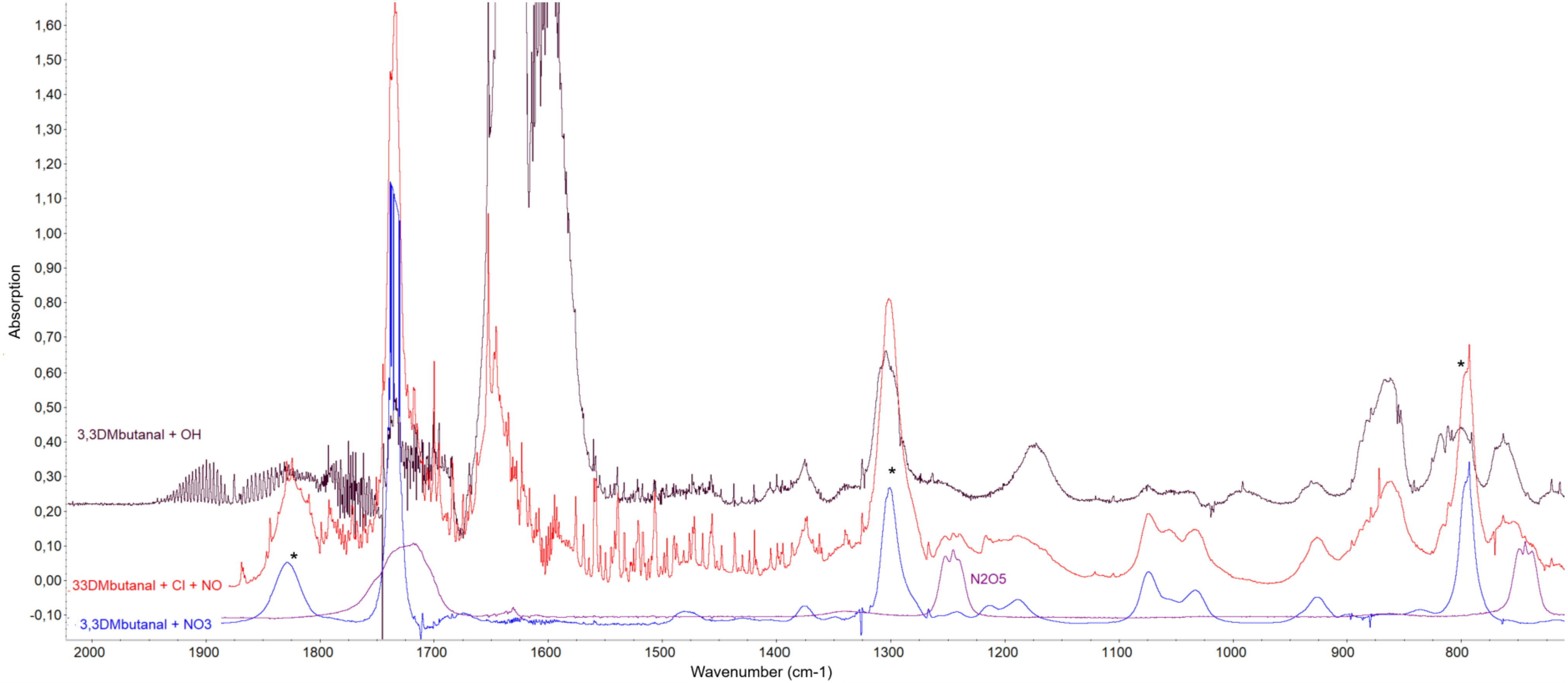
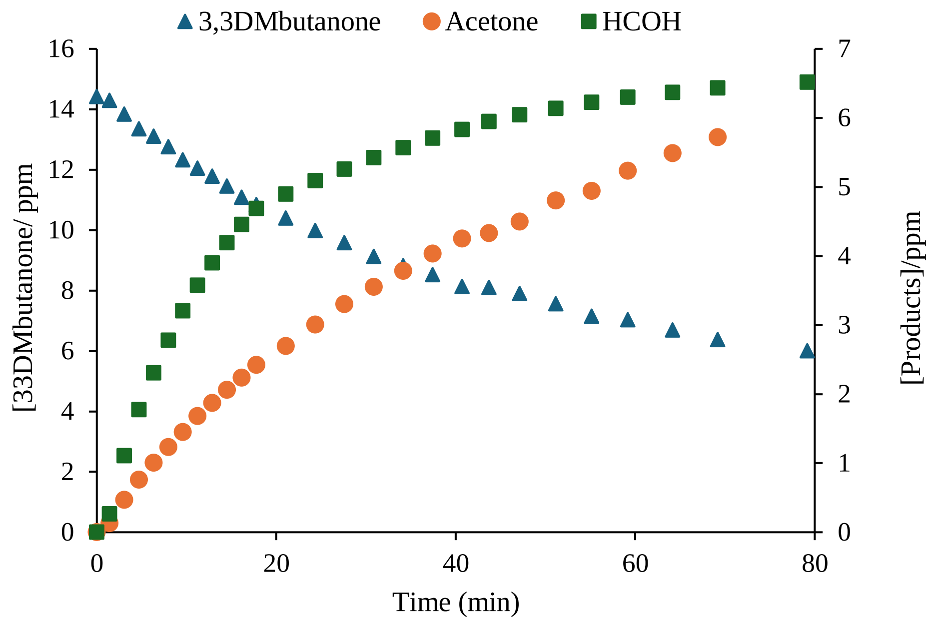


Figure 2S. IR absorption bands characteristic of alcoxy nitrates ($RONO_2$ ~1663, 1284, 853 cm^{-1}) peroxy nitrates ($ROONO_2$ ~1718, 1300 and 793 cm^{-1}) and (*) peroxycarbonyl nitrates ($ROO(CO)NO_2$~1830, 1300 and 793 cm^{-1}) formed in the reaction of 33DMbutanal +Cl + NO; 33DMbutanal + OH and 33DMbutanal + NO. And reference spectra of N_2O_5 (synthesized sample).

a)



b)

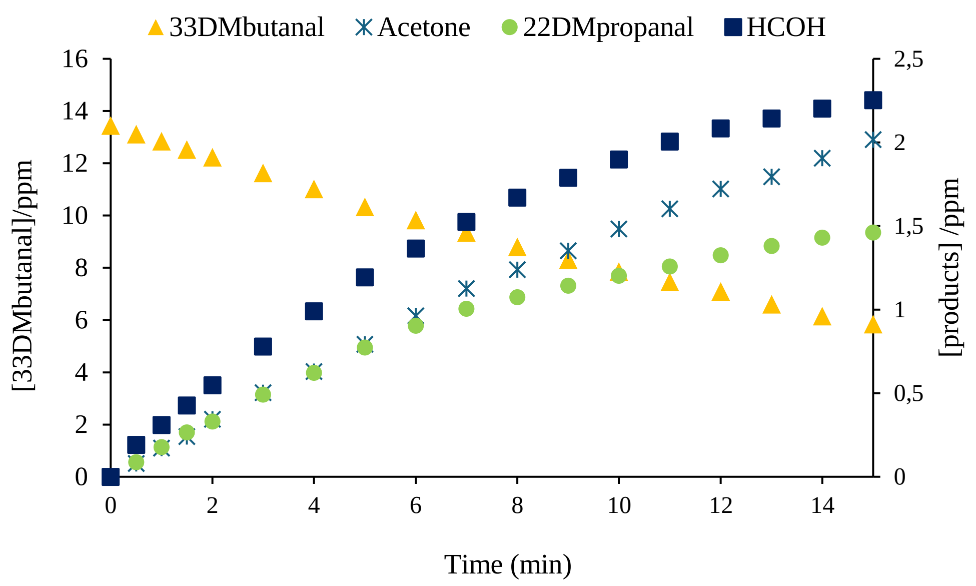


Figure 3S. Time-concentration profiles of the products formed and the carbonyl reactanted for the reaction of 33DMbutanone (a) and 33DMbutanal with Cl (b).

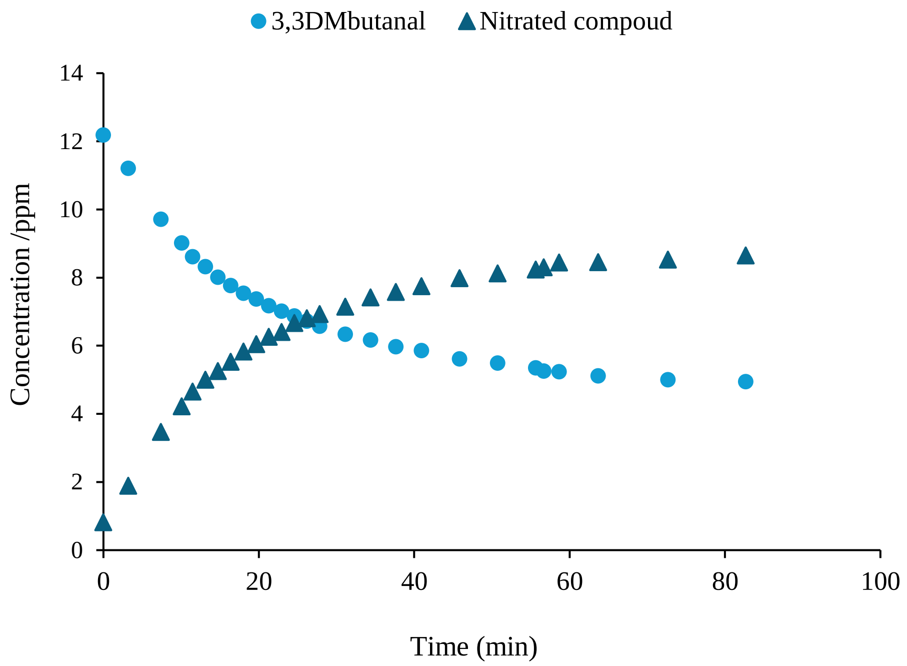


Figure 4S. Time-concentration profiles of the nitrated compounds formed for the reaction of 33DMbutanal with NO_3.

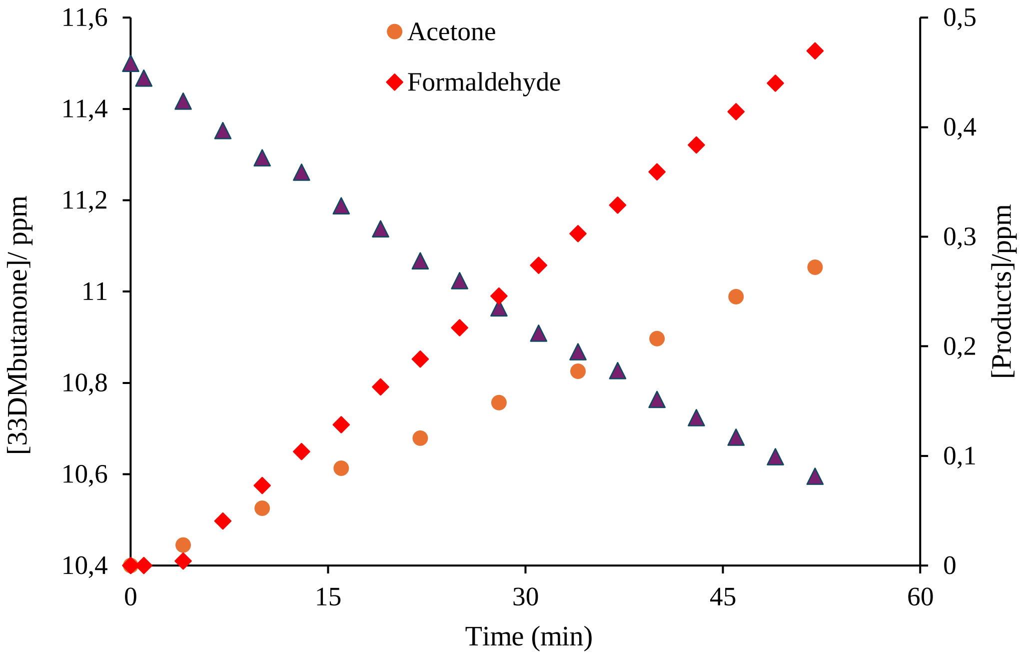
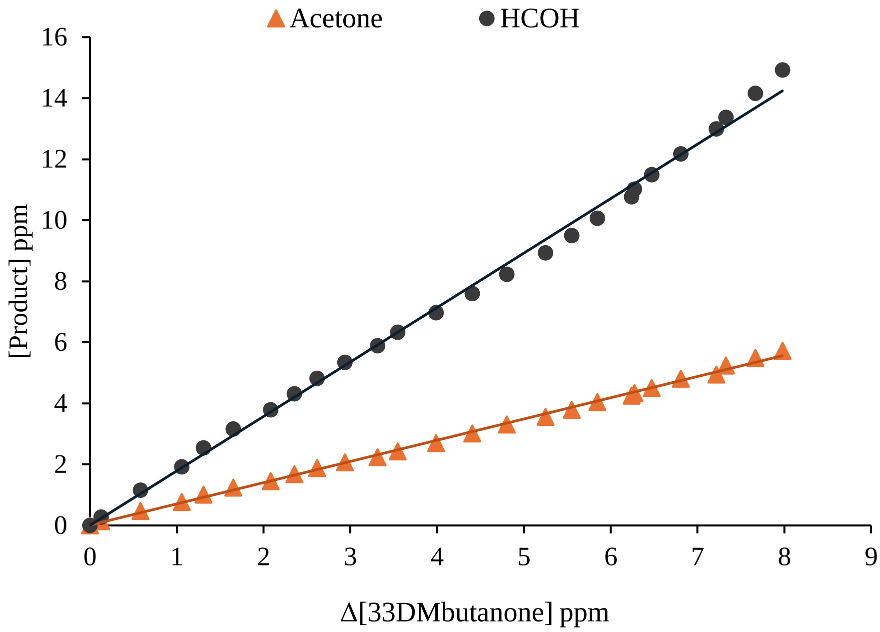


Figure 5S. Time-concentration profiles of product formed and the carbonyl reactanted for the reaction of 33DMbutanone with OH in the absence of NO.

a)



b)

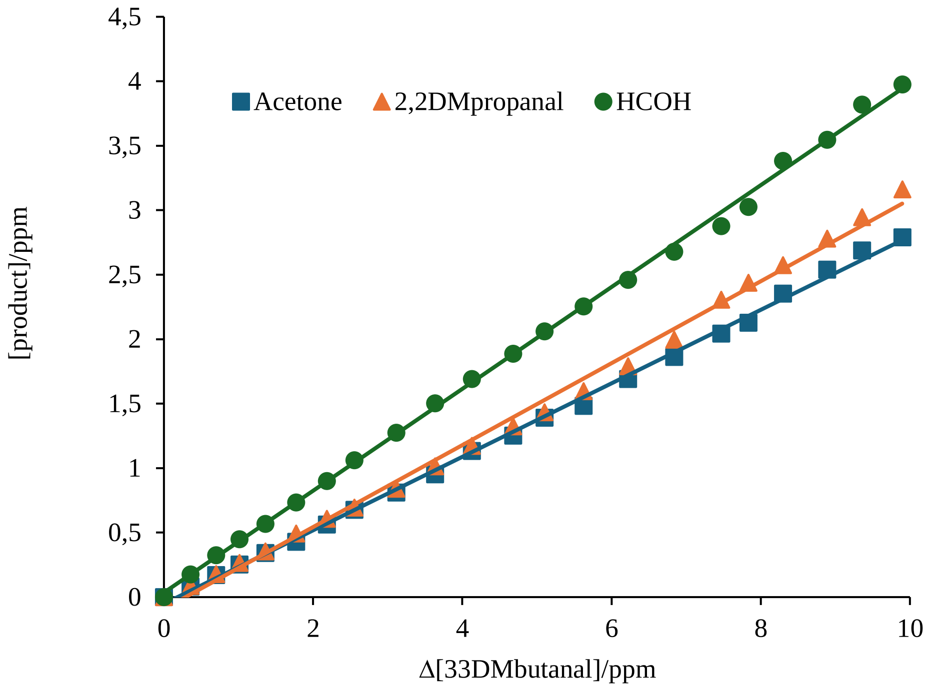


Figure 6S. Plots of the reaction product formed versus the consumption of carbonyl in the reaction of Cl atoms with 33DMbutanone (a) and with 33DMbutanal (b).

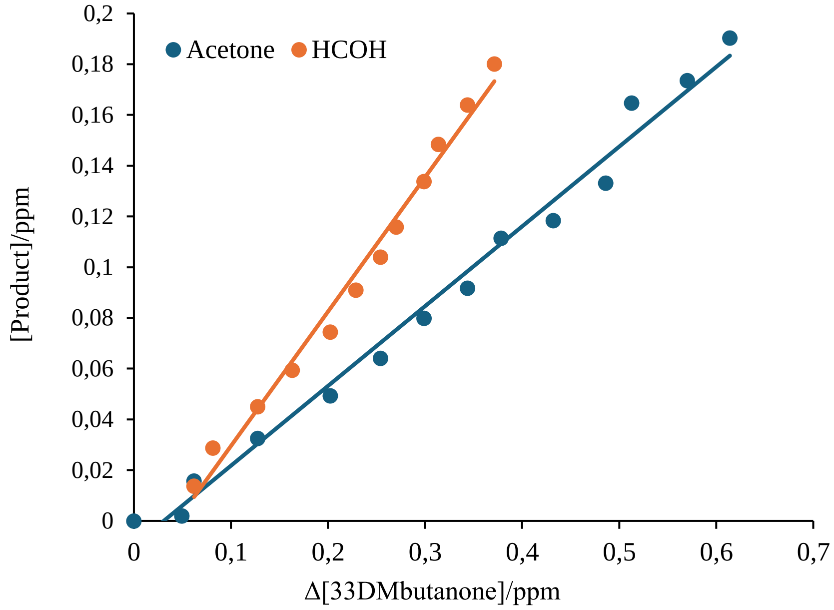
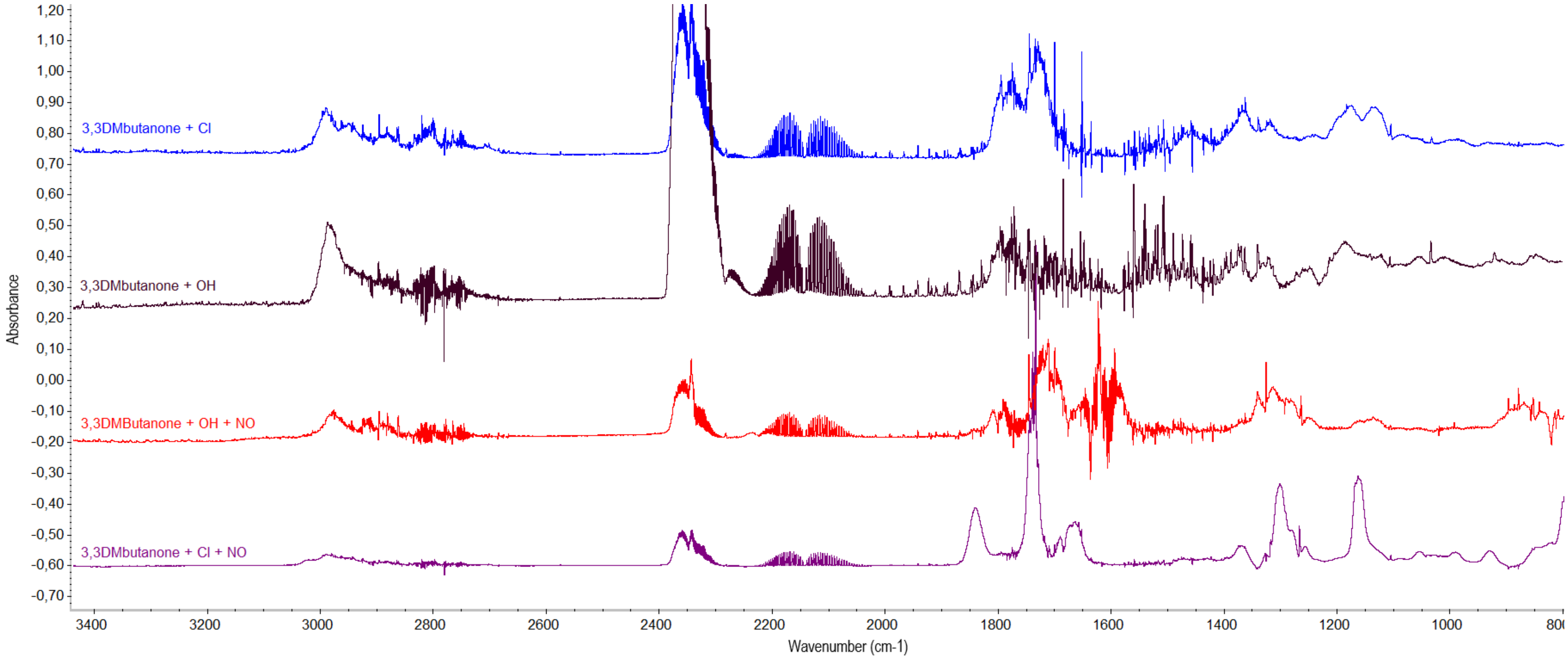


Figure 7S. Plots of the reaction product formed versus the consumption of 33DMbutanone in the reaction with OH in the absence of NO.

a)



3,3DMbutanone + Cl
3,3DMbutanone + OH
3,3DMButanone + OH + NO
3,3DMbutanone + Cl + NO
Absorbance
Wavenumber (cm-1)
1,20
1,10
1,00
0,90
0,80
0,70
0,60
0,50
0,40
0,30
0,20
0,10
0,00
-0,10
-0,20
-0,30
-0,40
-0,50
-0,60
-0,70
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000

b)

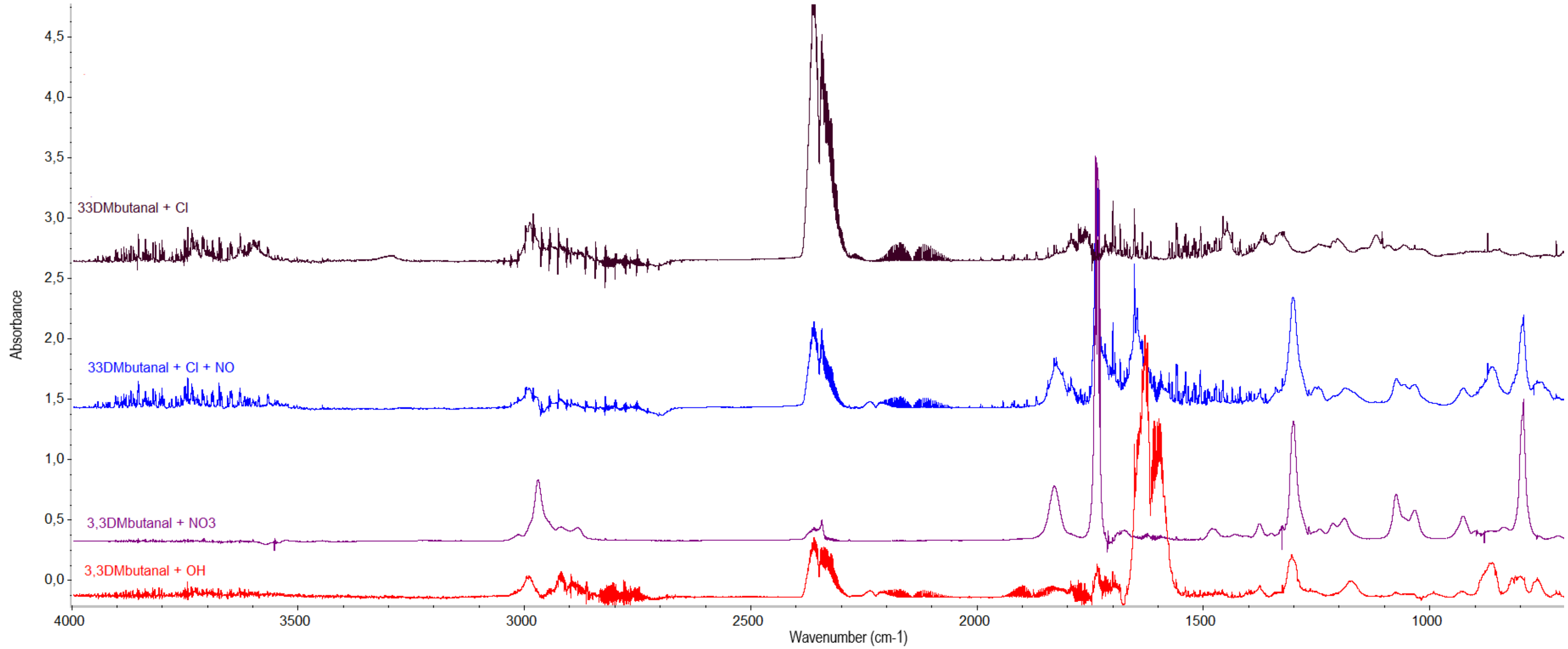


Figure 8S. Residual FTIR spectra of the reaction of (a) 33DMbutanone and (b) 33DMbutanal with atmospheric oxidants.

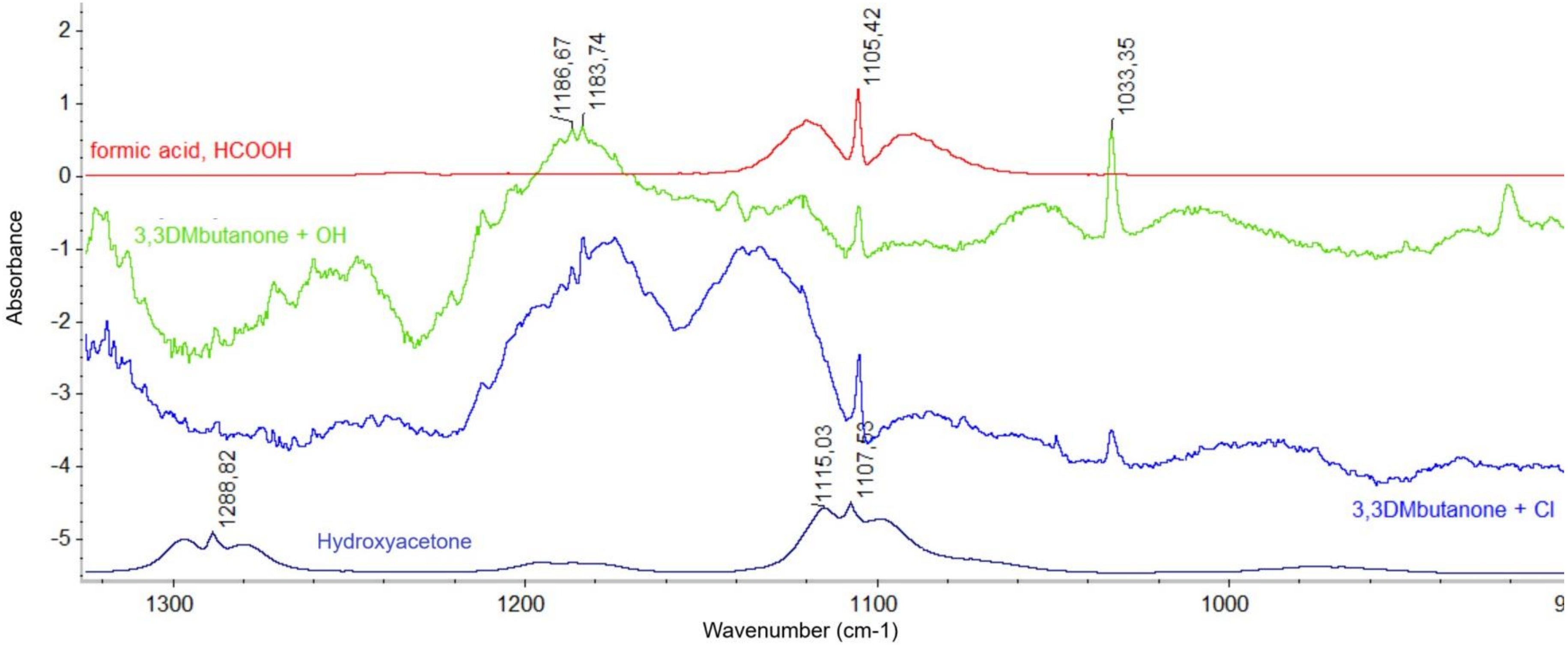


Figure 9S. Amplified Spectra for the 33DMbutanone + Cl and OH reactions and reference spectra of hydroxyacetone and formic acid.

(49 %)

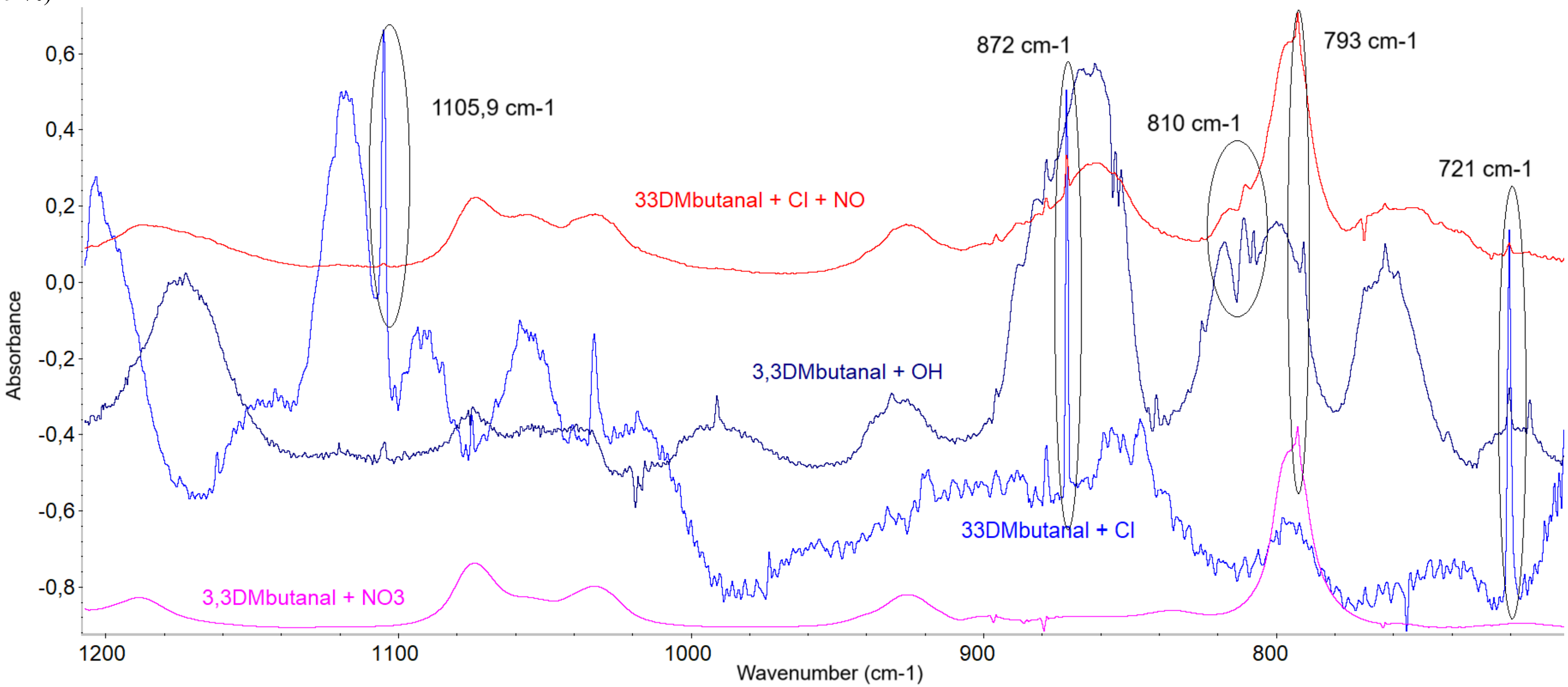


Figure 10S. Amplified Spectra for the 33DMbutanal + atmospheric oxidants reactions. Relation of common IR absorption bands; 1105,9 cm^{-1} reaction of 33DMbutanal + Cl and 33DMbutanal + Cl + NO (not nitrated compounds); 872 cm^{-1} reaction of 33DMbutanal + Cl; 33DMbutanal + Cl + NO and 33DMbutanal + OH (not nitrated compounds); 810 cm^{-1} reaction 33DMbutanal + Cl + NO and 33DMbutanal + OH (nitrated compound); 793 cm^{-1} reaction of 33DMbutanal + Cl + NO; 33DMbutanal + OH and 33DMbutanal + NO_3 (nitrated compound); 721 cm^{-1} reaction of 33DMbutanal + Cl; 33DMbutanal + Cl + NO and 33DMbutanal + OH (not nitrated compound).

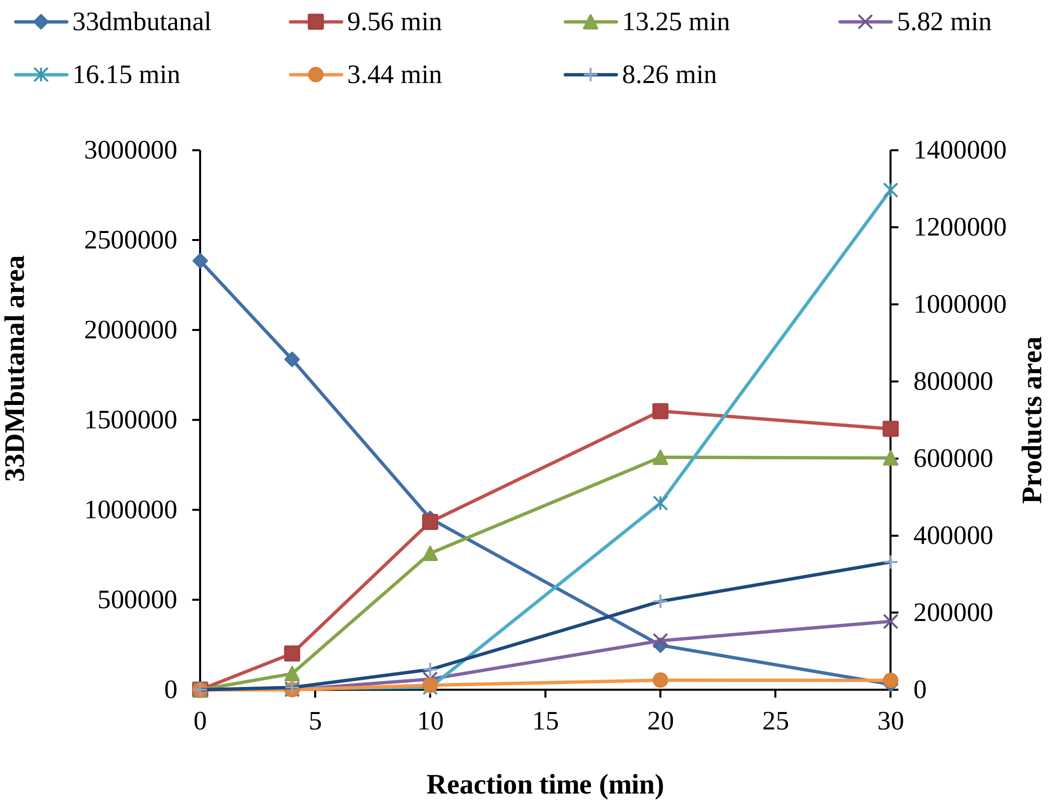


Figure 11S. Time evolution of the areas of chromatographic peaks of the reactant and products for the reaction of 33DMbutanal with Cl.

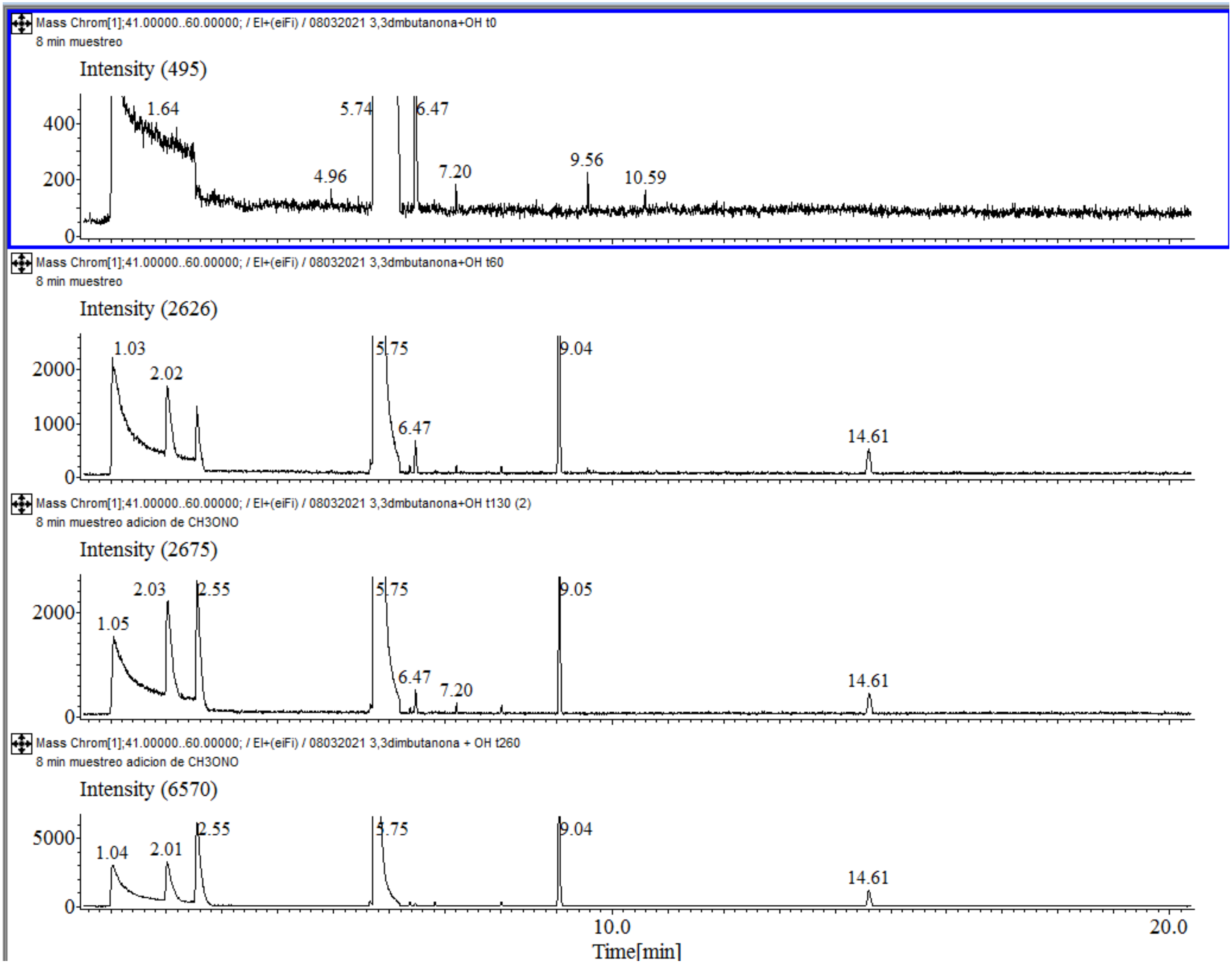


Figure 12S. GC-TOFMS generated chromatograms for the 33DMbutanone + OH +NO at different reaction times using EI ionization mode. Chromatograms have been magnified to better identification.

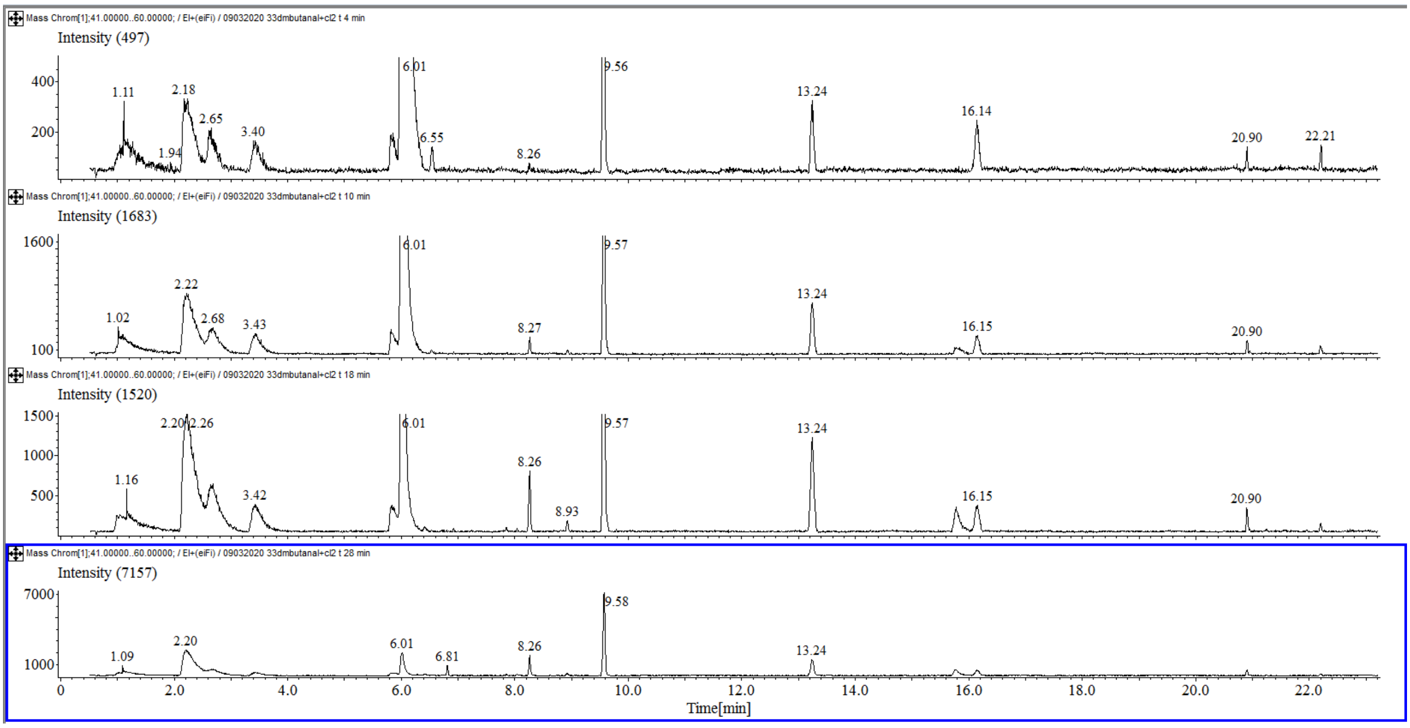


Figure 13S. GC-TOFMS generated chromatograms of 33DMbutanal + Cl at different reaction times using EI ionization mode. Chromatograms have been magnified to better identification.

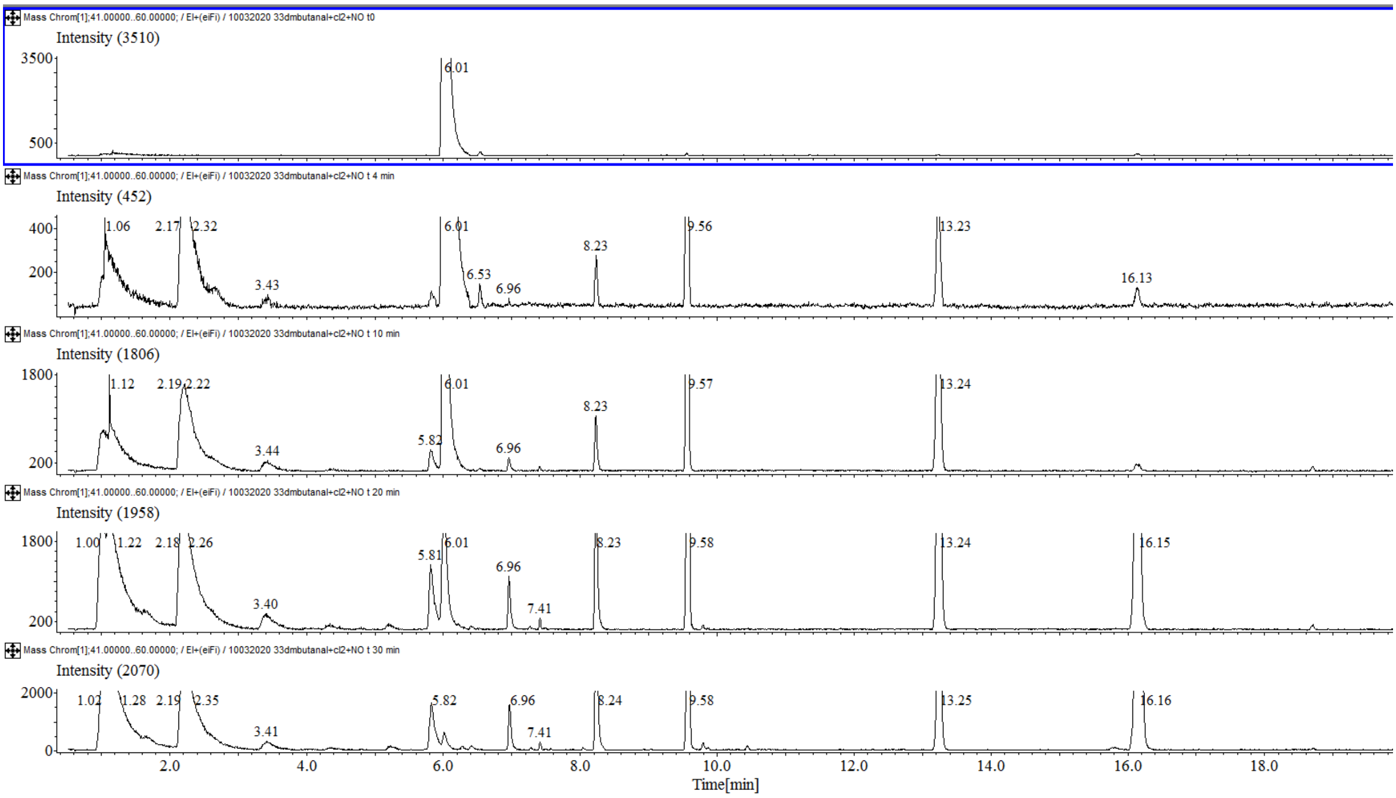


Figure 14S. GC-TOFMS generated chromatograms 33DMbutanal + Cl + NO at different reaction times using EI ionization mode. Chromatograms have been magnified to better identification.

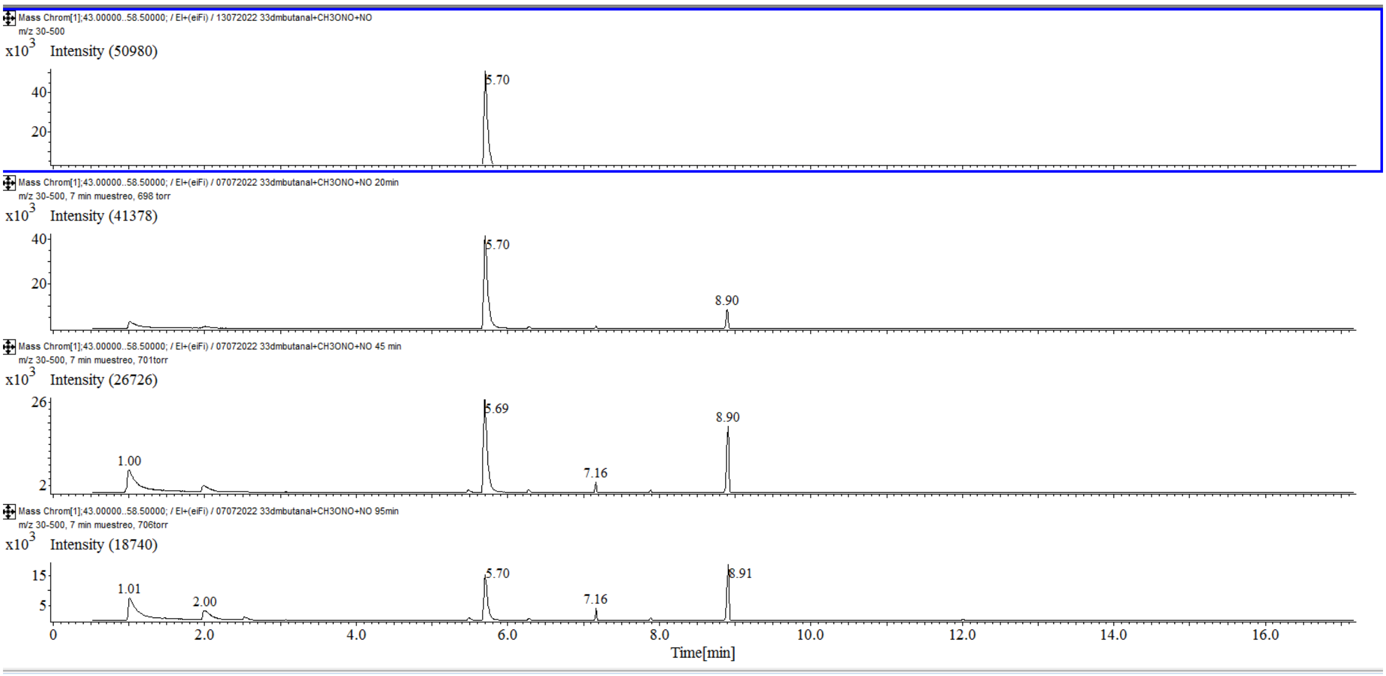


Figure 15S. GC-TOFMS generated chromatograms of 33DMbutanal + OH reaction at different reaction times using EI ionization mode.

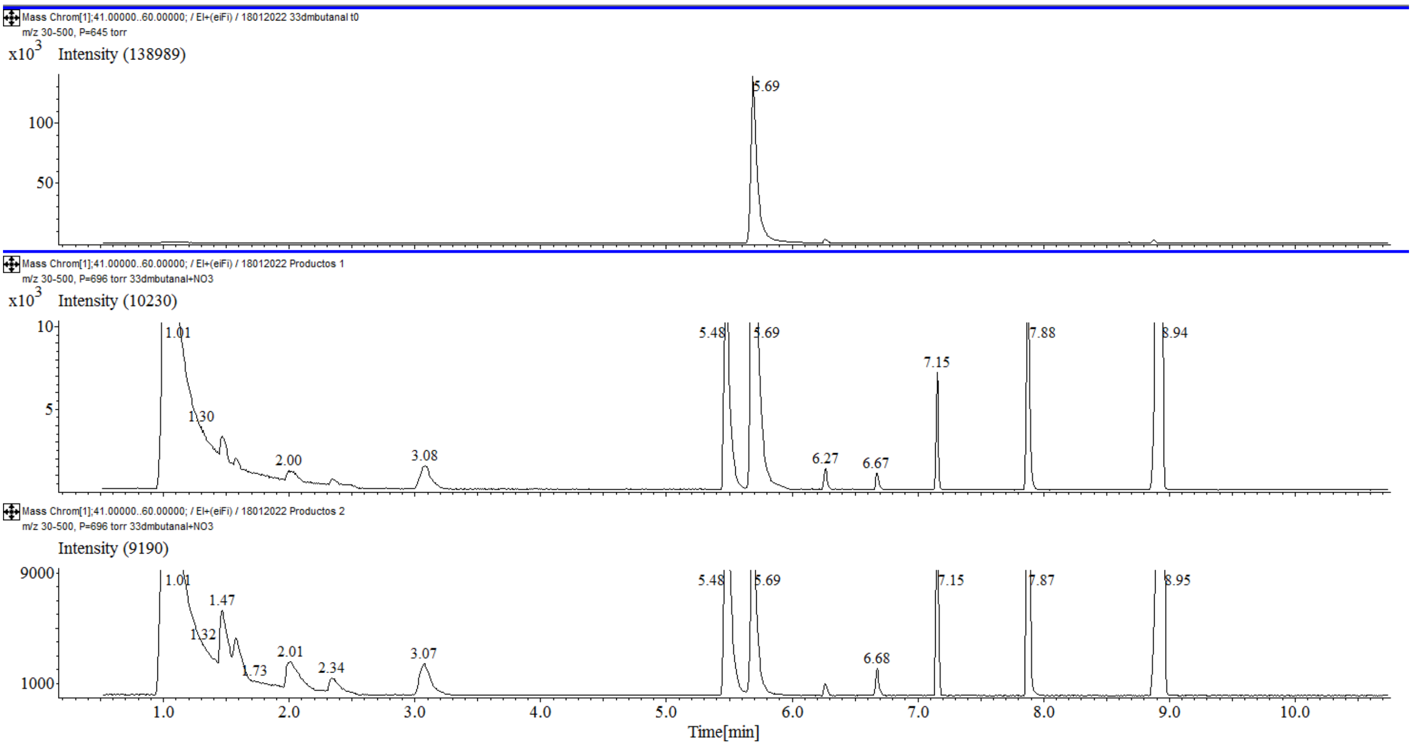
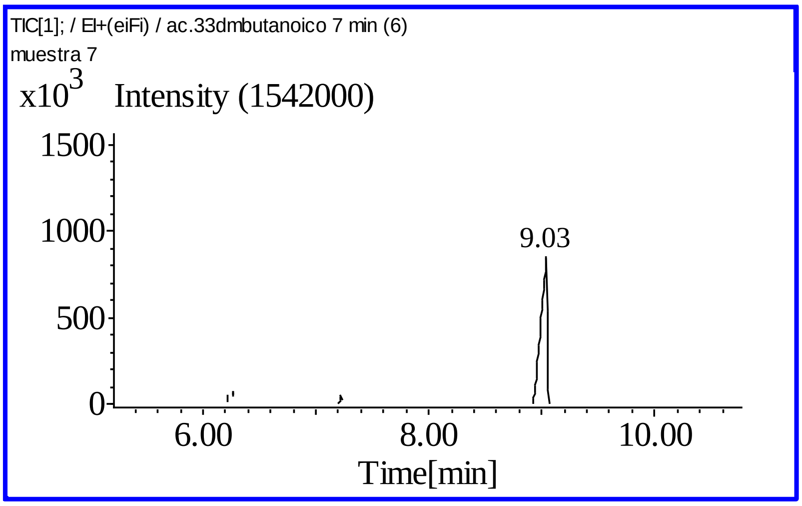


Figure 16S. GC-TOFMS generated chromatograms of 33DMbutanal + NO_3 reaction at different reaction times using EI ionization mode. Chromatograms Product 1 and 2 have been magnified to better identification.

(a)



(b)

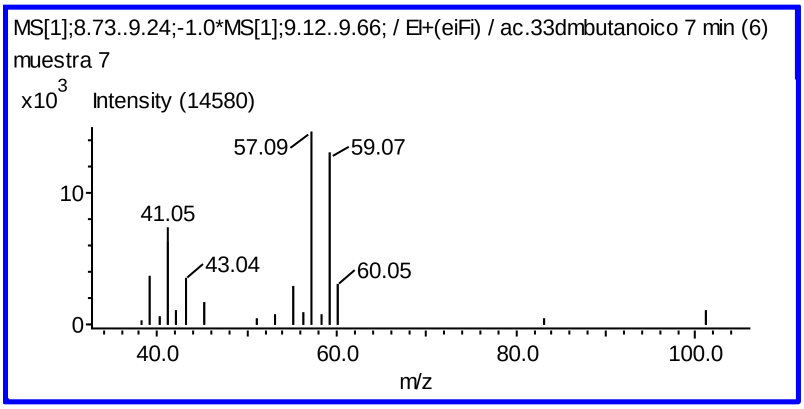


Figure 17S. GC-TOFMS chromatogram (a) and mass spectrum (b) of a commercial sample of 33DMbutanoic acid.

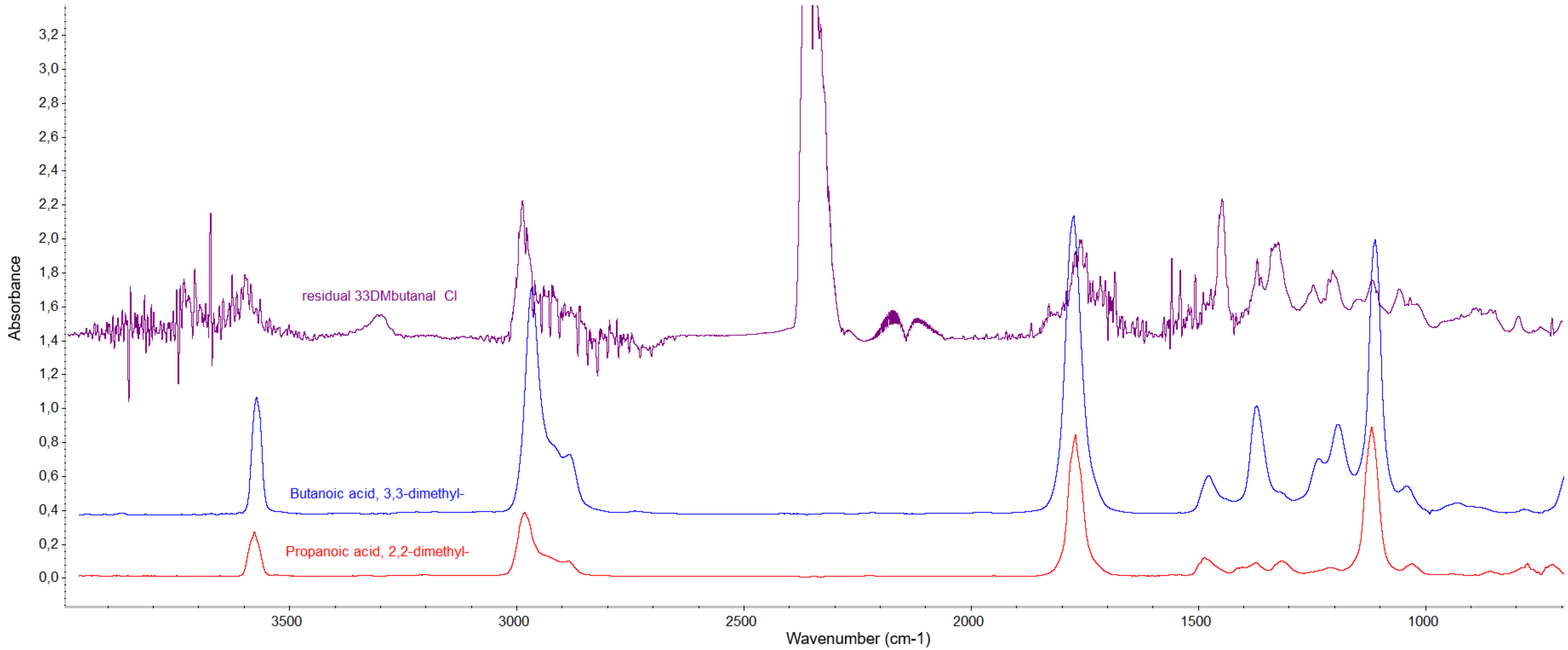
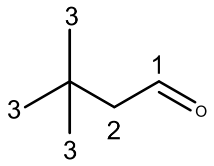
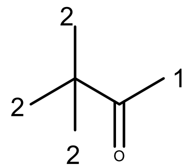


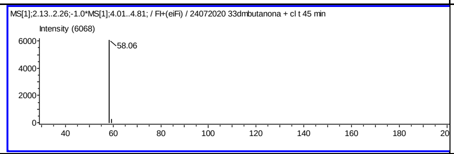
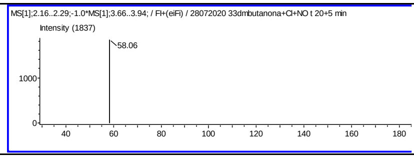
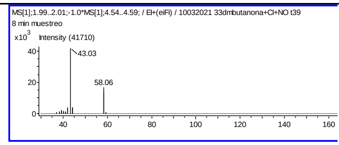
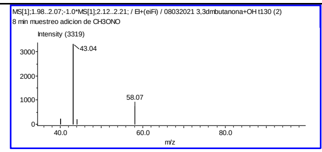
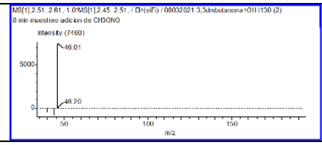
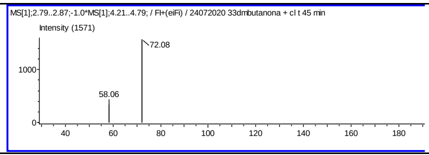
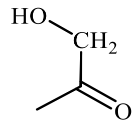
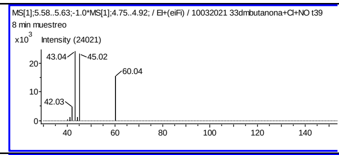
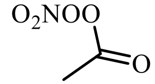
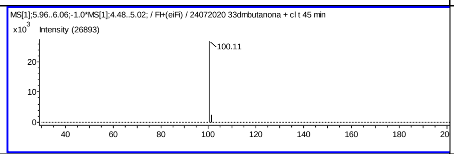
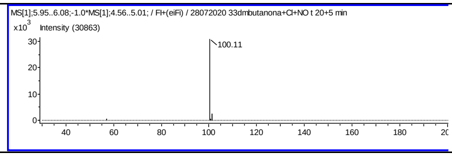
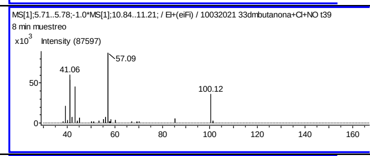
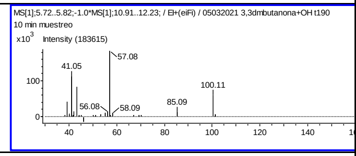
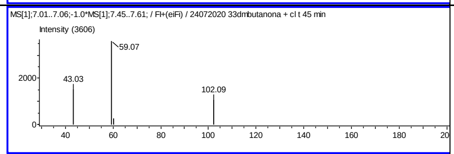
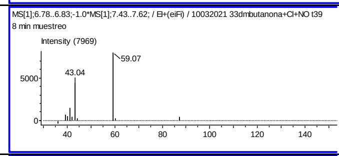
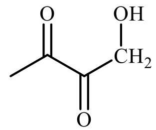
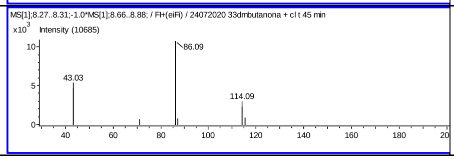
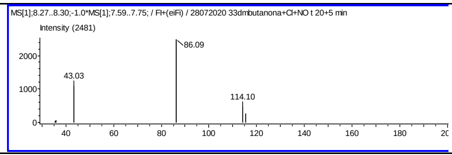
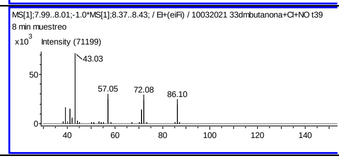
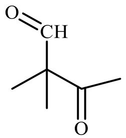
Figure 18S. Amplified Spectra for the 33DMbutanal + Cl atoms in the absence of NO together with the references spetra of 33DMbutanoic acid and 22DMpropanoic acid.

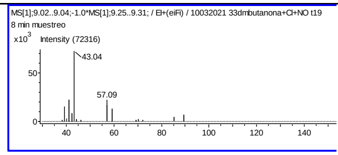
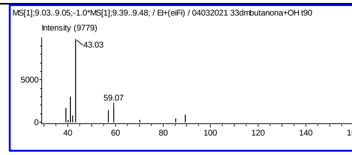
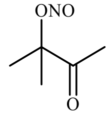
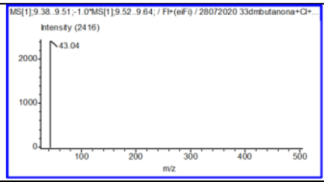
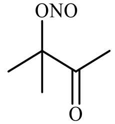
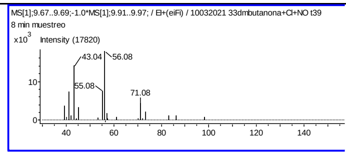
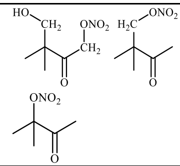
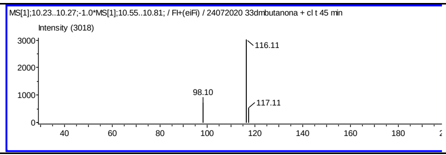
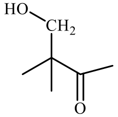
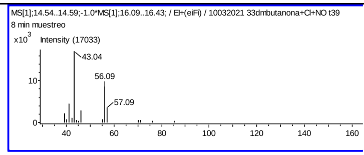
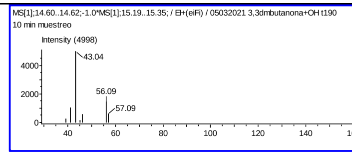
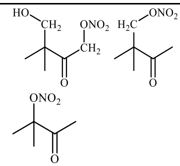
Table 1S. Attack Percentage in the different sites in the reaction of 33DMbutanal and 33DMbutanone with atmospheric oxidants base on SAR methods

Compound		33DMbutanal			33DMbutanone	
Structure						
* SAR method		$k_{abs} = 3(k_{prim}F(C)) + k_{sec}F(C)F(-CHO) + k_{-COH}F(CH_2)$			$k_{abs} = 3(k_{prim}F(-CR_2CO-)) + (k_{prim}F(-CO-)$	
Attack site		1	2	3**	1	2**
Rate coefficient (cm^3 $molecule^{-1}$ s^{-1})	*a Cl	0.405	0.282	0.224	0.0105	0.159
	*b OH	20.75	0.861	0.167	0.102	0.53
	*c NO_3	1.274	0.743	0.0002	-	
Overall rate coefficient (k_{abs}) (cm^3 $molecule^{-1}$ s^{-1})	a Cl	0.405+0.282+0.224x3=1.361			0.0105+0.159x3=0.49	
	b OH	20.75+0.861+0.167x3=22.11			0.102+0.53x3=1.69	
	c NO_3	1.274+0.743+0.0002x3=2.017			-	
Attack Percentages (%)	Cl	~30	~21	~49	~2	~98
	OH	~94	~4	~2	~6	~94
	NO_3	~63	~37	0	-	

[a]10^{-10}; [b]10^{-12}; [c]10^{-14}. *SAR parameters Cl reaction from Calvert et al 2011, Farrugia et al 2015 and Carter et al 2021; EPA Suit™ for OH reaction and Kerdouci et al 2014 for NO_3 reactions. **3 attack site.

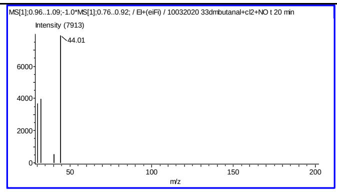
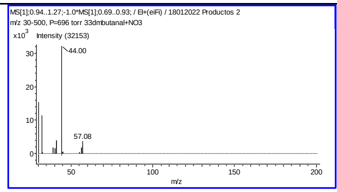
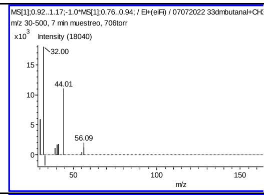
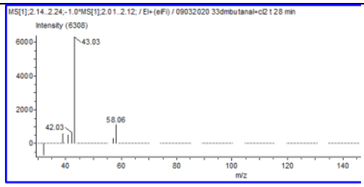
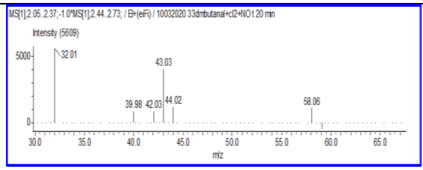
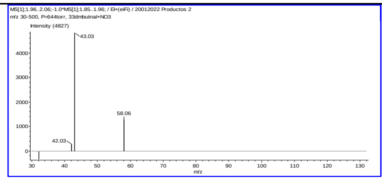
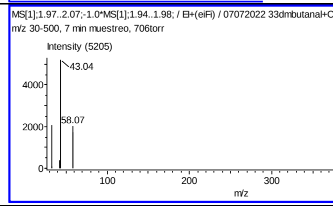
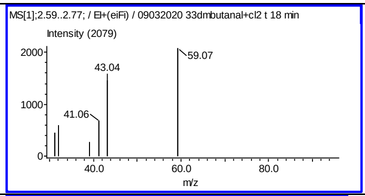
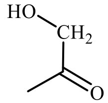
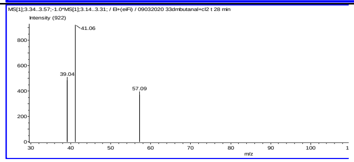
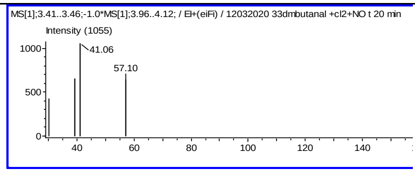
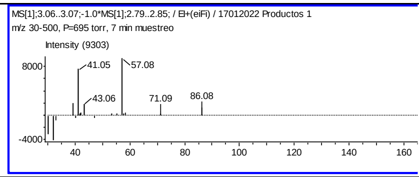
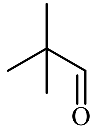
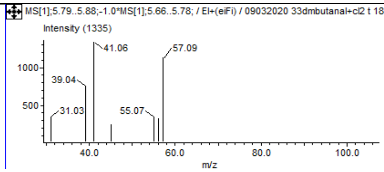
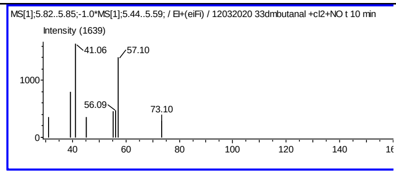
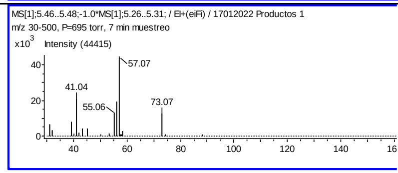
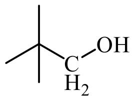
Table 2S. Mass spectra of the reaction products generate in the reactions of 33DMbutanone with Cl with and without NO using Field and Electron Ionization and 33DMbutanone with OH in presence of NO and electron ionization. Only the more intensity peaks have been considered.

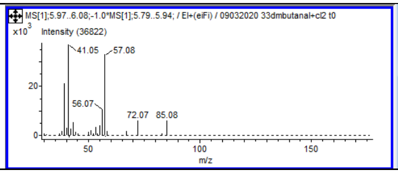
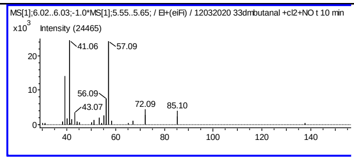
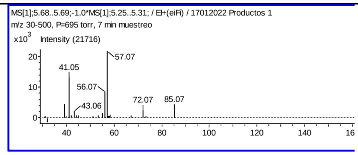
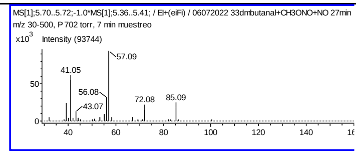
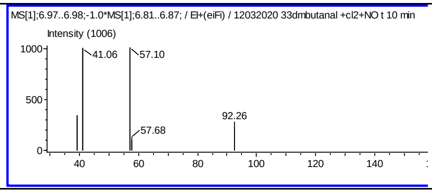
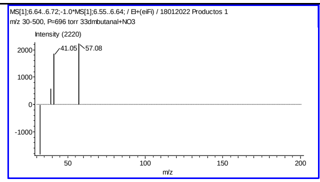
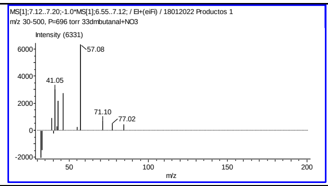
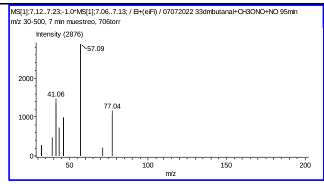
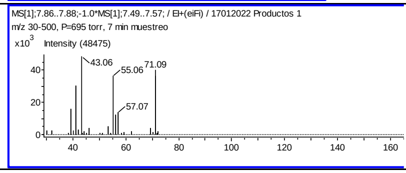
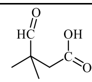
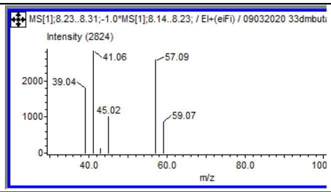
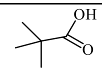
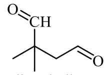
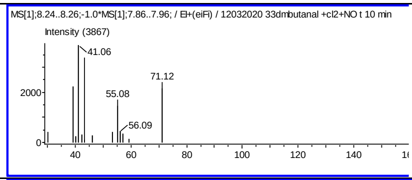
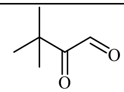
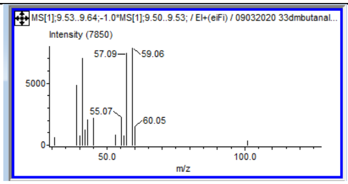
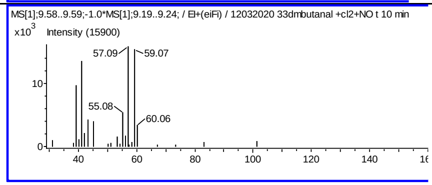
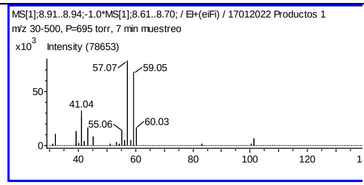
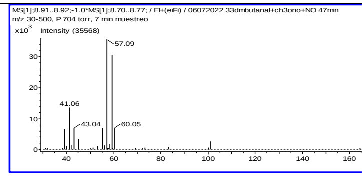
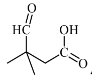
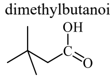
tr (min)	Mass Spectrum					Reaction product
	Field Ionization		tr (min)	Electron ionization		
	Without NO	With NO		Cl	OH	
				With NO	With NO	
2.2 All channels			2*			Acetone
2.55						Nitrated compound
2.87						
5.59			5.59			 (PAN)
6			5.73*			33DMbutanone (reactant)
7.03			6.81*			
8.28			8.00*			

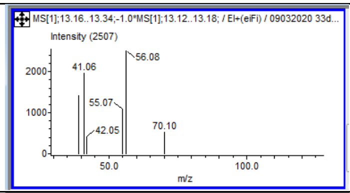
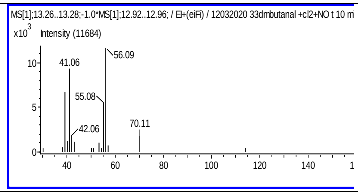
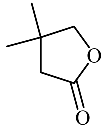
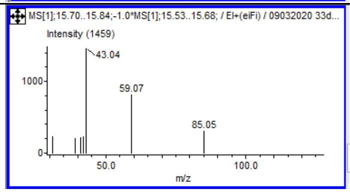
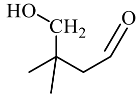
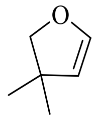
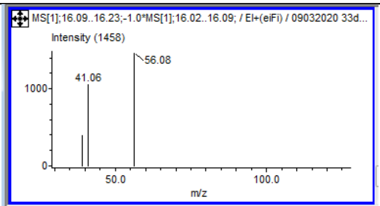
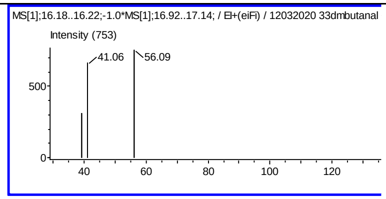
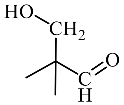
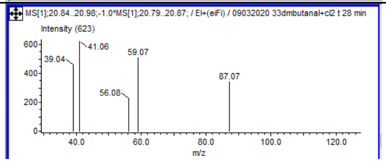
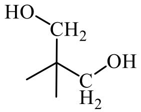
9.04			9.04*			 2,2-dimethyl-3-butyl peroxynitrite
9.44						
9.68			9.68			
10.26			10.26			
			14.57			

*Shorter Time retention than FI experiment due to a new chromatographic column.

Table 3S. Mass spectra of the reaction products for the reactions of 33DMbutanal with Cl (with and without NO) and NO_3 and OH radical, using Electron Impact ionization.

t_r (min)	Reaction 3,3DMbutanal +				Reaction product
	Cl		NO_3	OH	
	Without NO	With NO			
1					Unidentified
2.18 All channels					Acetone
2.65 Channel III					 Hydroxyacetone
3.43 (3.08) Channel I and II					 2,2-dimethyl-propanal
5.82 (5.48) Channel I					2,2-dimethylpropan-1-ol 

6.01 (5.70)*					3,3-dimethyl-butanal (reactant)
6.97(6.68)* Channel II					Nitrated compound
7.16 Channel I					Nitrated compound
7.88 Channel II					4-oxo-3,3-dimethylbutanoic acid??
8.23**					2,2-dimethylpropanoic acid 2,2-dimethylbutanodial
8.26					3,3-dimethyl-2-oxo-butanal
9.56 (8.95)* Channel I					4-oxo-3,3-dimethylbutanoic acid?? 3,3dimethylbutanoic acid

13.25 Channel III					2,2-dimethyl tetrahydrofuran-2-one
15.78 Channel III					4-hydroxy-3,3-dimethyl butanal Or 2,3-dihydro-4,4-dimethylfuran
16.15 Channel III					3-hydroxy-2,2-dimethyl-propanal
20.91 Channel III					2,2-dimethylpropane-1,3-diol

- *tr for OH and NO_3 experiment. Shorter Time retention than Cl experiments due to a new chromatographic column.
- **Secondary product. At large time reaction