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Supplement of

Reactivity study of 3,3-dimethylbutanal and 3,3-dimethylbutanone: kinetics, reaction products, mechanisms, and atmospheric implications

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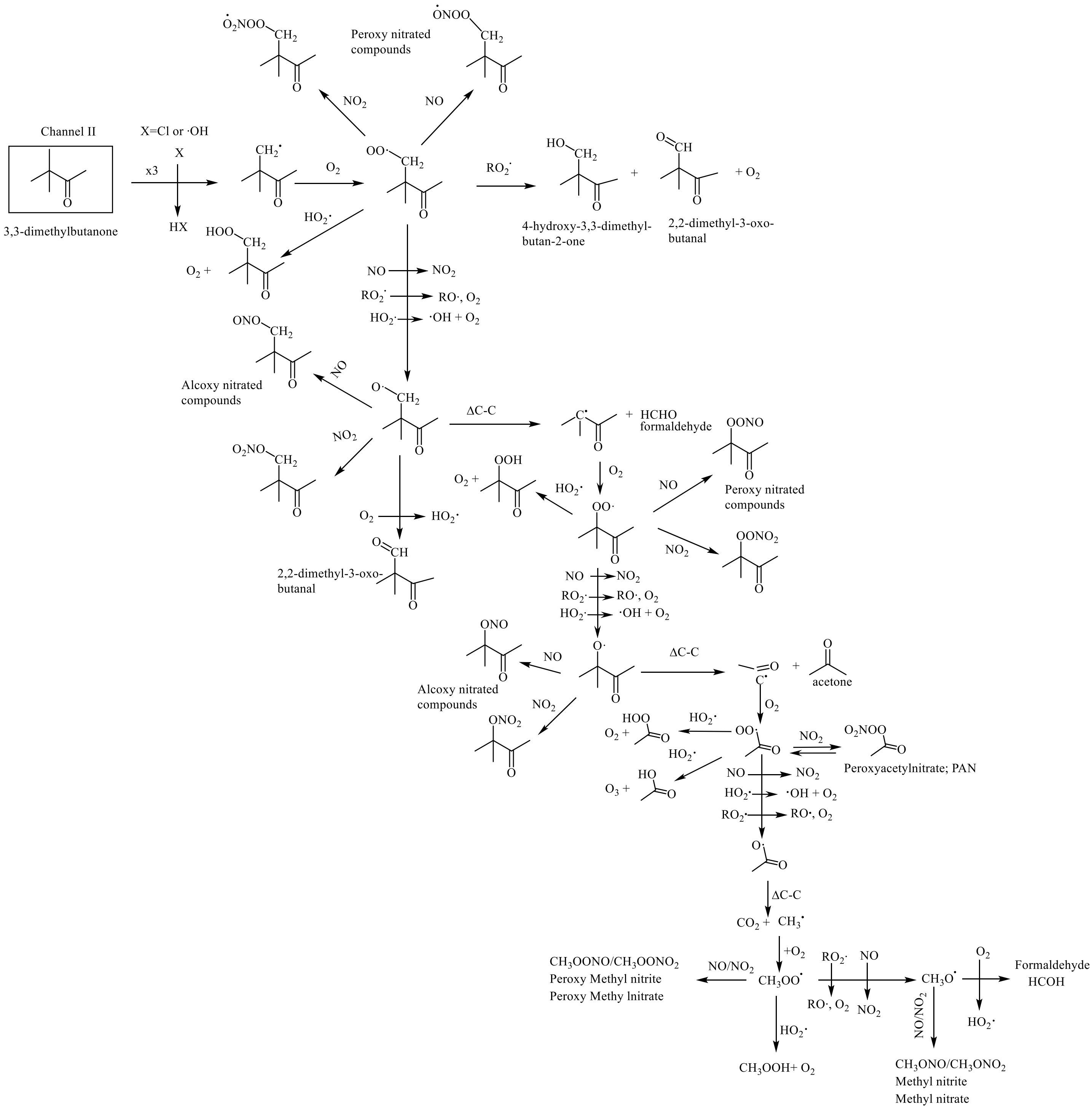
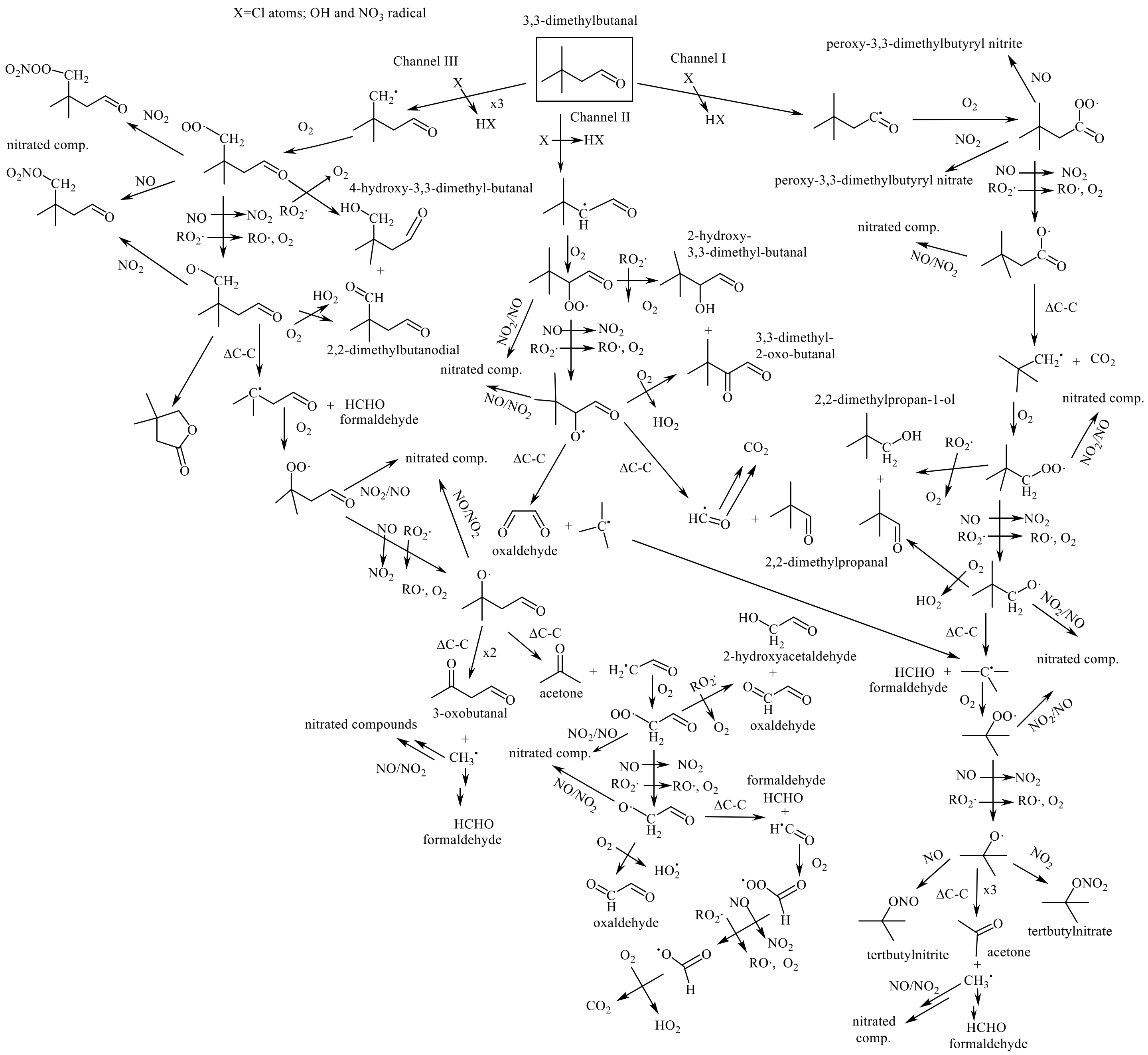
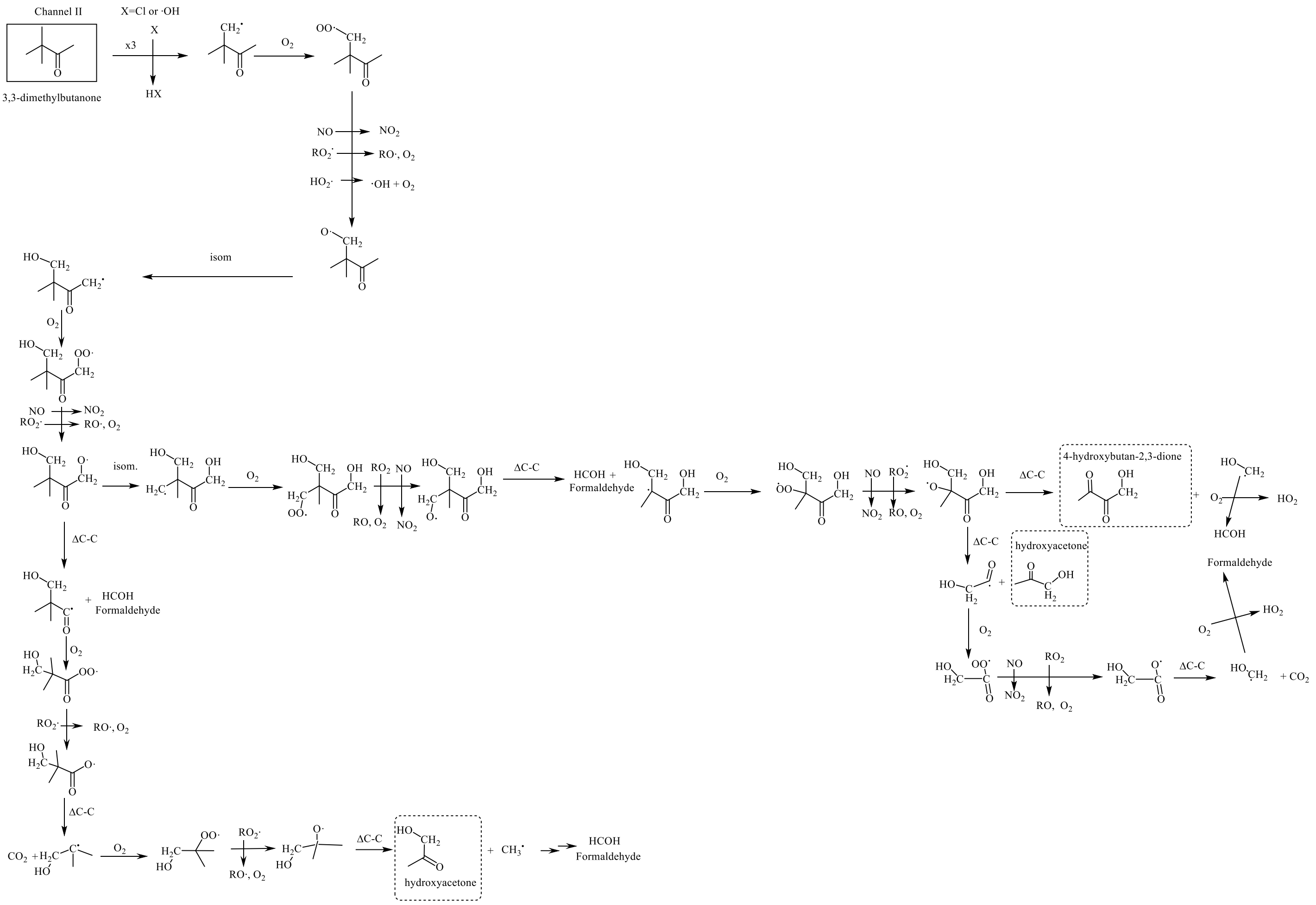
S1. Schemes



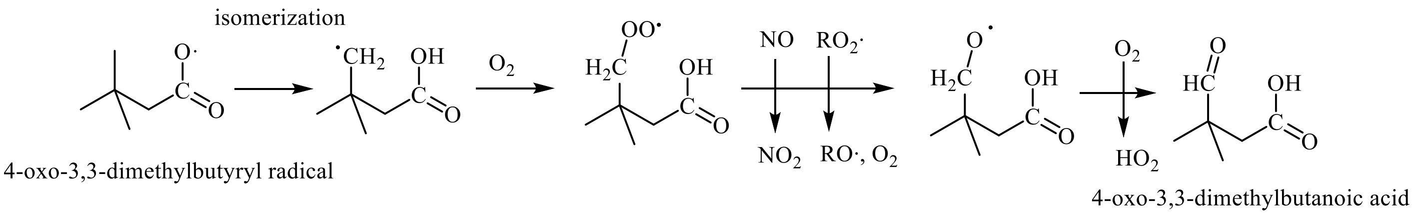
Scheme S1: General mechanism proposed for the reactions of 33DMbutanone with Cl atoms and OH radicals in the presence and absence of NO, including only the major channel. x3 indicates three equivalent attack positions.



Scheme S2. General mechanism for the reactions of 33DMbutanal with the main atmospheric oxidants. The $RO_2\cdot + HO_2\cdot$ reactions are excluded to avoid further complicating the mechanism for 33DMbutanal, as they are significant only in the absence of NOx, that is, in remote unpolluted atmospheres.



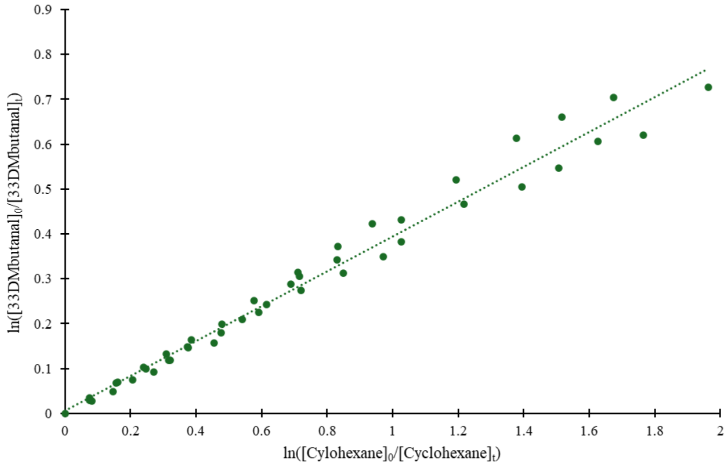
Scheme S3. Pathway proposed to explain the formation of hydroxyacetone and 4-hydroxybutan-2,3-dione in the reaction of 33DMbutanona with Cl atoms and OH radicals.



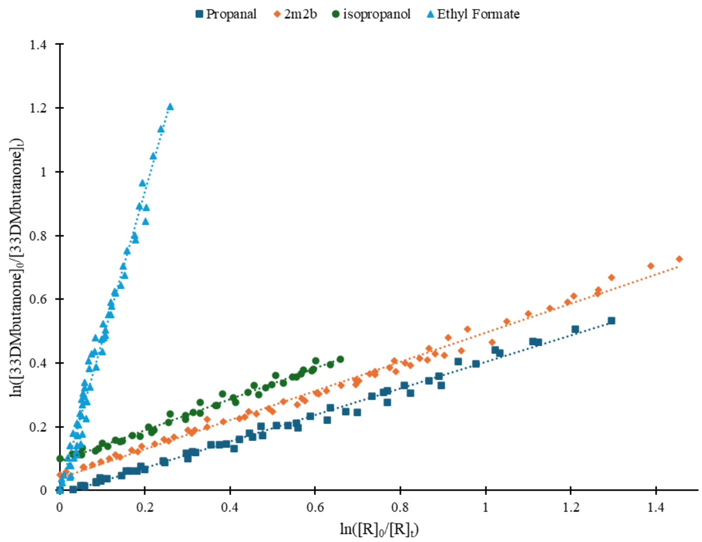
Scheme S4. Pathway proposed to explain the formation of 4-oxo-3,3-dimethylbutanoic acid in the reaction of 33DMbutanal with Cl atoms and OH and NO_3 radicals.

S2. Figures

a)



b)



c)

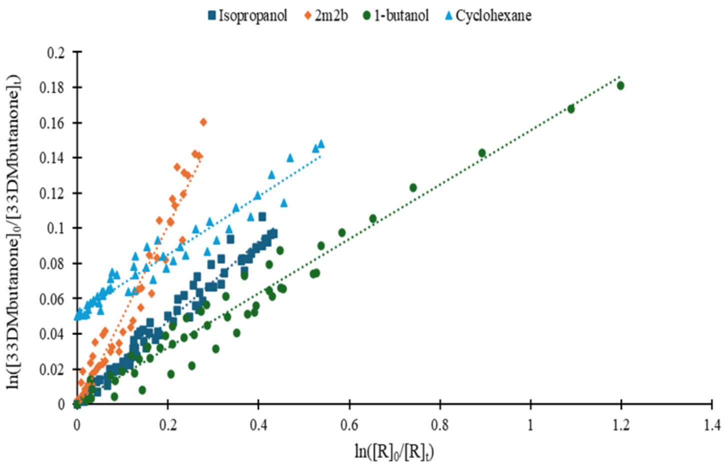
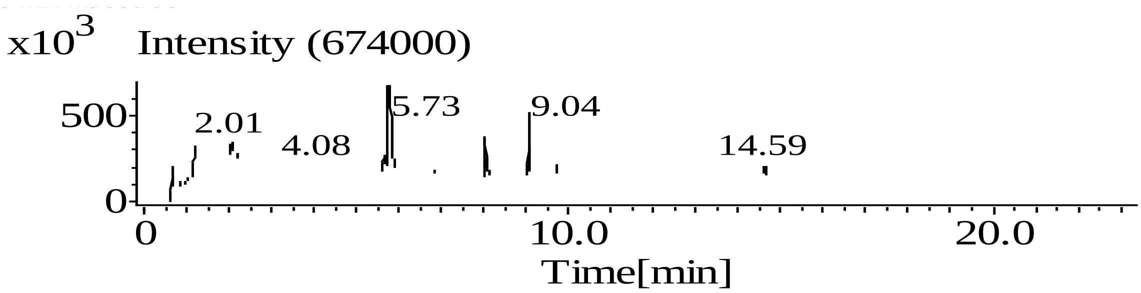


Figure S1. Plot of Eq. (I) for the reaction of 33DMbutanal with Cl atoms using cyclohexane as reference compound (a) and for 33DMbutanone with Cl atoms (b) and OH radical (c) using different references compounds. In some cases, the plots have been displaced for clarity.

a)



b)

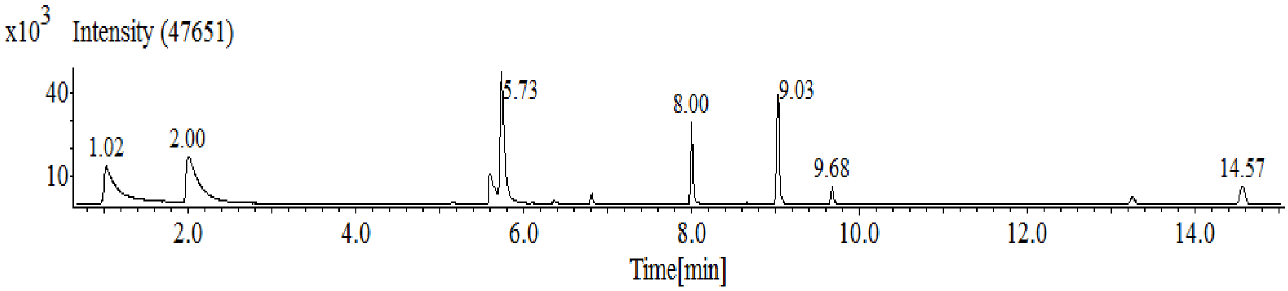


Figure S2. GC-TOFMS original chromatogram (a) and chromatogram generated using the specific tools of software of mass spectrometer, m/z range (41-60) (b).

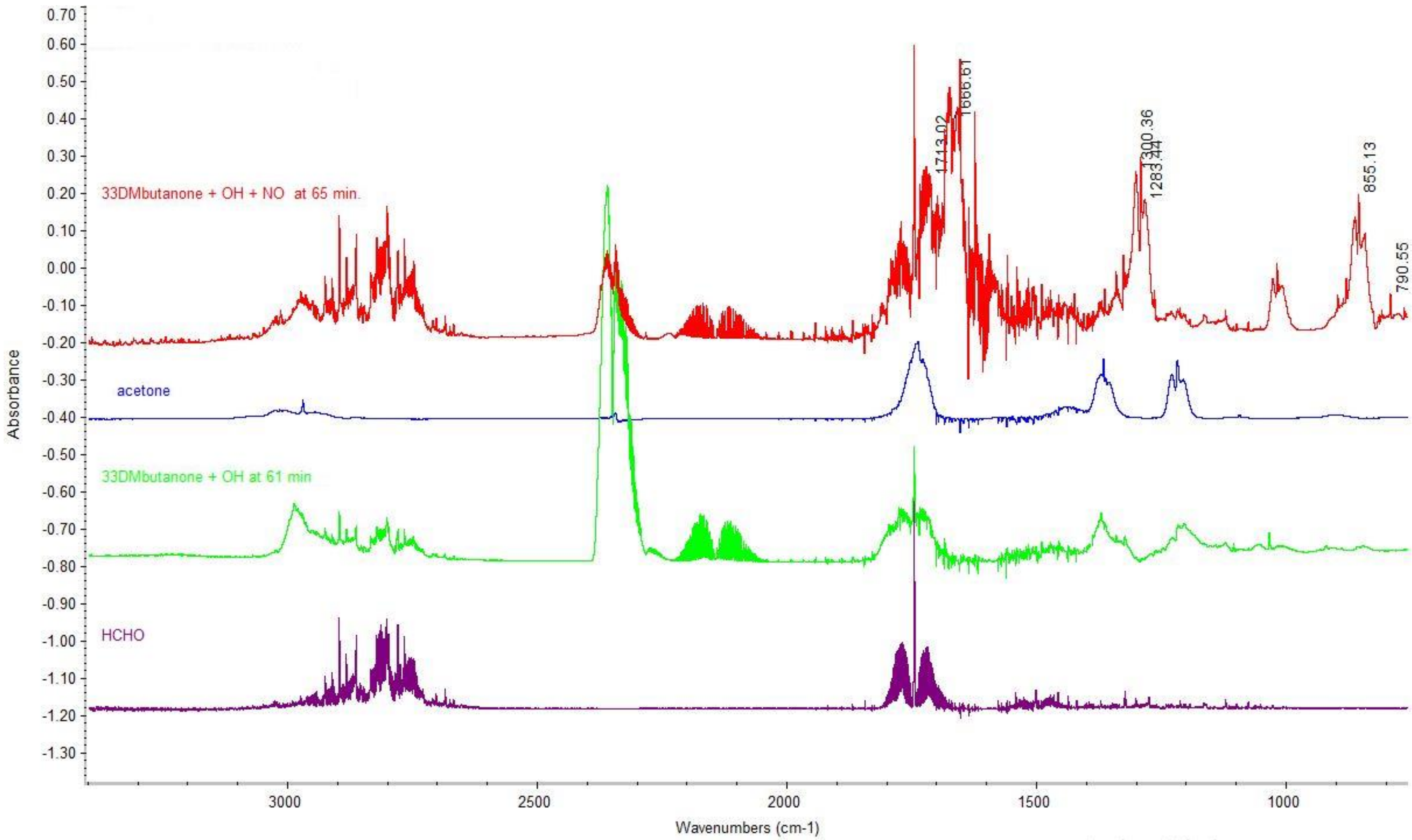


Figure S3. Residual FTIR spectra for the reaction of 33DMbutanone with OH radical in the presence and absence of NO. IR absorption bands characteristic of alcoxy nitrates ($RONO_2$ ~1663, 1284, 853 cm^{-1}) peroxy nitrates ($ROONO_2$ ~1710, 1300 and 793 cm^{-1}). IR spectrum of HCHO (Eurochamp 2020 database https://data. eurochamp.org/data-access/spectra/) last access: 9 July 2024) and acetone (commercial sample). The spectra have been displaced for clarity.

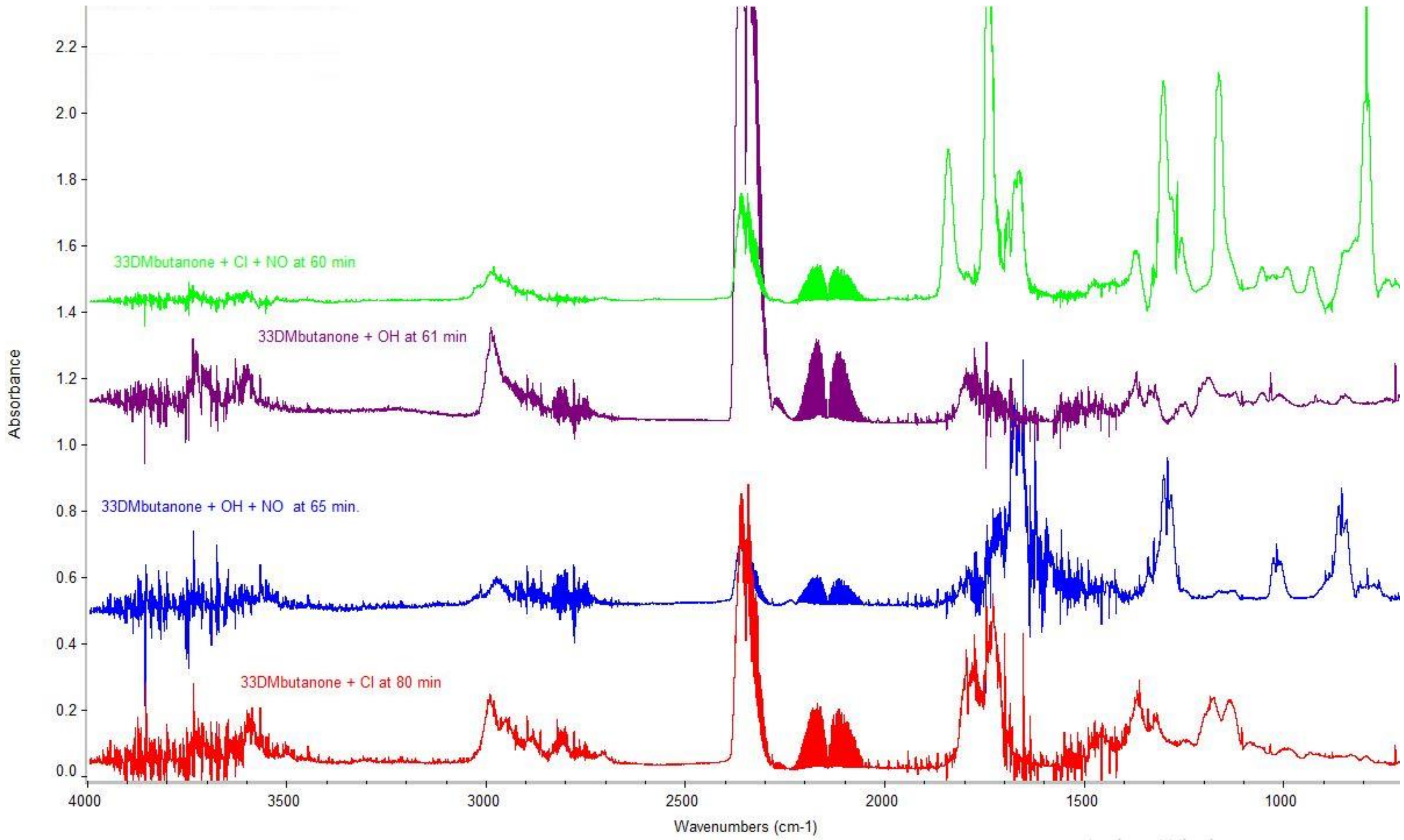


Figure S4. FTIR spectra for the reactions of 33DMbutanone with atmospheric oxidants obtained after elimination of acetone and HCHO from Figure 2 and 3S.

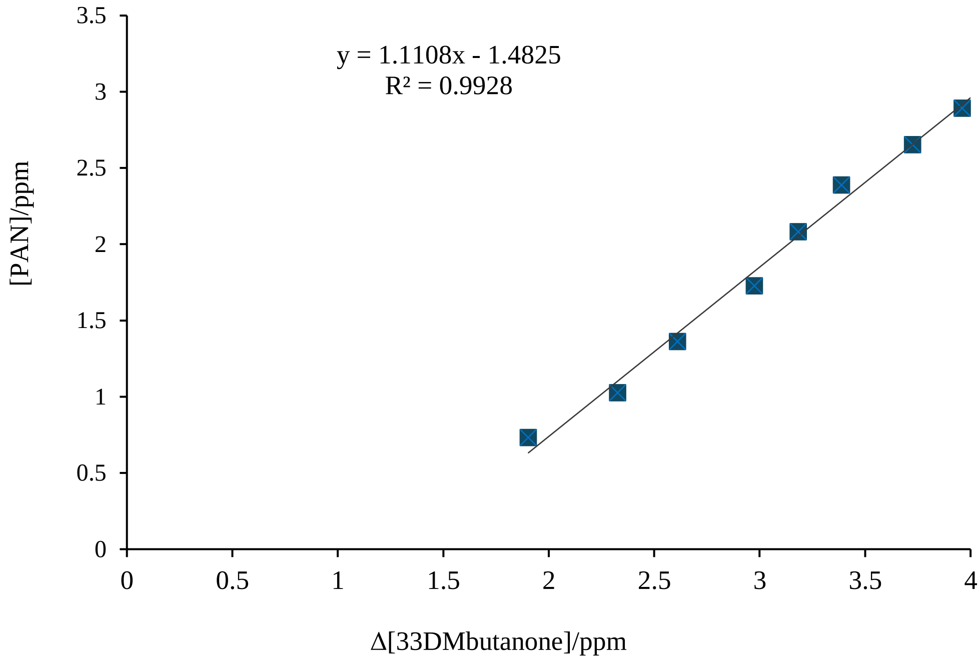
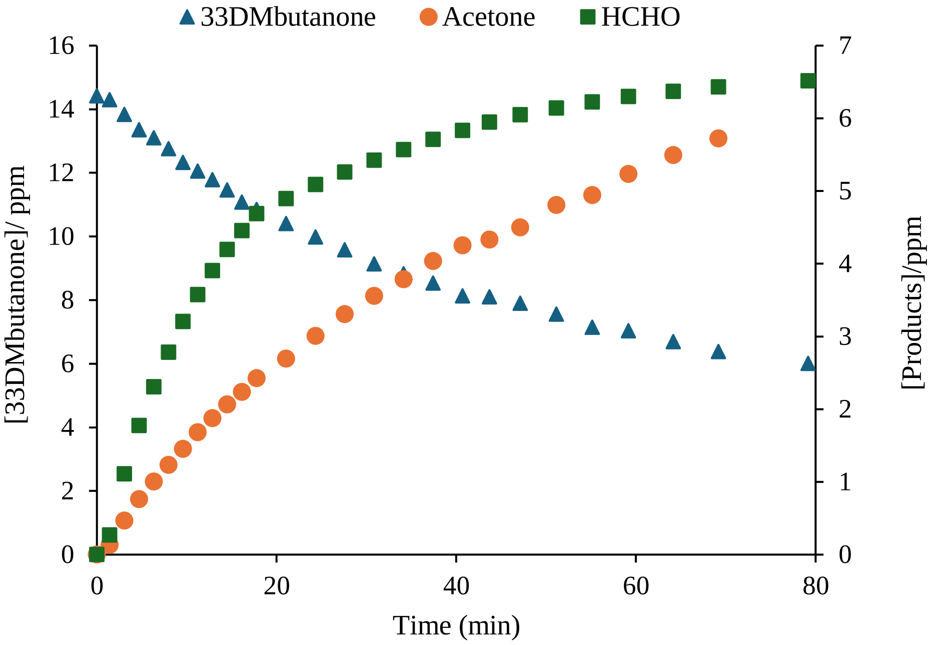


Figure S5. Plot of the PAN formed versus the consumption 33DMbutanone in the reaction of Cl + NO.

a)



b)

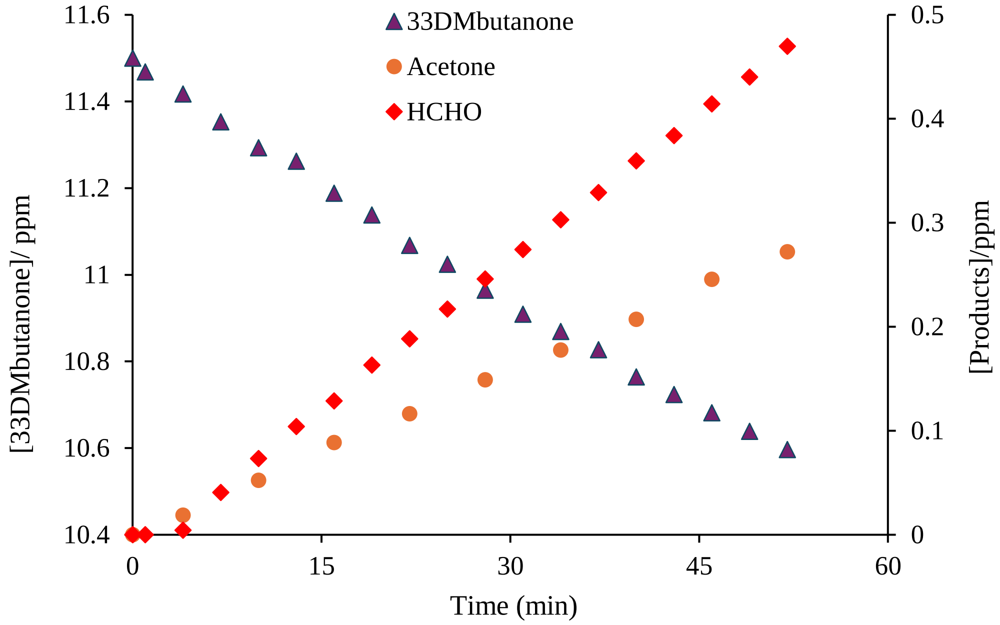
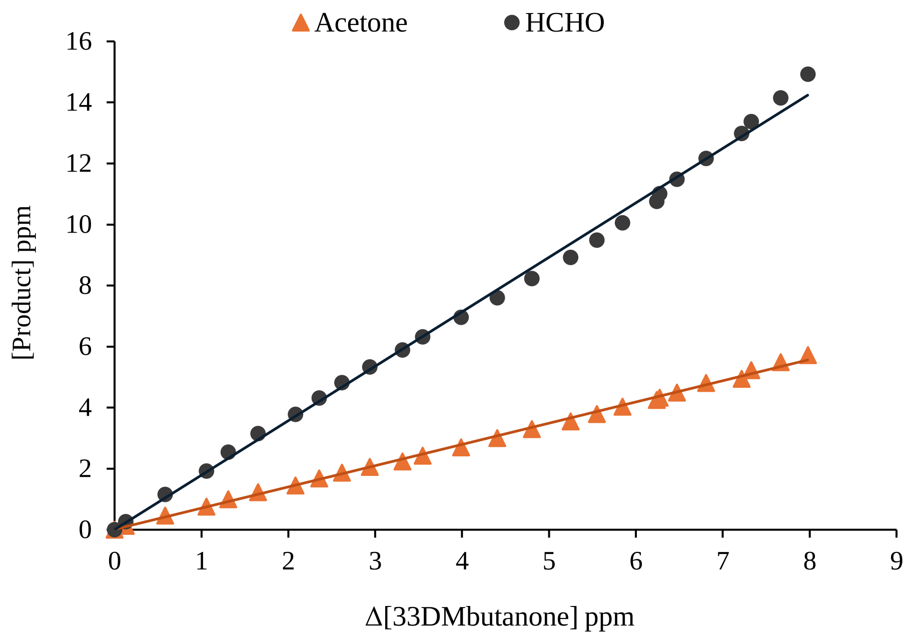


Figure S6. Concentration-time profiles of the products and 33DMbutanone for the reaction of Cl atoms (a) and OH radicals (b) in the absence of NO.

a)



b)

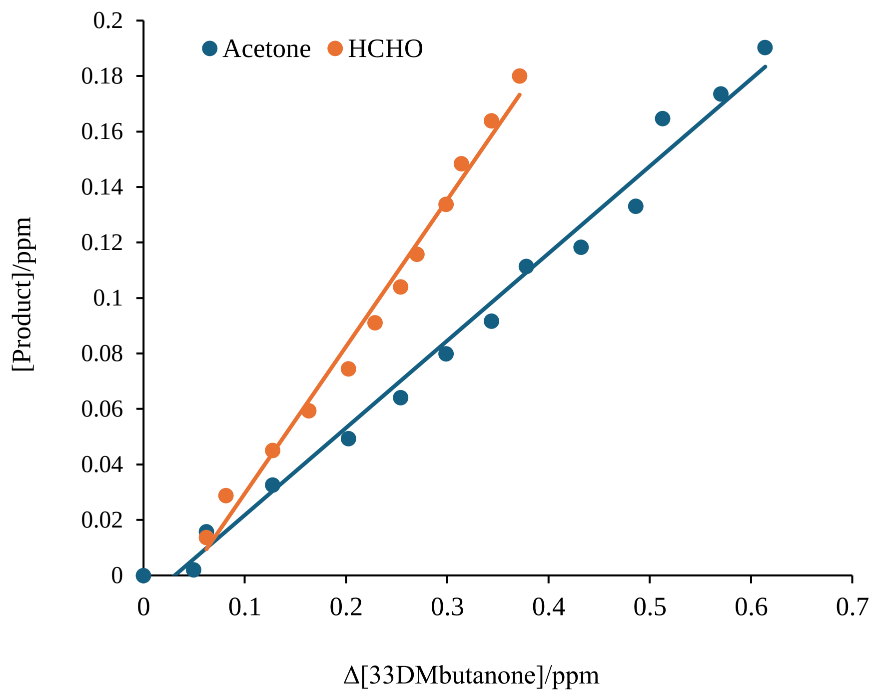


Figure S7. Plots of the reaction products formed versus consumption of 33DMbutanone in the reaction of Cl atoms (a) and OH radicals (b) in the absence of NO.

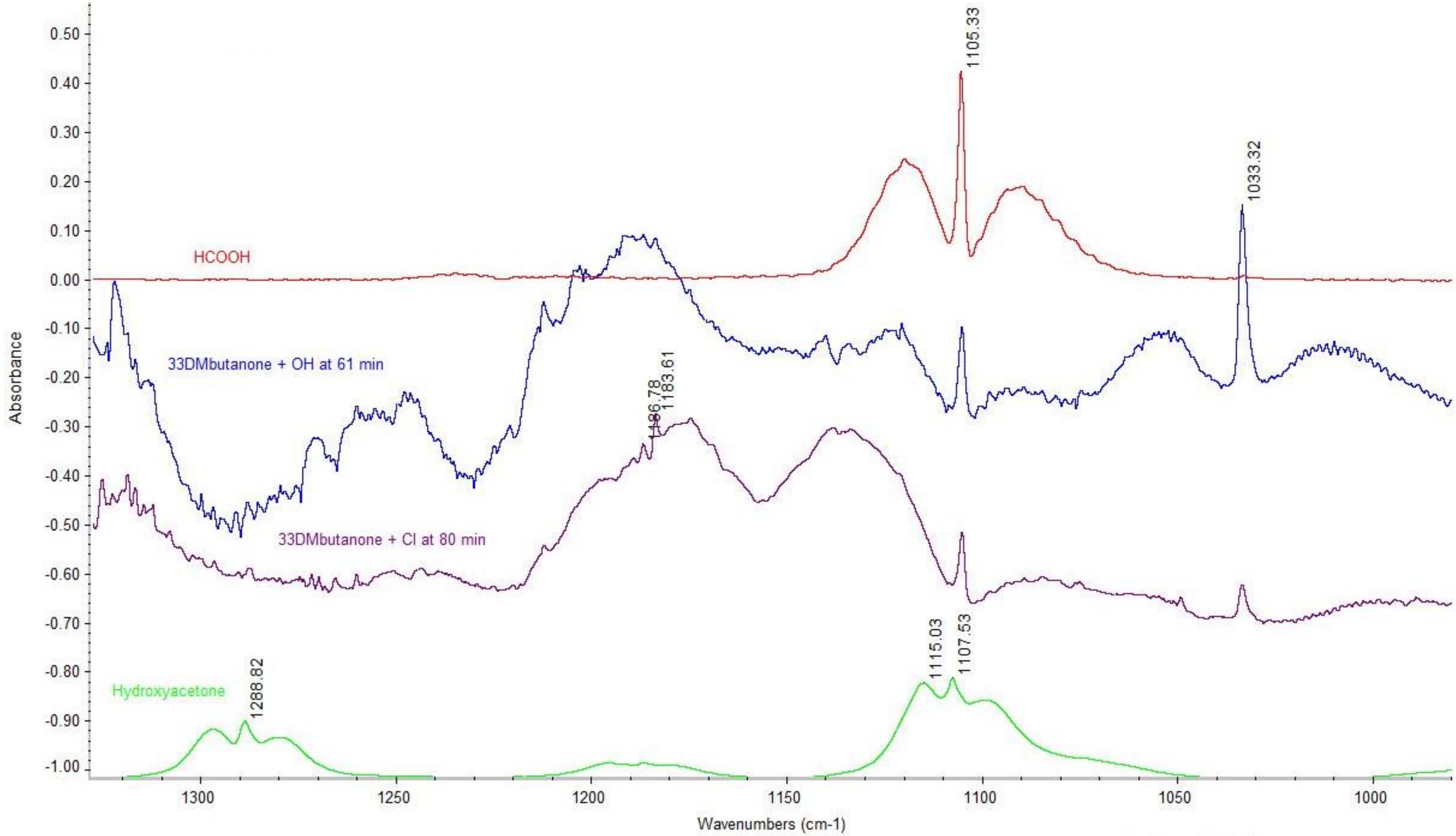


Figure S8. Amplified spectra for the 33DMbutanone + Cl and ·OH reactions and reference spectra of hydroxyacetone and formic acid.

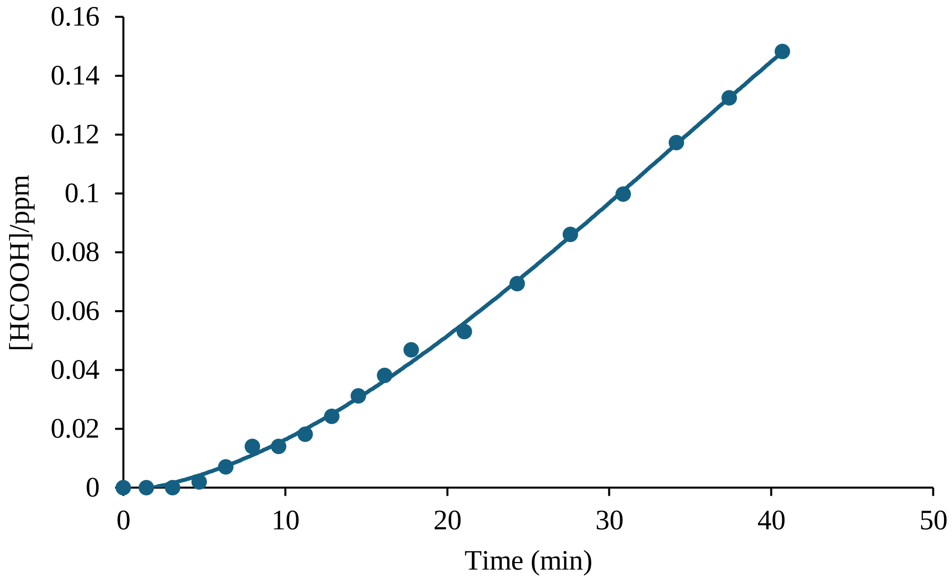
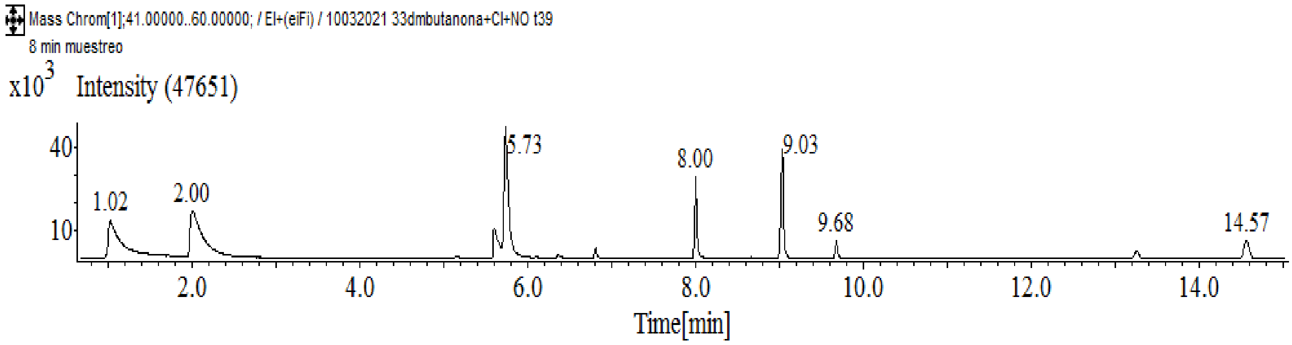


Figure S9. Concentration-time profile of the formic acid in the reaction of 33DMbutanone with Cl atoms in the absence of NO.

a)



b)

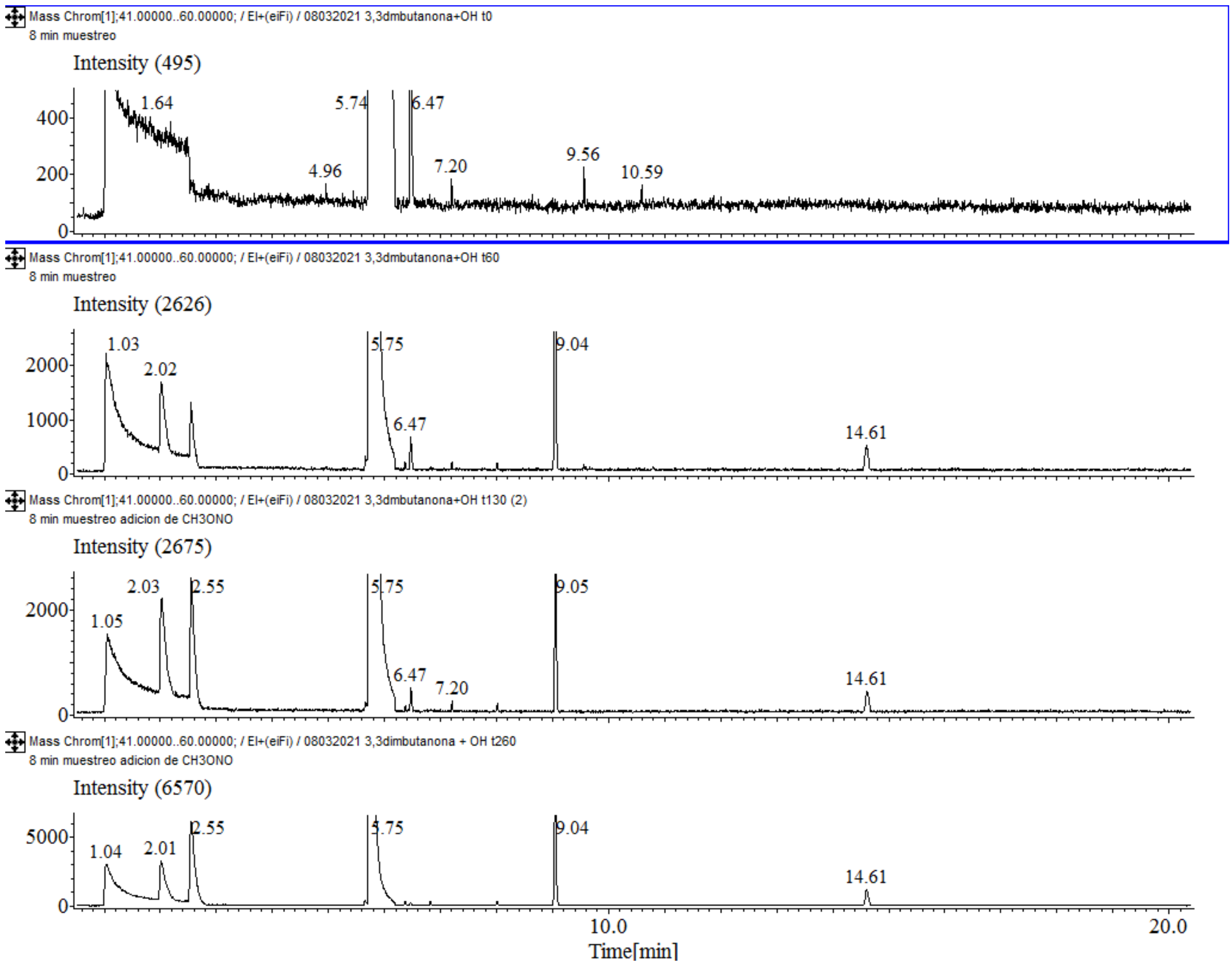


Figure S10. GC-TOFMS generated chromatograms for the 33DMbutanone + Cl + NO at t= 39 min (a) and for ·OH + NO at t = 0, 60, 130 and 260 minutes (listed from top to bottom), using EI ionization mode (b). Chromatograms have been magnified to better identification.

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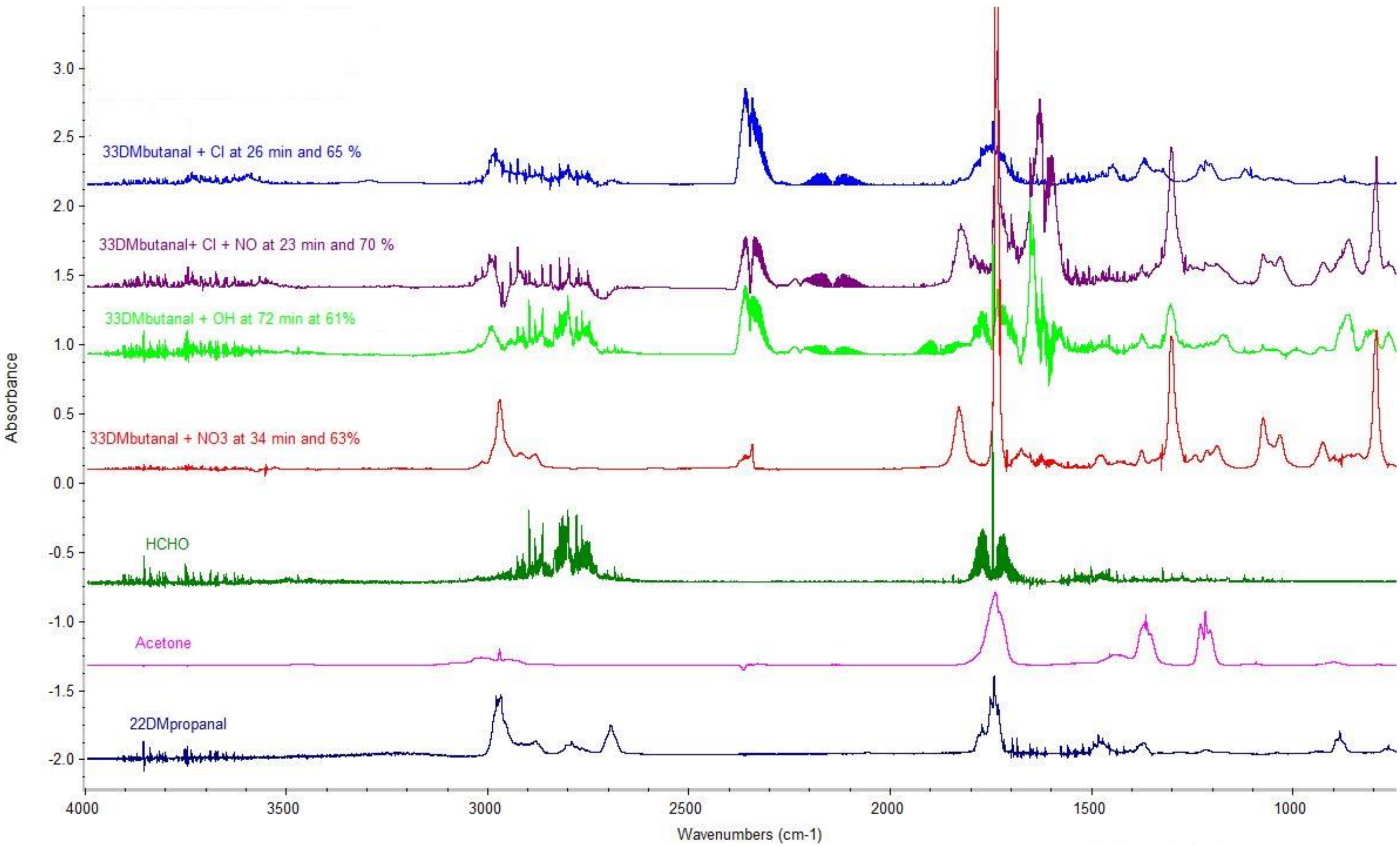


Figure S11. Residual FTIR spectra of the reaction of 33DMbutanal with atmospheric oxidants and reference spectra of HCHO, acetone and 22DMpropanal.

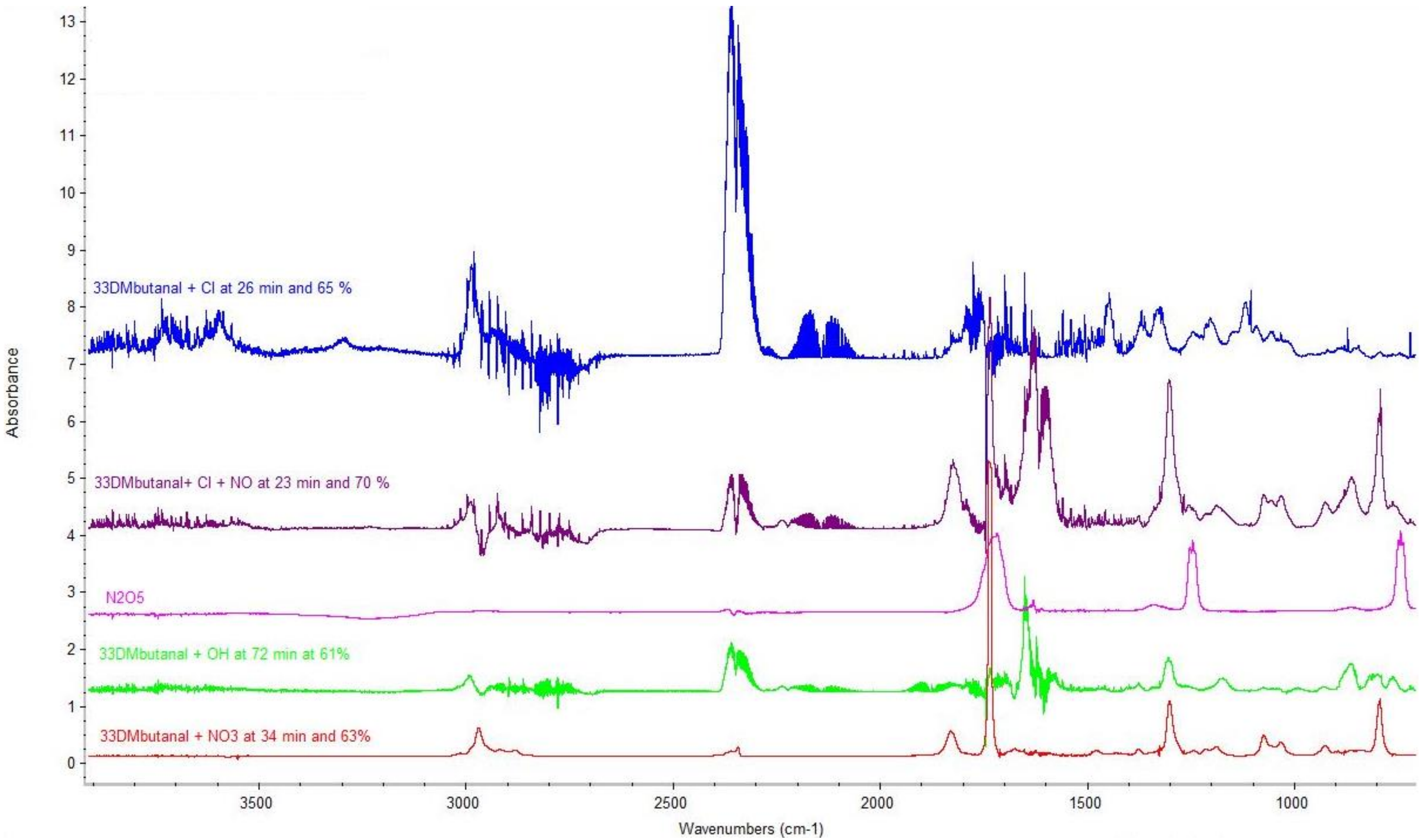


Figure S12. Residual FTIR spectra of the reaction of 33DMbutanal with atmospheric oxidants (obtained after elimination of 22DMpropanal, acetone and HCHO from Figure 11S) and N_2O_5 reference spectrum.

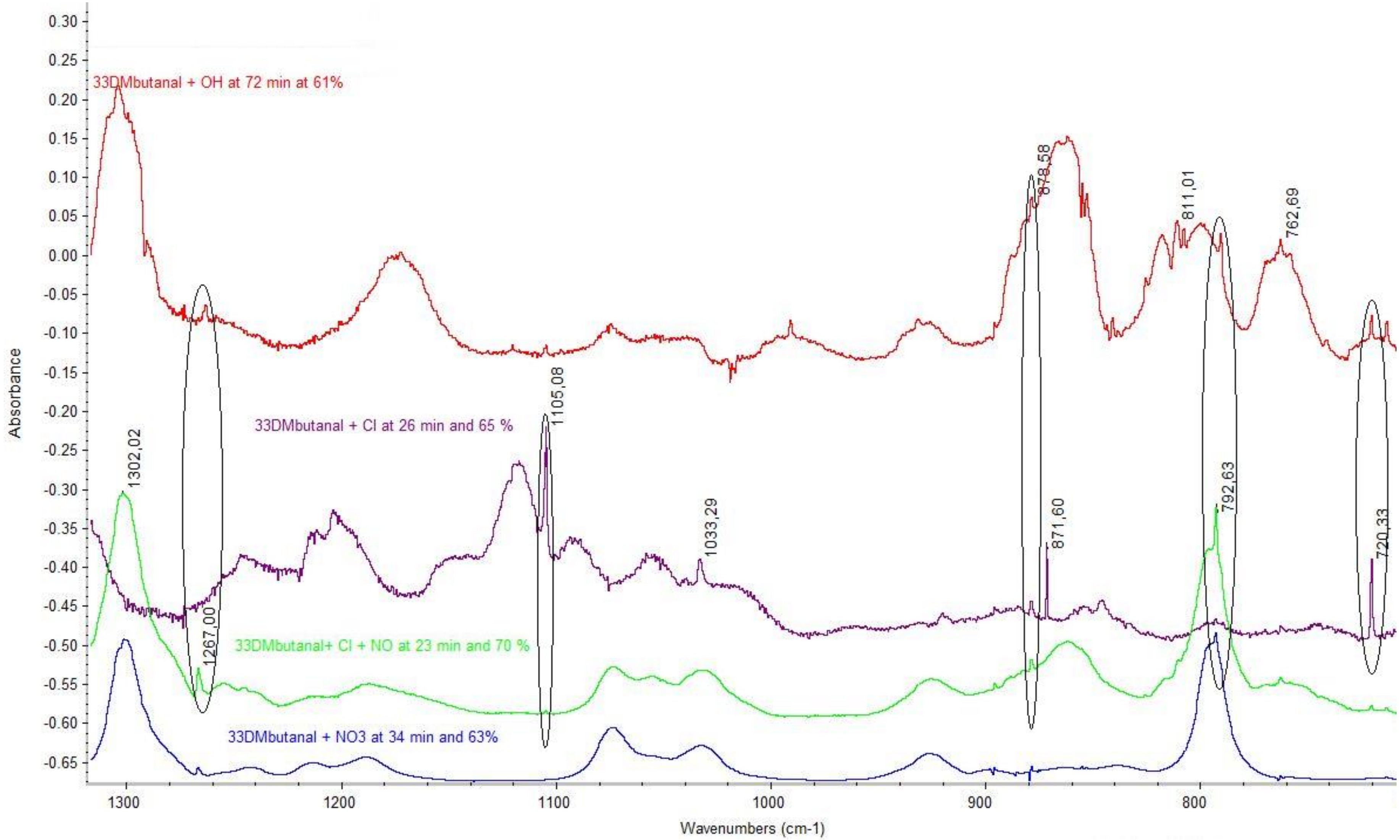
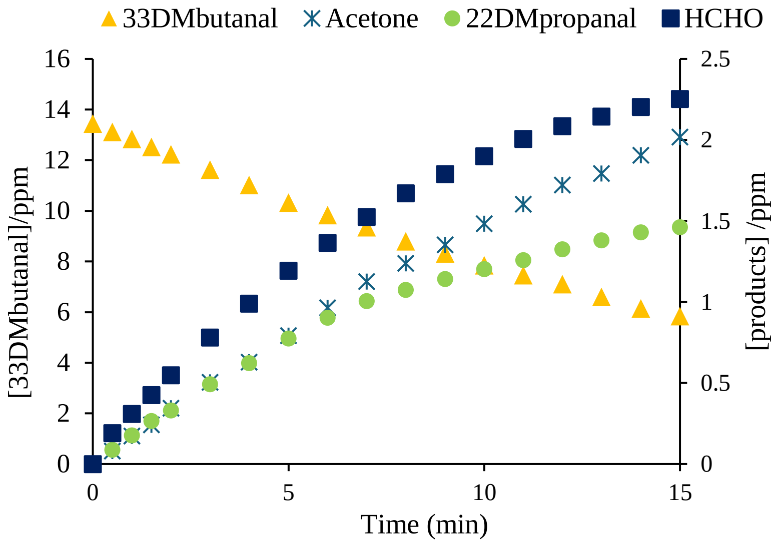
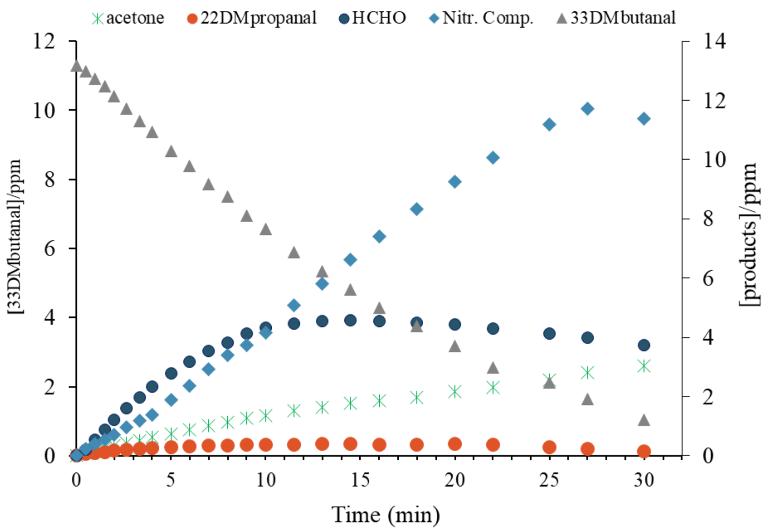


Figure S13. Amplified spectra of Figure 12S for the 33DMbutanal + atmospheric oxidants reactions. Relation of common IR absorption bands; at ~1105 cm^{-1} reaction of 33DMbutanal + Cl and 33DMbutanal + Cl + NO (not nitrated compounds); ~872 cm^{-1} reaction of 33DMbutanal + Cl, 33DMbutanal + Cl + NO 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).

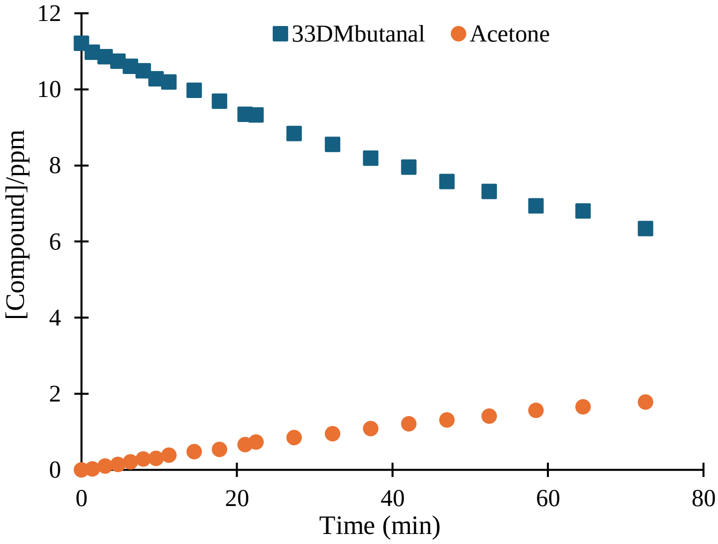
a)


33DMbutanal
Acetone
22DMpropanal
HCHO
[33DMbutanal]/ppm
[products] /ppm
Time (min)
0
5
10
15
0
2
4
6
8
10
12
14
16
0
0.5
1
1.5
2
2.5

b)


acetone
22DMpropanal
HCHO
Nitr. Comp.
33DMbutanal
[33DMbutanal]/ppm
[products]/ppm
Time (min)
0
5
10
15
20
25
30
0
2
4
6
8
10
12
0
2
4
6
8
10
12
14

c)


33DMbutanal
Acetone
[Compound]/ppm
Time (min)
0
20
40
60
80
0
2
4
6
8
10
12

d)

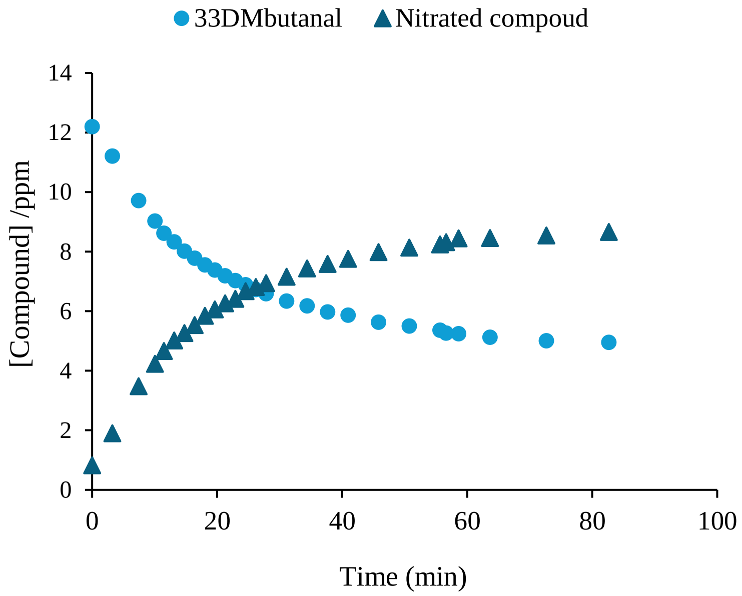
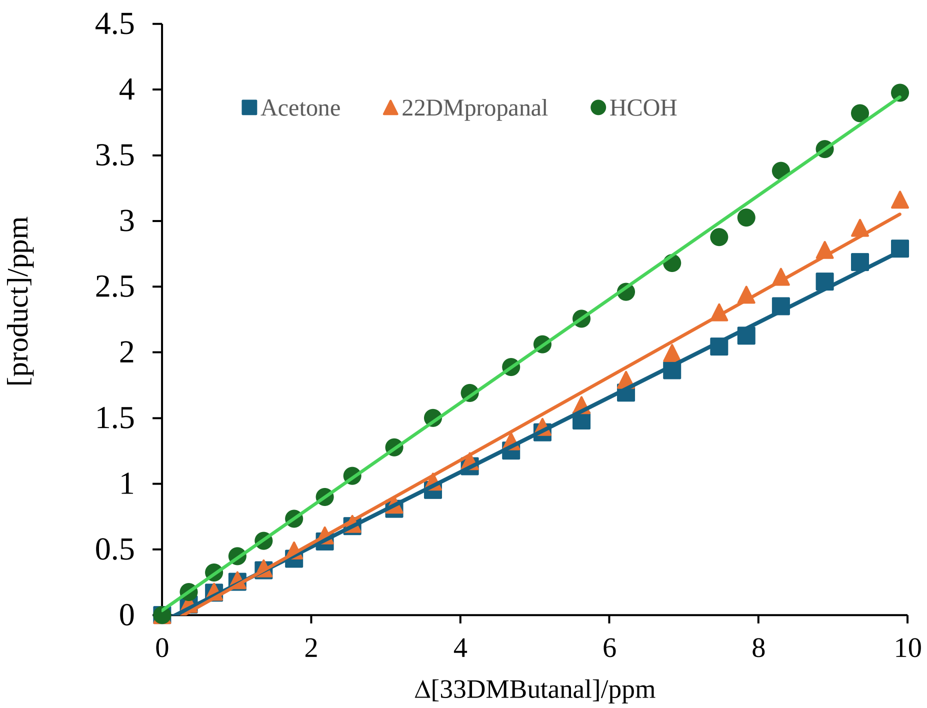


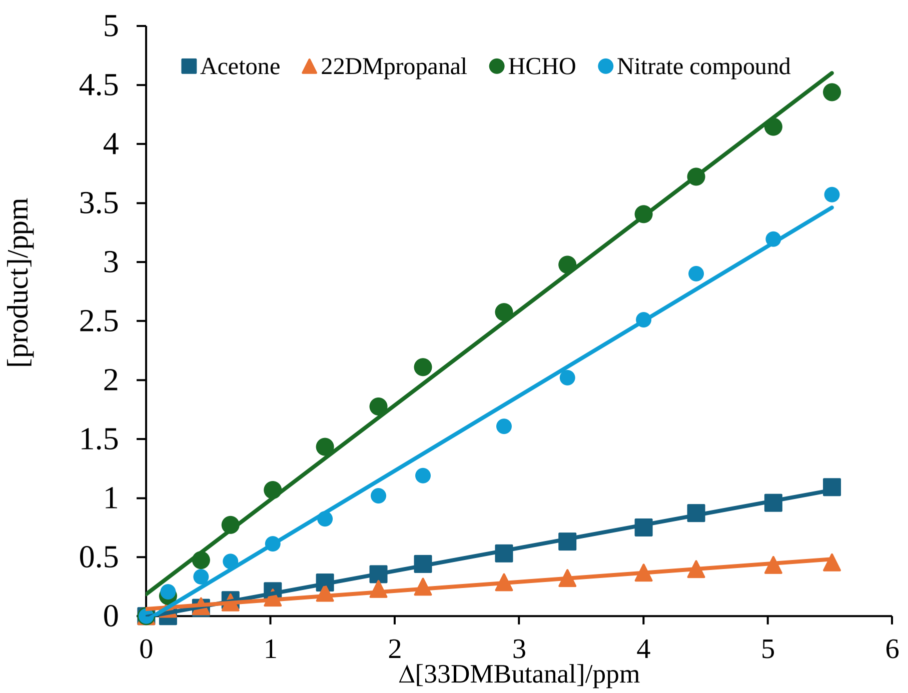
Figure S14. Concentration-time profiles of the 33DMbutanal and products formed for the reaction of 33DMbutanal with Cl atoms in the absence (a) and presence of NO (b), with ·OH (c) and with NO_3 radicals (d).

a)



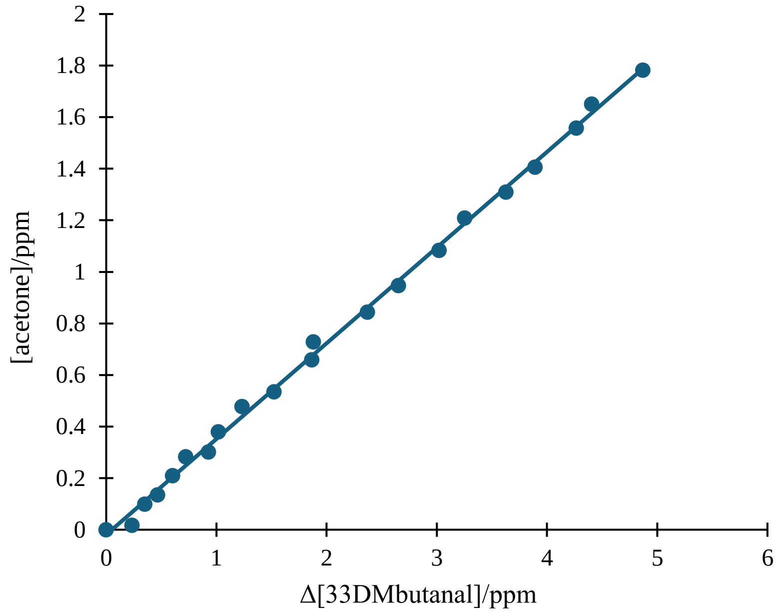
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
[product]/ppm
Acetone
22DMpropanal
HCOH
0
2
4
6
8
10
Δ[33DMButanal]/ppm

b)



5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
[product]/ppm
Acetone
22DMpropanal
HCHO
Nitrate compound
0
1
2
3
4
5
6
Δ[33DMButanal]/ppm

c)



d)

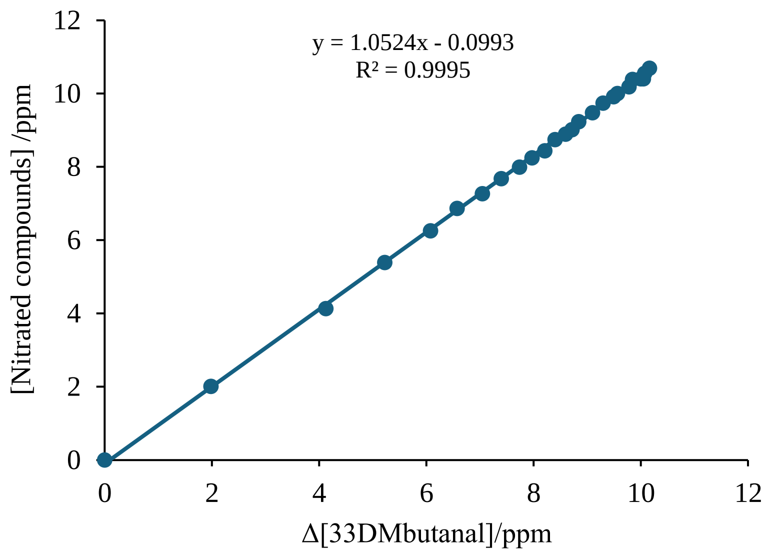


Figure S15. Plots of reaction product formed versus the consumption of 33DMbutanal in the reaction with Cl atoms in the absence (a) and presence of NO (b), with ·OH (c) and with NO_3 radical (d).

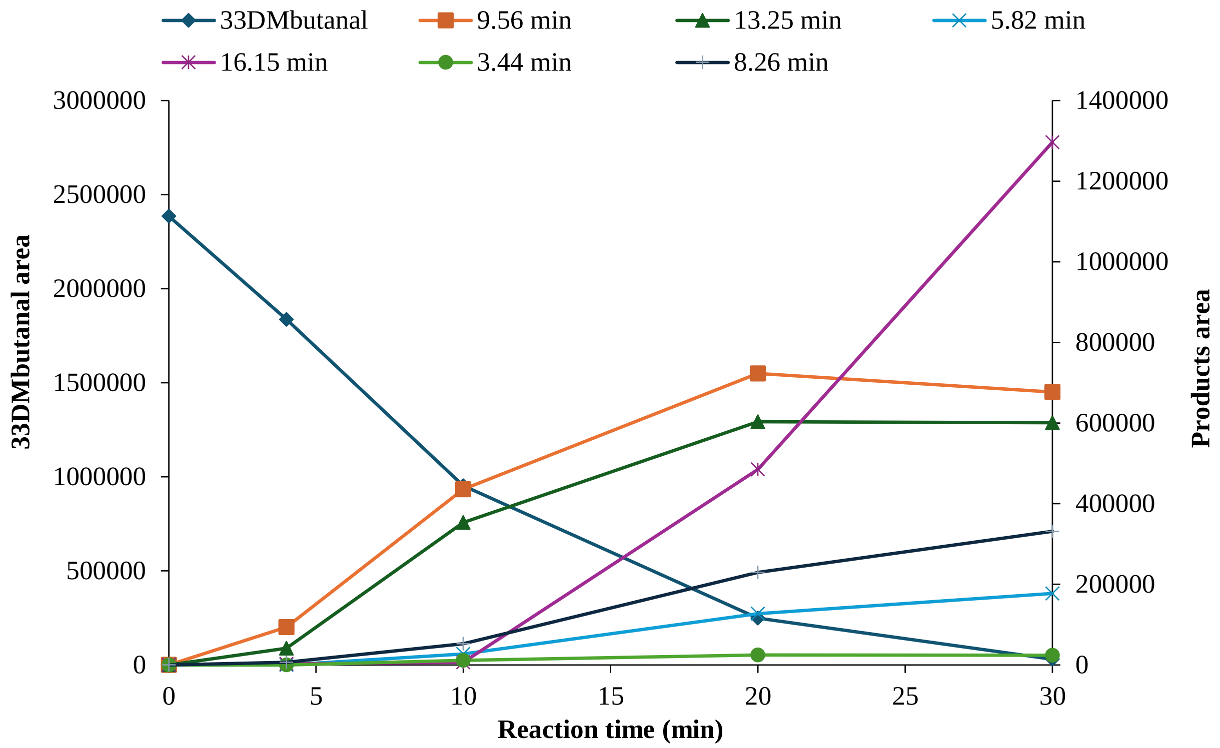


Figure S16. Time evolution of the areas of chromatographic peaks of the 33DMbutanal and products for the reaction with Cl atoms.

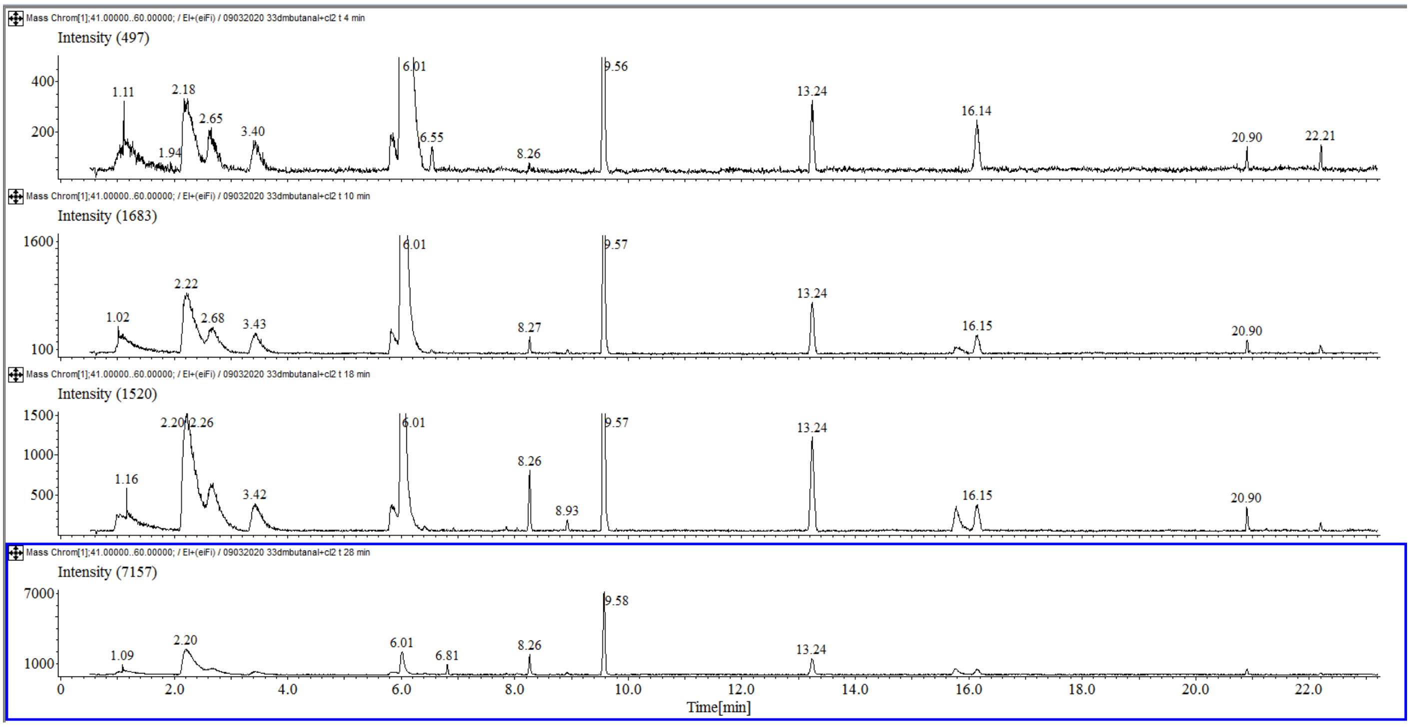


Figure S17. GC-TOFMS generated chromatograms of 33DMbutanal + Cl at different reaction times (t=4, 10, 18 and 28 min, listed from top to bottom) using EI ionization mode. Chromatograms have been magnified to better identification.

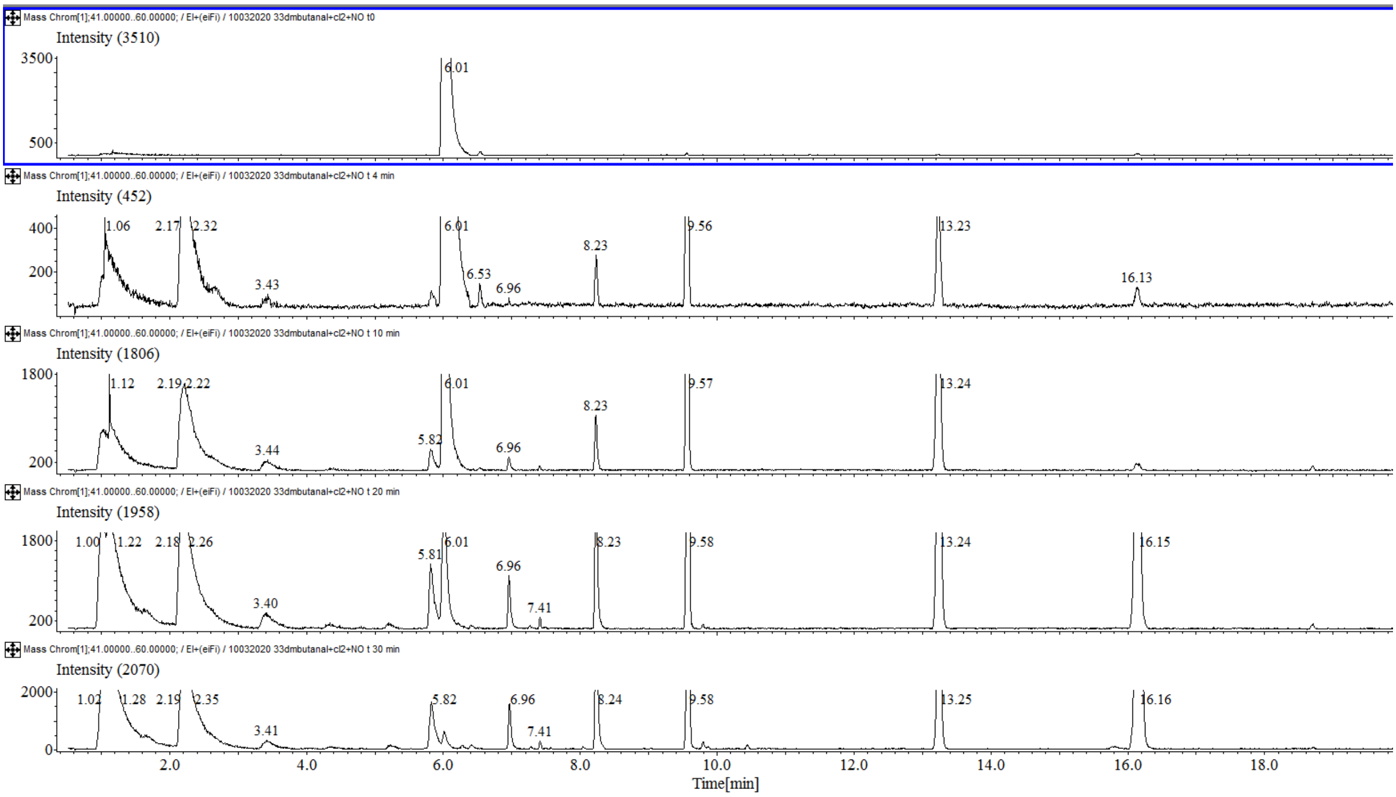


Figure S18. GC-TOFMS generated chromatograms 33DMbutanal + Cl + NO at different reaction times (t=0, 4, 10, 20 and 30 min, listed from top to bottom) using EI ionization mode. Chromatograms have been magnified to better identification.

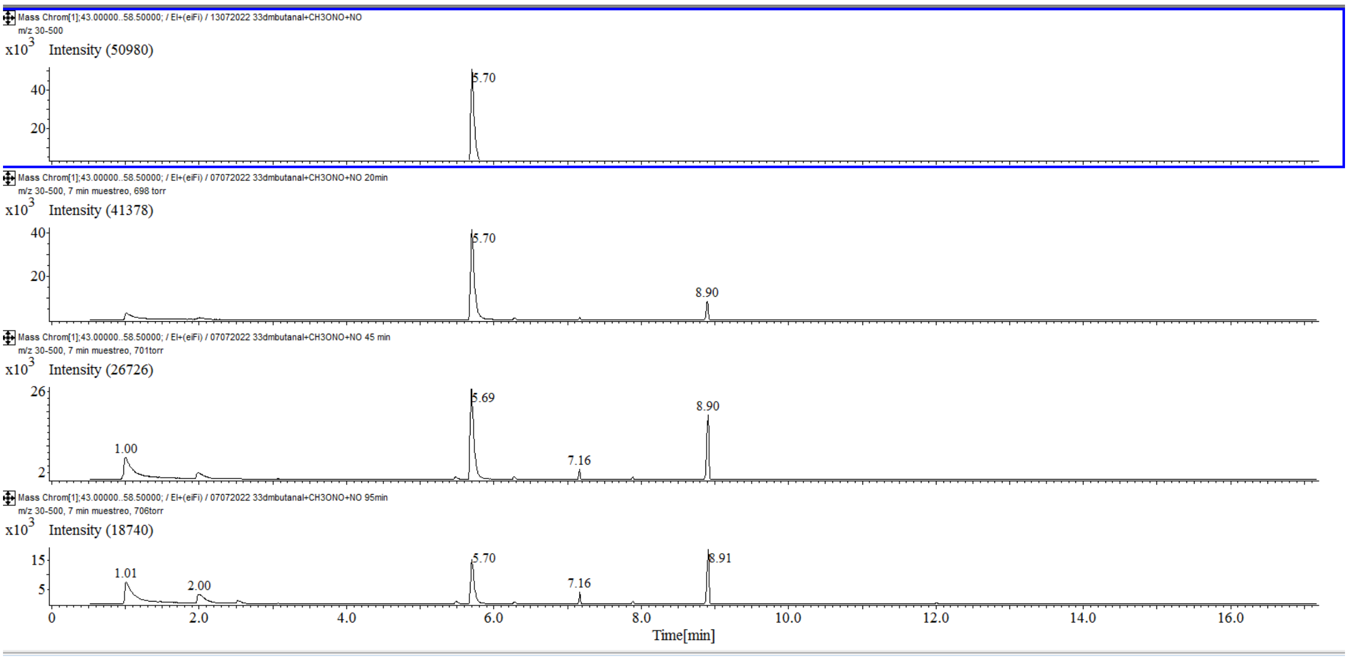


Figure S19. GC-TOFMS generated chromatograms of 33DMbutanal + ·OH reaction at different reaction times (t=0, 20, 45 and 95 min, listed from top to bottom) using EI ionization mode.

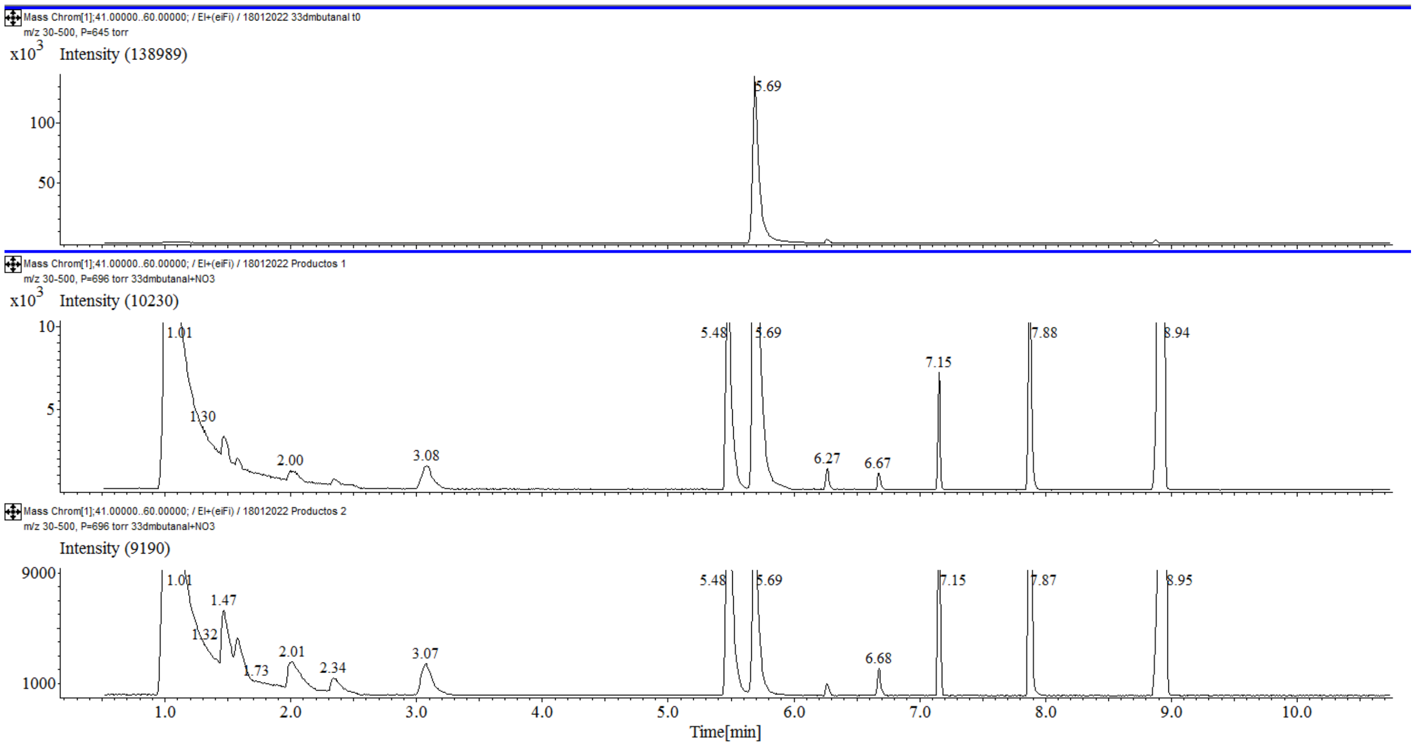
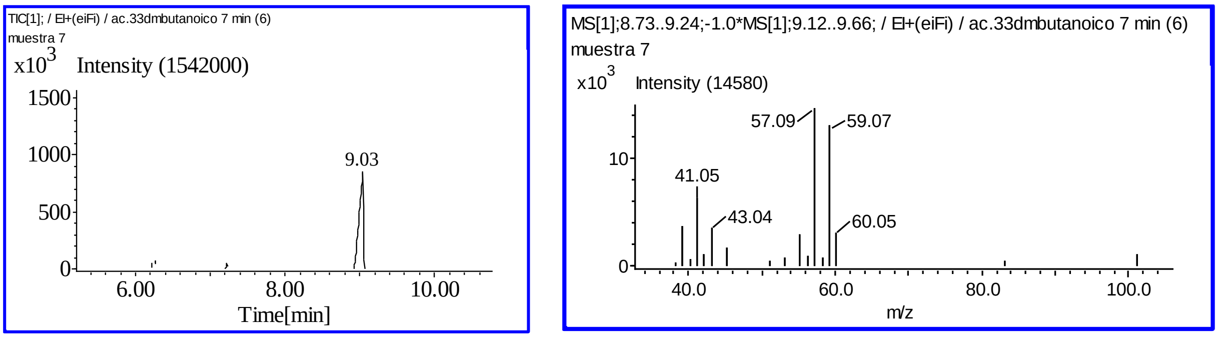


Figure S20. GC-TOFMS generated chromatograms of 33DMbutanal + NO_3 radical reaction at different reaction times (t=7 and 35 min) using EI ionization mode. Chromatograms Product 1 (t= 7 min) and 2 (t=35 min) have been magnified to better identification.

a)



b)

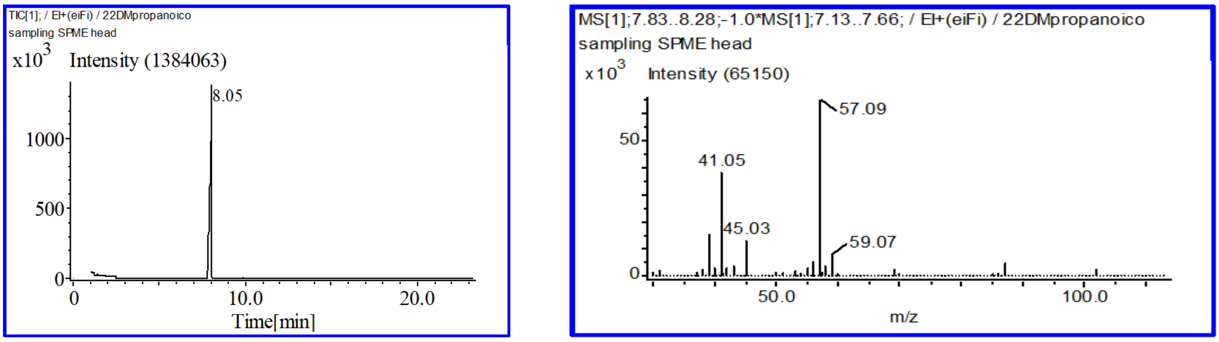


Figure S21. GC-TOFMS chromatograms and mass spectra of a commercial sample of 33DMbutanoic acid (a) and 22DMpropanoic acid (b).

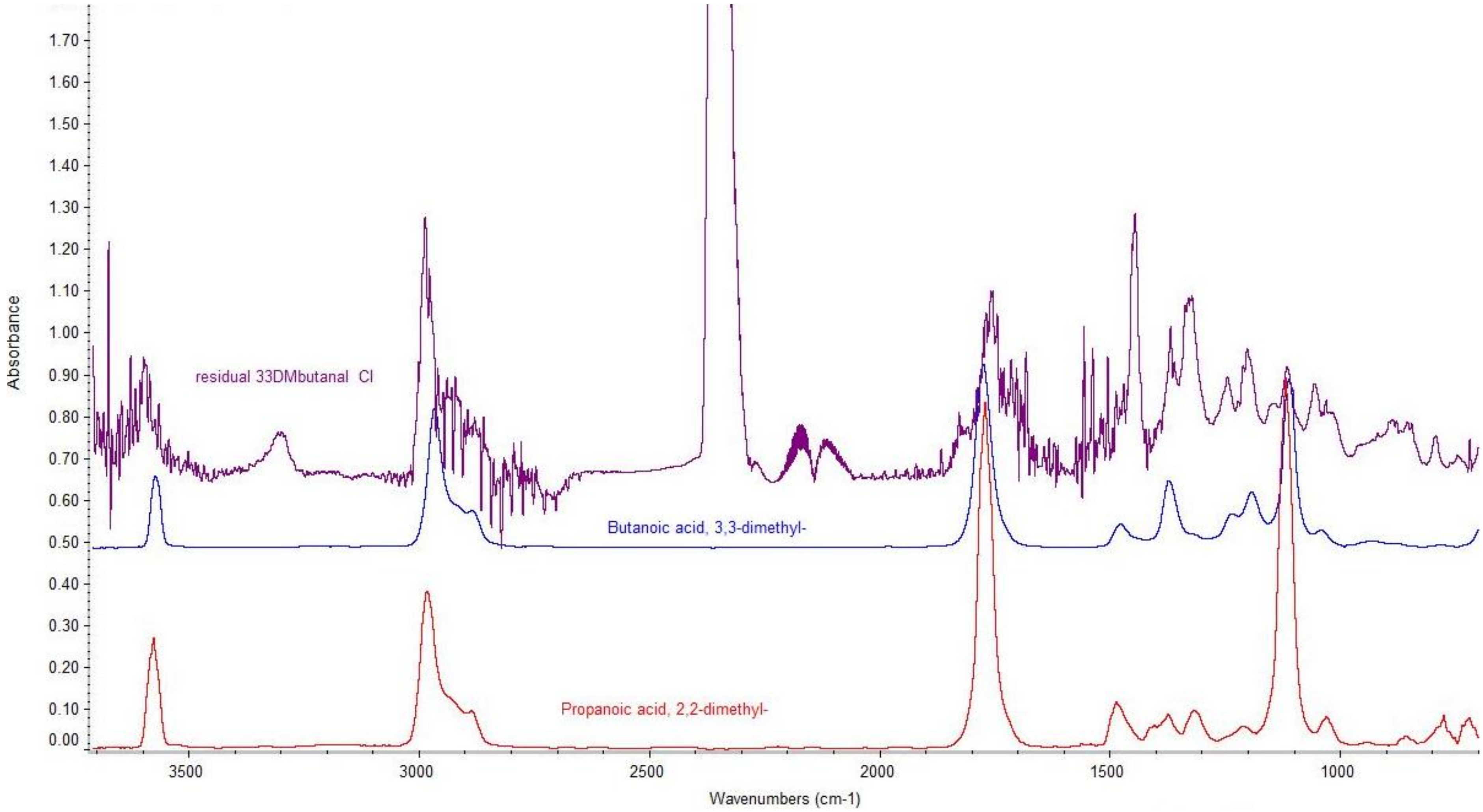
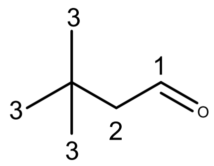
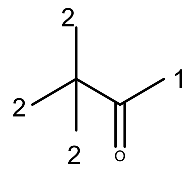


Figure S22. Amplified IR spectra for the 33DMbutanal + Cl atoms in the absence of NO together with the references spetra of 33DMbutanoic acid and 22DMpropanoic acid.

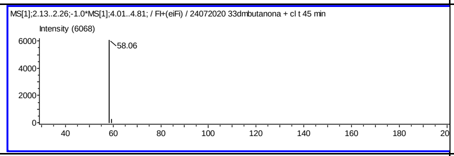
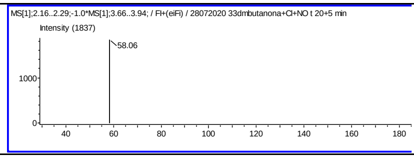
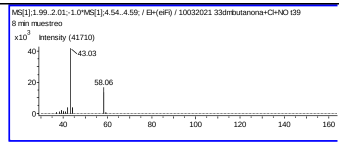
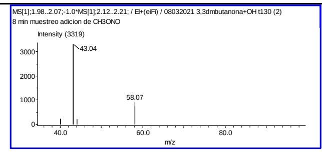
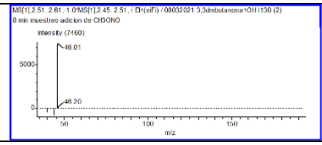
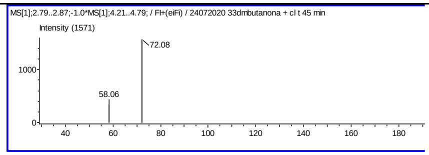
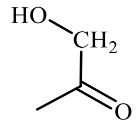
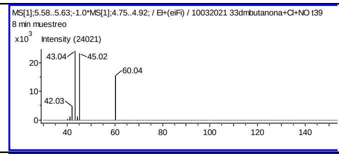
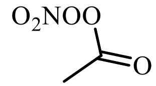
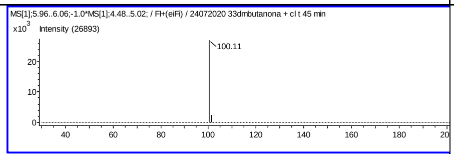
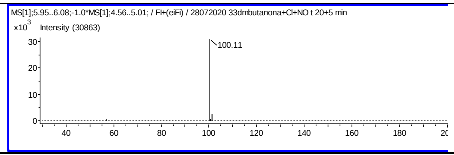
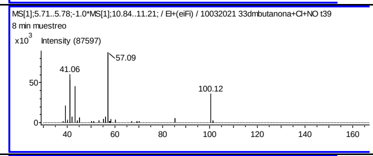
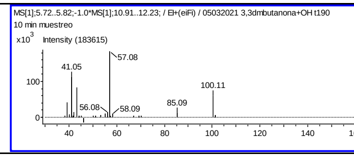
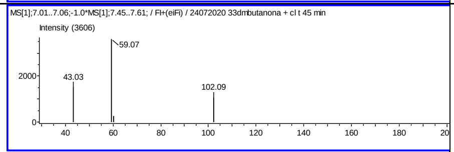
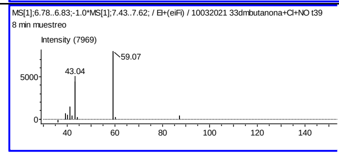
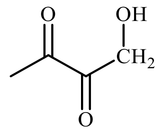
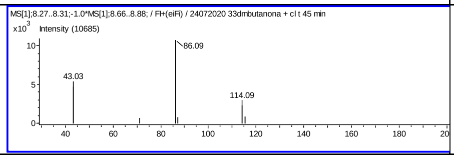
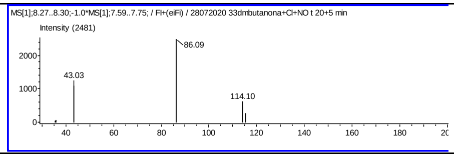
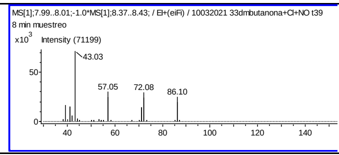
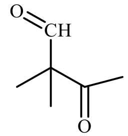
S3. Tables

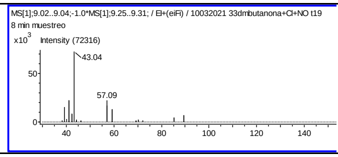
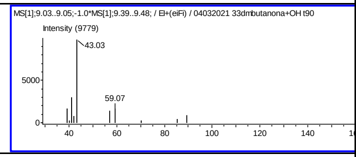
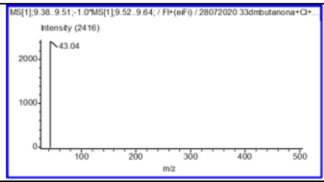
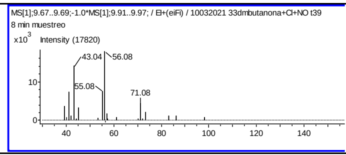
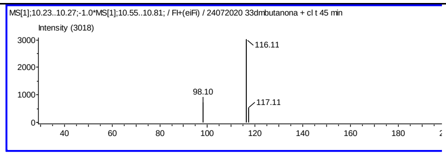
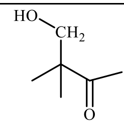
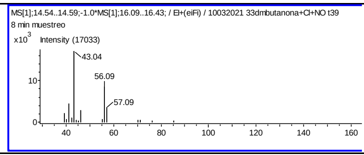
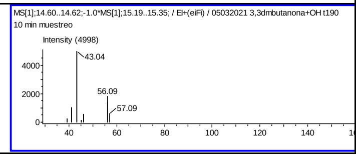
Table S1. Attack Percentage in the different sites in the reaction of 33DMbutanal and 33DMbutanone with atmospheric oxidants base on SAR methods

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})	*aCl	0.405	0.282	0.224	0.0105	0.159
	*bOH	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})	aCl	0.405+0.282+0.224x3=1.361			0.0105+0.159x3=0.49	
	bOH	20.75+0.861+0.167x3=22.11			0.102+0.53x3=1.69	
	cNO_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 (k_{prim}=2.84 × 10^{-11}; k_{sec}=8.95 × 10^{-11}; k_{-CHO}=5.13 × 10^{-11} ; k_{ter}=6.48 × 10^{-11}; k in cm^3 $molecule^{-1}$ s^{-1}) from Calvert et al., 2011, Farrugia et al., 2015 and Carter et al., 2021; EPA Suit™ for OH reaction (AOPWIN™) and Kerdouci et al, 2014 for NO_3 reactions. **3 attack site.

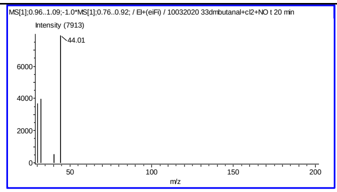
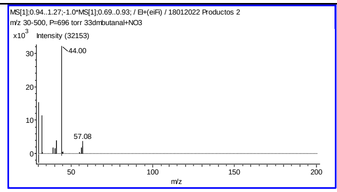
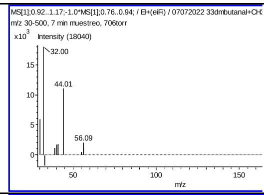
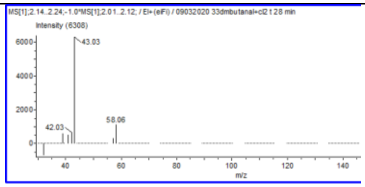
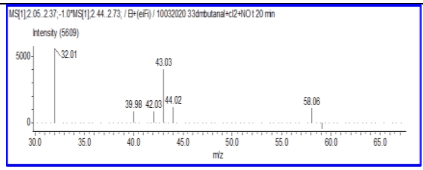
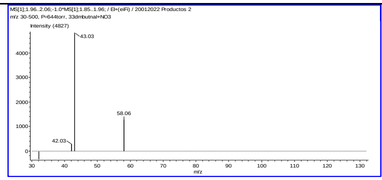
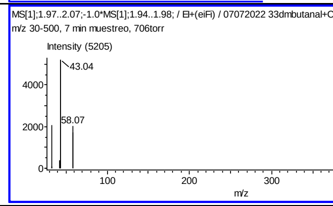
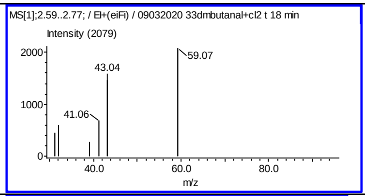
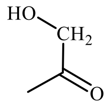
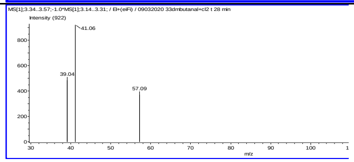
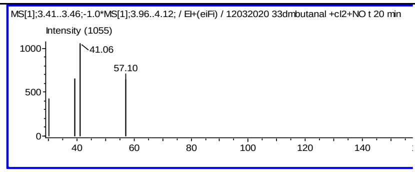
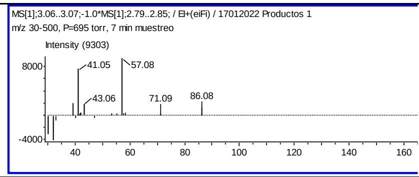
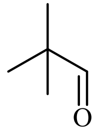
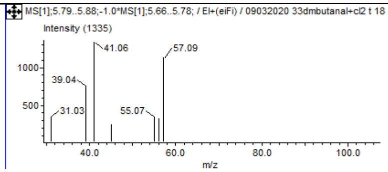
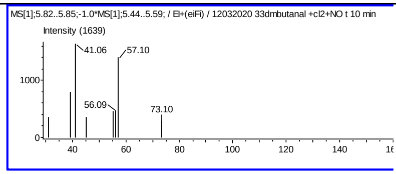
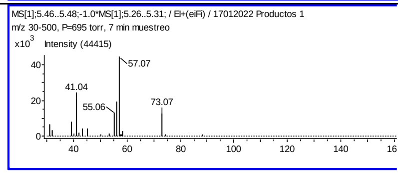
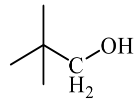
Table S2. Mass spectra of the reaction products formed in the reactions of 33DMbutanone with Cl (with and without NO) using FI and EI ionization modes and 33DMbutanone with OH in presence of NO using EI ionization mode. Only the more intensity peaks have been considered.

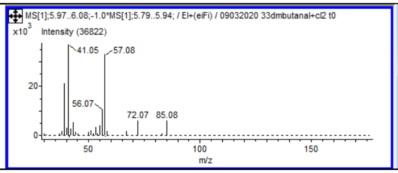
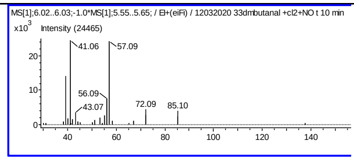
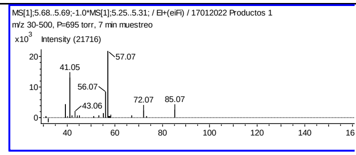
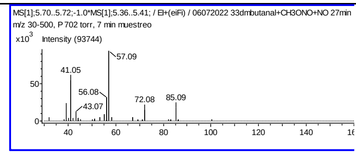
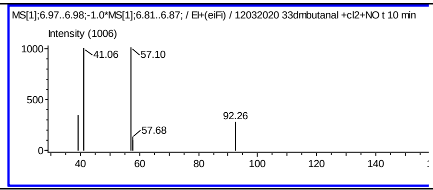
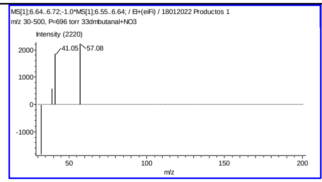
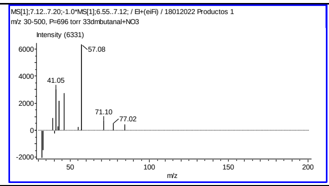
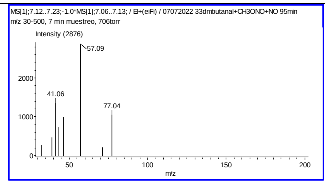
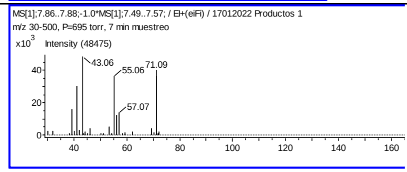
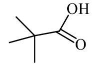
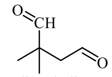
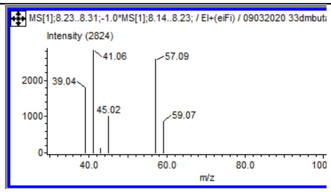
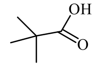
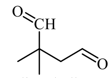
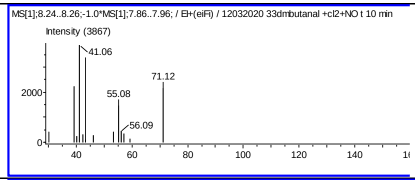
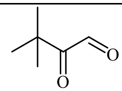
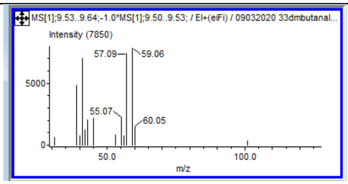
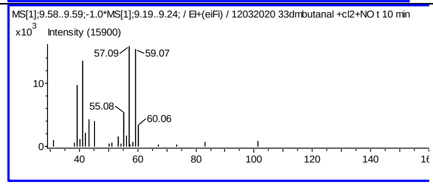
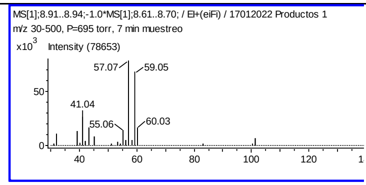
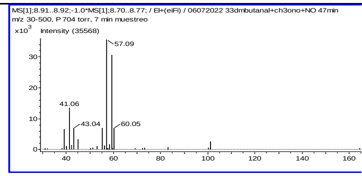
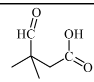
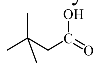
tr (min)	Mass Spectrum					Reaction product
	Field Ionization		tr (min)	Electron ionization		
	Without NO	With NO		Cl	OH	
				With NO	With NO	
2.2 All channels			2*			Acetone 98 % similitude index (NIST database
2.55						Nitrated compound
2.87						 Hydroxyacetone
5.59			5.59			 (PAN)
6			5.73*			33DMbutanone (reactant)
7.03			6.81*			 4-hydroxy-butan-2,3-dione
8.28			8.00*			

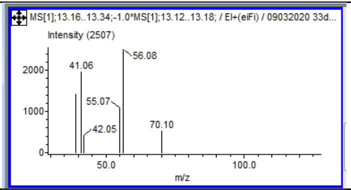
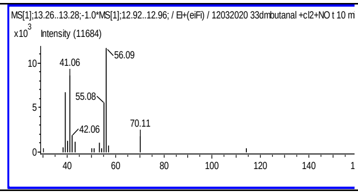
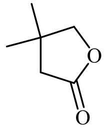
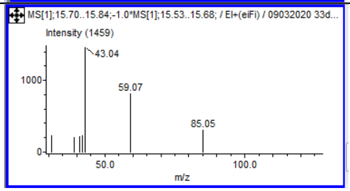
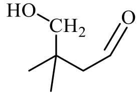
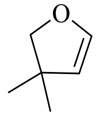
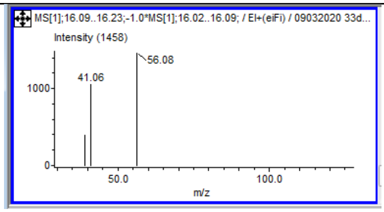
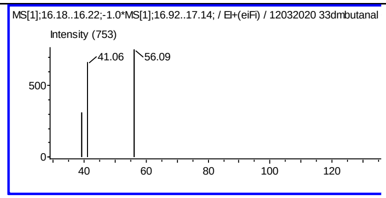
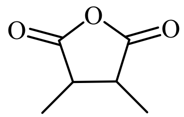
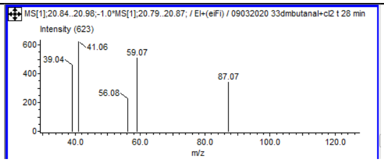
						2,2-dimethyl-3-oxobutanal
9.04			9.04*			Nitrated compounds
9.44						Nitrated compounds
9.68			9.68			Nitrated compounds
10.26			10.26			 4-hydroxy-3,3-dimethylbutanone
			14.57			Nitrated compounds

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

Table S3. Mass spectra of the reaction products formed for the reactions of 33DMbutanal with Cl (with and without NO) and NO_3 and OH radical, using EI ionization, along with a possible assignment of the reaction products.

t_r (min)	Reaction 33DMbutanal +				Reaction product
	Cl		NO_3	OH	
	Without NO	With NO			
1					Unidentified
2.18 All channels					Acetone 98 % similitude index (NIST database)
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  73.5% similitude index (NIST database)

6.01 (5.70)*					33DMbutanal (reactant)
6.97(6.68)* Channel II					Peroxy-3,3-dimethylbutyryl nitrate
7.16 Channel I					Peroxy nitrated compound
7.88 Channel II					 2,2-dimethylpropanoic acid  2,2-dimethylbutanodial
8.23**					 2,2-dimethylpropanoic acid  2,2-dimethylbutanodial
8.26 Channel II					 3,3-dimethyl-2-oxo-butanal
9.56 (8.95)* Channel I					 4-oxo-3,3-dimethylbutanoic acid??  3,3dimethylbutanoic acid

					87.2 % similitude index (NIST database)
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					62% similitude index (NIST database)  3,4-Dimethyldihydrofuran-2,3-dione
20.91					Unidentified

- *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