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-Table 3S. Mass spectra of the reaction products for the reactions of 33DMbutanal with Cl (with and without NO) and NO₃ and OH radical, using Electron Impact ionization.



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

X=Cl atoms; OH and NO3 radical



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 (RONO₂ ~1663, 1284, 853 cm⁻¹) peroxy nitrates (ROONO₂ ~1718, 1300 and 793 cm⁻¹)

and (*) peroxycarbonyl nitrates (ROO(CO)NO₂~1830, 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).



Time (min)

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 NO₃.



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



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.







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.



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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 + NO₃ reaction at different reaction times using EI ionization mode. Chromatograms Product 1 and 2 have been magnified to better identification.



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		$\begin{array}{c} 3 \\ 3 \\ 3 \\ 3 \\ 3 \end{array} \xrightarrow{1}_{2} \\ 0 \end{array}$					
* 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	*aCl	0.405	0.282	0.224	0.0105	0.159	
$(cm^3 molecule^{-1} s^{-1})$	*bOH	20.75	0.861	0.167	0.102	0.53	
	*c NO ₃	1.274	0.743	0.0002	-		
Overall rate coefficient	^a Cl	0.405+0.282+0.224x3=1.361			0.0105+0.159x3=0.49		
(k _{abs})	bОН	20.75+0.861	20.75+0.861+0.167x3=22.11 1.274+0.743+0.0002x3=2.017			0.102+0.53x3=1.69	
$(cm^3 molecule^{-1} s^{-1})$	^c NO ₃	1.274+0.743				-	
Attack Percentages (%)	Cl	~30	~21	~49	~2	~98	
	ОН	~94	~4	~2	~6	~94	
	NO ₃	~63	~37	0	-		

^a10⁻¹⁰; ^b10⁻¹²; ^c10⁻¹⁴. *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 NO₃ 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					
	Field Ionization			Electron io	product	
	Without NO	With NO	(min)	Cl	ОН	
				With NO	With NO	
2.2 All channels	Mc(1)2.13.2.28/1.07Mc(1)4.01.4.81/FH(eF)/24072020333drbdatanona + cl + 45 min intensity (6068) 4000 4000 400 400 40 40 40 40	MS[1]:2.16.2.29-1.07MS[1]:3.66.3.94 / FH(eFF) / 28072020 33dimbdamona-CH/01 20-5 min intensity (1837) 1000- 40 60 80 100 120 140 160 180	2*	MST) 198.2.01; 17/16/RE(1),4.54.4.48; 16/8; 10/002021 32/8/mbutmoran-C-MD G9 # mm monstrom mm monstrom 1 10/002021 32/8/mbutmoran-C-MD G9 # 0 0.0 0.0 0.0 100 100 # 0 0.0 100 120 140 160	Megri 148 2.07.1 (7040[12:0:2:22:7:12:04F] / (2003202) 13.5846.4840447-04130 (2) Brinn maxime and on 40:00400 Namatry (519) 3000 40.0 60.0 mr2	Acetone
2.55					D0(1) 52 5 24 1 400(1) 24 3 23 / 0 Hold(1) 44 35 / 0 Hold(1) 4003221 3.384544 mean-Oli(130 (2)) 0 10 10 metrics (nois a CODOU 0 10 metric (nois) 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	Nitrated compound
2.87	MS(1):2.72 :2.87-1:01MS(1):4.21:4.79; /FH(eR) / 24072020 33dmbutanona + cl + 6 min Intensity (1571) 1000 40, 60, 80, 100, 120, 140, 160, 180					HO CH ₂
5.59			5.59	MST(1545.8.5.8)-(1/MST(1)4.75.4.92, / Br(eR)/ / 1002021 33dmbutarona+G+MD 09 8 min muster x10 ³ Intensity (24021) 20 40.04 		O ₂ NOO (PAN)
6	MC[1]5.58.6.08.10*MC[1]4.48.5.02, /FH(eF) / 24072020 33dmbutanona + c1t 45 min x10 [*] tetenstry (2885) 20 10 10 40 40 40 40 60 80 10 10 10 10 10 10 10 10 10 10 10 10 10	ME(1)5.65.6.08-10/ME(1)4.56.501./FH(eR)/28072020.30dmbutmonar-OH/0120-5 min 10 ³ 10 ³ 20 10 0 40 40 60 80 100 120 140 160 180 20 20 20 20 20 20 20 20 20 2	5.73*	Mc110571.5.78-107Mc110.084.1121; / EHeFF / 100322133dmbdmonaHCHH0 09 8 ms nuestree x10 ³ htems (87597) 4 1.08 90 4 1.09 4 0.09 4 0.09 100.12 4 0.00 4 0.09 100.12	MS(1):572.4.82-10/MS(1):10:91-12:22 / E9-(eB) / 65032021 3.3dmbutanona-GH1180 10 mm mustrico 10 mm mustrico 41.05 60 100 41.05 100 41.05 60 100 40 60 100 120 140	33DMbutanone (reactant)
7.03	MS(1)/2.01.7.06.101%S(1)/7.45.7.81, / PH(eF) / 24072020 33detbutanona + d1 45 min htematy (3006) 43.00 43.00 44.00 0 40 40 40 40 40 40 40 40 4	ä	6.81*	MS(1)(776.0.53-10745(1),7.43.7.42.7.164(476) / 10030021 333mbutanona+G+MO199 6 min muestreo htensaly (7969) 000 43.04 00 43.04 00 00 00 00 00 00 100 120 140		O OH CH ₂
8.28	MS(1)8.27.8.31.101%S(1)8.06.8.88,/PH(eR) / 24072020 33detbutanona + cl i 45 min x10 ³ memohy (10685) 10 43.03 5 43.03 6 40 60 80 100 120 140 160 180 2	MS(1)3.27.8.20-107MS(1)27.56.7.35; / FH(eFF) / 28072020 33dmbutenona+CH-ND 120+5 min Hetersby (2481) 2000 43.03 1000 43.03 114.10 40 60 80 100 120 140 160 180 20 180 20 180 20 180 20 180 20 20 20 20 20 20 20 20 20 2	8.00*	MS(1)(9.9.6.0)(-10*MS(1)6.37.8.43, /BH(eR) / 10032021 33dmbutanom+O+MO 199 6 min mestres x10 ³ hermaty (71199) 50 40 40 40 40 40 40 40 40 40 4		



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

Table 3S. Mass spectra of the reaction products for the reactions of 33DM butanal with Cl (with and without NO) and NO₃ and OH radical, using Electron Impact ionization.





13.25	MS[1];13.1613.34;-1.0*MS[1];13.1213.18; / EI+(eiFi) / 09032020 33d	MS[1]:13.2613.28;-1.0'MS[1]:12.9212.96; / EH(eiF) / 12032020 33dmbutanal +cl2+NO t 10 mi		
Channel III	niemský (2507)	10 41.06 56.09		
	55.07	55.08		\mathcal{A}
	1000	42.06 70.11		Ö
	0 ¹	о <mark>4 иш рын р 40 60 80 100 120 140 1</mark>		2,2-dimethyl tetrahydrofuran-2-one
15.78	₩2 MS[1];15.7015.84;-1.0*MS[1];15.5315.68; / EI+(eiFi) / 09032020 33d			
Channel III	Intensity (1459)			$\begin{bmatrix} CH_2 \\ I \end{bmatrix}$
	1000-59,07			\frown
	85,05			
				4-hydroxy-3,3-dimethyl
	m/z			butanai
				<u>_</u> 0_
				$\langle \rangle$
				Or 2.3-dihydro-4.4-
				dimethylfuran
16.15	MS[1];16.0916.23;-1.0*MS[1];16.0216.09; / EI+(eiFi) / 09032020 33d	MS[1];16.1816.22;-1.0*MS[1];16.9217.14; / EH(eiFi) / 12032020 33dmbutanal		HO
Channel III	Intensity (1458)	Intensity (753) 		CH ₂
	41.06	500		C ²⁰
				' H
				3-hydroxy-2,2-dimethyl-
	50.0 100.0 m/z	40 60 80 100 120		propanal
20.91	MS[1]:20.84.20.98[-1.0 ^{MS} [1]:20.79.20.87; / EI+(eIFi) / 09032020.33dmbutanal+ci2 t 28 min Intensity (623)			HO
Channel III	600- 39.04 41.06 59.07			$\downarrow $ OH
	400 87.07 200 56.08			
				•••2
	n/2 00.0 100.0 120.0			2,2-dimethylpropane-
				1,3-diol

• *tr for OH and NO₃ experiment. Shorter Time retention than Cl experiments due to a new chromatographic column.

• **Secondary product. At large time reaction