

Electronic Supplementary Information

The Reaction of Organic Peroxy Radicals with Unsaturated Compounds Controlled by a non-Epoxyde Pathway under Atmospheric Conditions

By Barbara Nozière,^a Olivier Durif,^a Eloé Dubus,^a Stephanie Kylington,^a Åsa Emmer,^a Fabienne Fache,^b Felix Piel,^c and Armin Wisthaler^c

^a KTH, Royal Institute of Technology, Department of Chemistry, 114 28 Stockholm, Sweden

^b Université Lyon 1 and CNRS, UMR 5246, ICBMS, 69626 Villeurbanne, France

^c University of Oslo, Department of Chemistry, 0315 Oslo, Norway

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Table S1: List of the experiments and experimental conditions. All the concentrations are in cm.⁻³

3

C₅H₁₁O₂ + 2,3DMB			
Expt. n°	F_{air} (sLm)	[C₅H₁₁]	[2,3DMB]
PTr-MS FUSION analyses			
Alk35	3.5/1.75	3.4 × 10 ¹³	2.0 × 10 ¹³ / 5.1 × 10 ¹³
Alk36	3.5/1.0	3.4 × 10 ¹³	2.0 × 10 ¹³ / 5.1 × 10 ¹³
Alk37	3.0/1.0	6.0 × 10 ¹³	7.2×10 ¹³ / 1.4×10 ¹⁴ / 1.8×10 ¹⁴ / 2.7×10 ¹⁴
Alk38	3.0/1.0	6.0 × 10 ¹³	7.2×10 ¹³ / 1.4×10 ¹⁴ / 1.8×10 ¹⁴ / 2.7×10 ¹⁴
Alk48	1.0	6.0 × 10 ¹³	7.2×10 ¹³ / 1.4×10 ¹⁴ / 1.8×10 ¹⁴ / 2.7×10 ¹⁴
GC/MS analyses			
Alk39	3.0/1.0	6.0 × 10 ¹³	sample 3: Lights OFF, 2.7 × 10 ¹⁴ samples 4 and 6: Lights ON, 2.7 × 10 ¹⁴ samples 5 and 7: Lights ON, 7.2 × 10 ¹³
Alk40	3.0/1.0	6.0 × 10 ¹³	sample 3: Lights OFF, 2.7 × 10 ¹⁴ samples 4 and 6: Lights ON, 2.7 × 10 ¹⁴ samples 5 and 7: Lights ON, 7.2 × 10 ¹³
C₅H₁₁O₂, + isoprene (PTr-MS FUSION analyses only)			
		[C₅H₁₁]	[isoprene]
Alk41	3.5/1.0	3.4 × 10 ¹³	2.3 × 10 ¹³ / 4.6 × 10 ¹³
Alk42	3.5/1.0	3.4 × 10 ¹³	4.6 × 10 ¹³ / 1.2 × 10 ¹⁴
Alk43	3.0/1.0	3.4 × 10 ¹³	4.3 × 10 ¹³ / 6.5 × 10 ¹³ / 8.6 × 10 ¹³
Alk44	3.0/1.0	6.0 × 10 ¹³	4.3 × 10 ¹³ / 6.5 × 10 ¹³ / 8.6 × 10 ¹³
CH₃O₂ + 2,3DMB (PTr-MS FUSION analyses only)			
		[CH₃I]	[2,3DMB]
Alk45	3.0/1.0	2.3 × 10 ¹⁴	1.8×10 ¹⁴ / 3.5×10 ¹⁴
Alk46	3.0/1.0	7.7 × 10 ¹⁴	1.4×10 ¹⁴ / 1.8×10 ¹⁴ / 2.7×10 ¹⁴ / 3.5×10 ¹⁴
Alk47	3.0/1.0	5.5 × 10 ¹⁴	1.4×10 ¹⁴ / 1.8×10 ¹⁴ / 2.7×10 ¹⁴ / 3.5×10 ¹⁴

Table S2: Main ions in the experiments C₅H₁₁O₂ + 2,3 DM2B

<i>m/z</i>	Intensity (Baseline/Product)	Ion sum formula	Neutral sum formula	Interpretation and comments
19.018	10 ⁵ / -	H ₃ O ⁺	H ₂ O	Source
31.018	10 ³ / 10 ⁴	CH ₂ OH ⁺	CH ₂ O	Formaldehyde, product
43.018	10 ⁴ / 5x10 ⁴	C ₂ H ₂ OH ⁺	C ₂ H ₄ O ₂	Fragment of C ₂ H ₄ O ₂ H ⁺
45.033	- / 5x10 ⁴	C ₂ H ₄ OH ⁺	C ₂ H ₄ O	Acetaldehyde, product side-chemistry
59.049	5x10 ⁴ / 5x10 ⁴	C ₃ H ₆ OH ⁺	C ₃ H ₆ O	Acetone, 2,3DM2B product
61.028	10 ⁴ / 10 ⁴	C ₂ H ₄ O ₂ H ⁺	C ₂ H ₄ O ₂	Acetic acid/hydroxyacetaldehyde, product
67.054	10 ⁴ / 10 ⁴	C ₅ H ₇ ⁺	/	Fragment, autoxidation C ₅ H ₁₁ O ₂
69.070	10 ⁵ / 5x10 ⁴	C ₅ H ₈ H ⁺	/	Fragment, autoxidation C ₅ H ₁₁ O ₂
71.049	5x10 ³ / 10 ⁴	C ₄ H ₆ OH ⁺	/	Fragment, autoxidation C ₅ H ₁₁ O ₂
83.049	5x10 ³ / 10 ⁴	C ₅ H ₆ OH ⁺	/	Fragment, autoxidation C ₅ H ₁₁ O ₂
85.065	10 ⁴ / 10 ⁴	C ₅ H ₈ OH ⁺	C ₅ H ₁₀ O ₂	3-hydroxy-3-methyl-2-butanone + pentanoic acid (dehydrated ion)
85.101	10 ⁵ / 5x10 ³	C ₆ H ₁₂ H ⁺	C ₆ H ₁₂	2,3DM2B
87.080	10 ³ / 5x10 ³	C ₅ H ₁₀ OH ⁺	C ₅ H ₁₀ O	Pentanal
97.065	10 ³ / 10 ³	C ₆ H ₈ OH ⁺	C ₆ H ₈ O	Product C ₅ H ₁₁ O ₂ + 2,3DM2B
99.044	5x10 ³ / 5x10 ³	C ₅ H ₆ O ₂ H ⁺	C ₅ H ₆ O ₂	Product RO ₂ + 2,3DM2B
99.080	5x10 ³ / 5x10 ³	C ₆ H ₁₀ OH ⁺	C ₆ H ₁₀ O	Product RO ₂ + 2,3DM2B
101.060	10 ³ / 10 ⁴	C ₅ H ₈ O ₂ H ⁺	C ₅ H ₁₀ O ₃	Fragment, autoxidation C ₅ H ₁₁ O ₂
101.096	10 ⁵ / 10 ⁴	C ₆ H ₁₂ OH ⁺	C ₆ H ₁₂ O	Tetramethyl oxirane + 210 isomers
103.075	- / 10 ³	C ₅ H ₁₀ O ₂ H ⁺	C ₅ H ₁₀ O ₂	3-hydroxy-3-methyl-2-butanone + pentanoic acid
105.018	- / 5x10 ²	C ₃ H ₄ O ₄ H ⁺	/	Fragment, side-chemistry
105.033	- / 10 ²	C ₇ H ₄ OH ⁺	/	Fragment, RO ₂ + 2,3DM2B
125.096	5x10 ² / 5x10 ³	C ₈ H ₁₂ OH ⁺	/	Product C ₅ H ₁₁ O ₂ + 2,3DM2B
126.9	10 ³ / 5x10 ³	I ⁺	I	Iodine atom
127.112	5x10 ² / 10 ³	C ₈ H ₁₄ OH ⁺	/	Product C ₅ H ₁₁ O ₂ + 2,3DM2B
139.075	10 ³ / 5x10 ³	C ₈ H ₁₀ O ₂ H ⁺	/	Product C ₅ H ₁₁ O ₂ + 2,3DM2B
253.82	- / 5x10 ³	I ₂ ⁺	I ₂	di-Iodine

Table S3: Main ions in the experiments C₅H₁₁O₂ + isoprene.

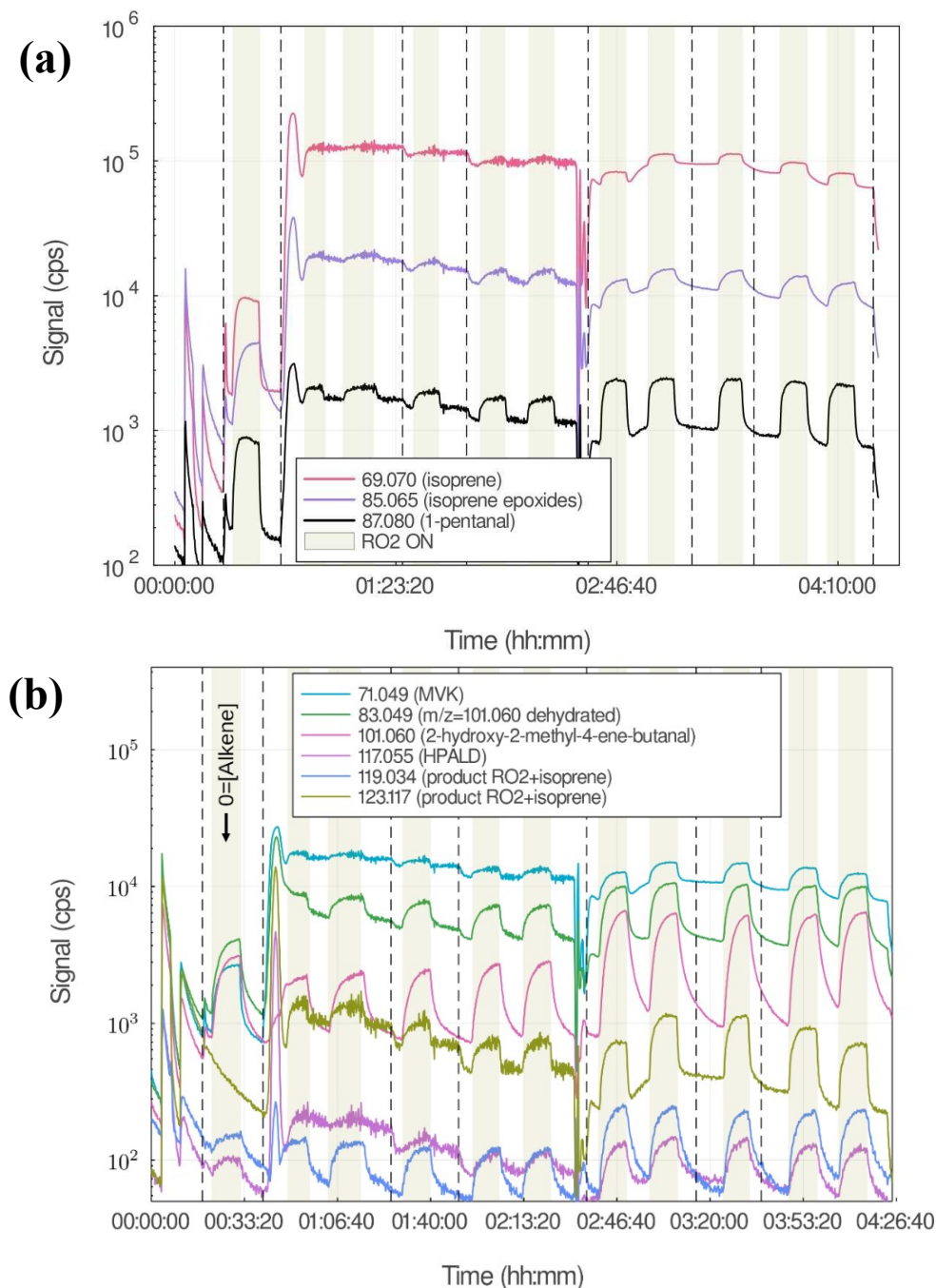
<i>m/z</i>	Intensity (Baseline/Product)	Ion sum formula	Neutral sum formula	Interpretation and comments
19.018	10 ⁵ / -	H ₃ O ⁺	H ₂ O	Source
31.018	5x10 ³ / 10 ³	CH ₂ OH ⁺	CH ₂ O	Formaldehyde, product
43.018	5x10 ⁴ / 10 ⁴	C ₂ H ₂ OH ⁺	C ₂ H ₄ O ₂	Fragment of C ₂ H ₄ O ₂ H ⁺
45.033	5x10 ³ / 10 ⁴	C ₂ H ₄ OH ⁺	C ₂ H ₄ O	Acetaldehyde, product side-chemistry
55.018	10 ³ / 5x10 ²	C ₃ H ₂ OH ⁺	/	Fragment, side-chemistry
59.049	5x10 ⁴ / 2x10 ³	C ₃ H ₆ OH ⁺	C ₃ H ₆ O	Acetone, product
61.028	5x10 ³ / 5x10 ³	C ₂ H ₄ O ₂ H ⁺	C ₂ H ₄ O ₂	Acetic acid/hydroxyacetaldehyde, product side-chemistry
69.070	10 ⁵ / 10 ⁴	C ₅ H ₈ H ⁺	C ₅ H ₈	isoprene
71.049	10 ⁴ / 5x10 ³	C ₄ H ₆ OH ⁺	C ₄ H ₆ O	MACR or MVK
73.028	10 ³ / 10 ³	C ₃ H ₄ O ₂ H ⁺	C ₃ H ₄ O ₂	Product side-chemistry
83.049	5x10 ³ / 5x10 ³	C ₅ H ₆ OH ⁺	C ₅ H ₈ O ₂	2-hydroxy-2-methyl-3-butenal (dehydrated ion)
85.065	10 ⁴ / 5x10 ³	C ₅ H ₈ OH ⁺	C ₅ H ₈ O	Isoprene epoxide
87.080	5x10 ² / 10 ³	C ₅ H ₁₀ OH ⁺	C ₅ H ₁₀ O	Pentanal
101.060	10 ³ / 5x10 ³	C ₅ H ₈ O ₂ H ⁺	C ₅ H ₈ O ₂	2-hydroxy-2-methyl-3-butenal
103.075	10 ² / 10 ³	C ₅ H ₁₀ O ₂ H ⁺	C ₅ H ₁₀ O ₂	Pentanoic acid, product side-chemistry
105.018	50 / 10 ²	C ₃ H ₄ O ₄ H ⁺	/	Product side-chemistry
107.034	50 / 10 ²	C ₃ H ₆ O ₄ H ⁺	C ₃ H ₆ O ₄	Product side-chemistry
111.080	10 ² / 10 ²	C ₇ H ₁₀ O ₄ H ⁺	C ₇ H ₁₀ O ₄	Product side-chemistry
113.023	5x10 ² / 10 ²	C ₅ H ₄ O ₃ H ⁺	C ₅ H ₄ O ₃	Product side-chemistry
115.039	10 ² / 10 ²	C ₅ H ₆ O ₃ H ⁺	C ₅ H ₆ O ₃	Product side-chemistry
117.055	50 / 10 ²	C ₅ H ₈ O ₃ H ⁺	C ₅ H ₈ O ₃	HPALD
119.034	50 / 10 ²	C ₄ H ₆ O ₄ H ⁺	/	Product C ₅ H ₁₁ O ₂ + isoprene
121.028	10 ² / 10 ²	C ₇ H ₄ O ₂ H ⁺	C ₇ H ₄ O ₂	Product
123.117	5x10 ² / 5x10 ²	C ₉ H ₁₄ H ⁺	/	Fragment C ₅ H ₁₁ O ₂ + isoprene
126.9	5x10 ³ / 5x10 ³	I ⁺	I	Iodine atom
253.82	- / 5x10 ³	I ₂ ⁺	I ₂	di-Iodine

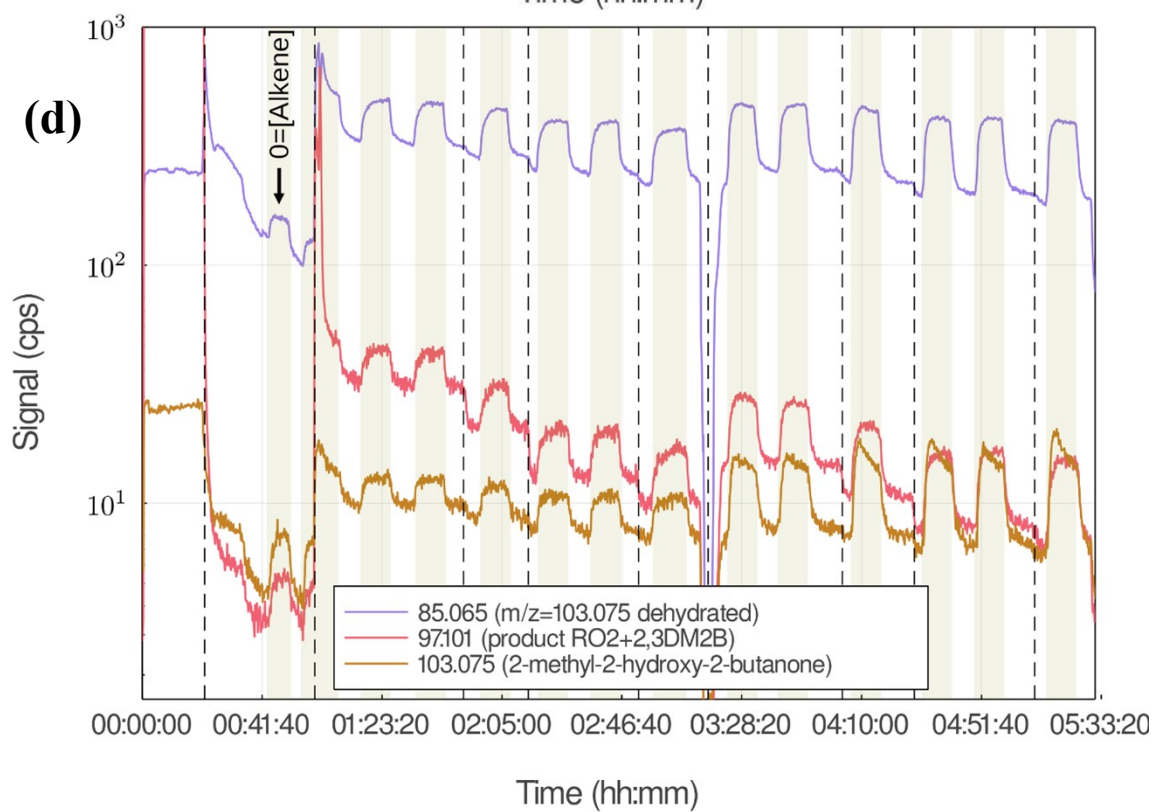
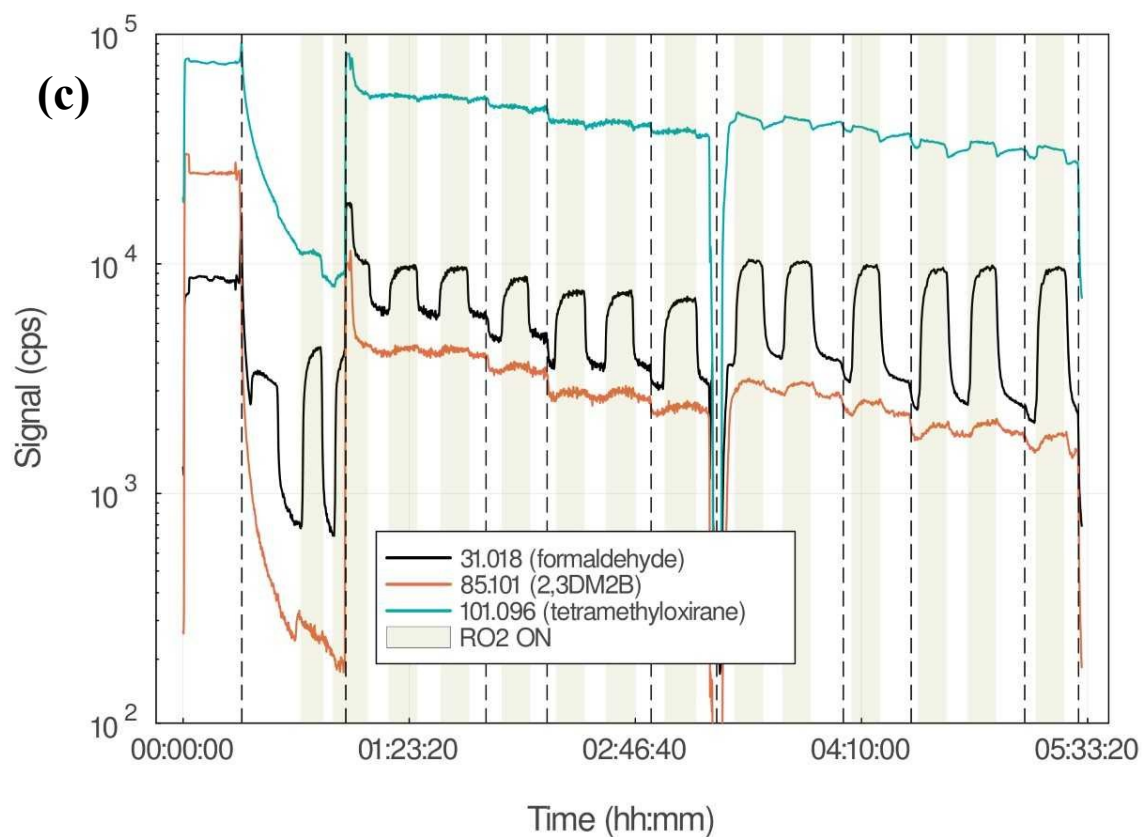
Table S4: Main ions in the experiments CH₃O₂ + 2,3DM2B.

<i>m/z</i>	Intensity (Baseline/Product)	Ion sum formula	Neutral sum formula	Interpretation and comments
19.018	10 ⁵ / -	H ₃ O ⁺	H ₂ O	Source
31.018	5x10 ³ / 10 ⁴	CH ₂ OH ⁺	CH ₂ O	Formaldehyde, product
43.018	5x10 ⁴ / 5x10 ³	C ₂ H ₂ OH ⁺	C ₂ H ₄ O ₂	Fragment of C ₂ H ₄ O ₂ H ⁺
45.033	5x10 ³ / 10 ³	C ₂ H ₄ OH ⁺	C ₂ H ₄ O	Acetaldehyde, product side-chemistry
47.013	10 ³ / 10 ³	CH ₂ O ₂ H ⁺	CH ₂ O ₂	Formic acid, product side-chemistry CH ₃ O ₂
47.049	- / 10 ³	C ₂ H ₆ OH ⁺	C ₂ H ₆ O	Product side-chemistry CH ₃ O ₂
55.054	5x10 ⁴ / 10 ⁴	C ₄ H ₆ H ⁺	/	Fragment, side-chemistry
59.049	5x10 ⁴ / 10 ⁴	C ₃ H ₆ OH ⁺	C ₃ H ₆ O	Acetone, product RO ₂ + 2,3DM2B
61.028	5x10 ³ / 10 ⁴	C ₂ H ₄ O ₂ H ⁺	C ₂ H ₄ O ₂	Acetic acid/hydroxyacetaldehyde, product side-chemistry
73.065	10 ³ / 5x10 ²	C ₄ H ₈ OH ⁺	C ₄ H ₈ O	Product side-chemistry
81.070	5x10 ³ / 10 ³	C ₆ H ₈ H ⁺	/	Fragment side-chemistry
83.049	5x10 ² / 5x10 ²	C ₅ H ₆ OH ⁺	/	Product side-chemistry
83.086	10 ⁴ / 5x10 ³	C ₆ H ₁₀ H ⁺	/	Fragment side-chemistry
85.065	10 ³ / 10 ³	C ₅ H ₈ OH ⁺	C ₅ H ₁₀ O ₂	2-methyl-2-hydroxy-2-butanone (dehydrated ion)
97.101	10 ² / 10 ²	C ₇ H ₁₁ H ⁺	C ₇ H ₁₁	Fragment CH ₃ O ₂ + 2,3DM2B
126.9	10 ⁵ / 10 ⁴	I ⁺	I	Iodine atom
253.82	10 ⁴ / 5x10 ⁴	I ₂ ⁺	I ₂	di-Iodine

Figure S5: Time-profiles and variations of the main aldehydes with alkene concentration in the experiments.

a) and b): Time profiles for $C_5H_{11}O_2$ + isoprene (Experiments Alk44); c) and d) Time profiles for CH_3O_2 + 2,3DM2B (experiment Alk46); The shaded areas correspond to RO_2 "ON" cycles. The dashed lines indicate different alkene concentrations (decreasing during the experiments, with the values given in Table S1). In all the experiments, the products were first studied at a reaction time of $t = 17$ s (first part of the experiment), then at a reaction time of $t = 53$ s (second part).e)-g) Variations of the aldehydes signal with alkene concentration.





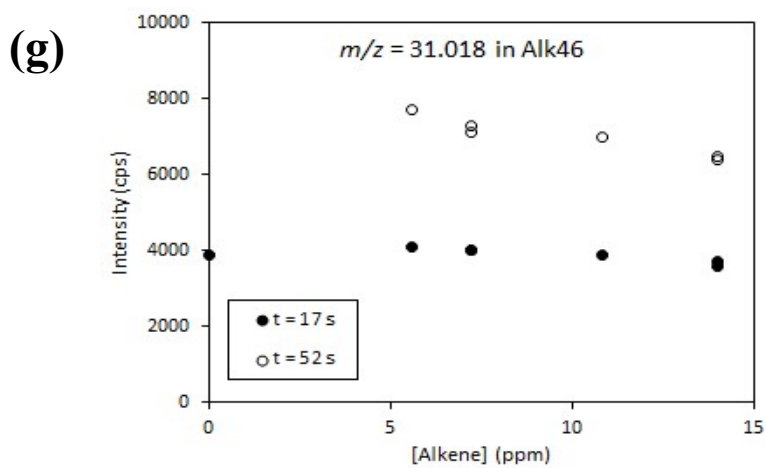
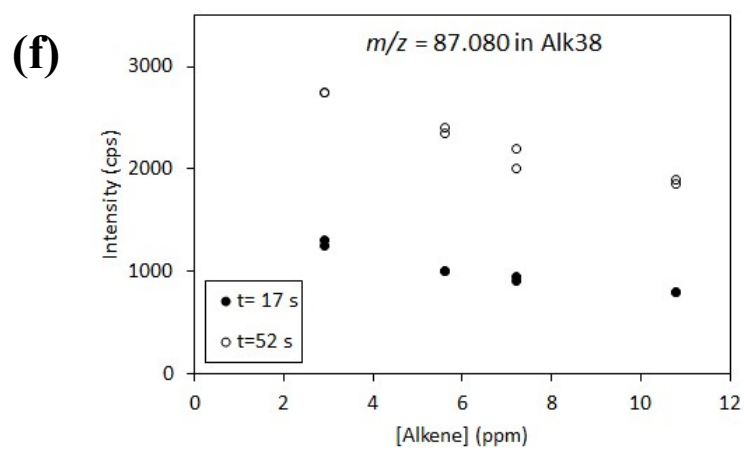
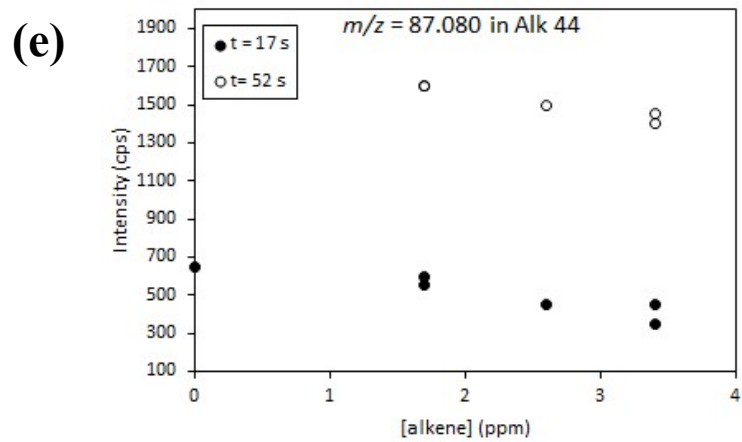


Figure S6: Chromatograms.

Chromatograms obtained in $C_5H_{11}O_2 + 2,3DM2B$ experiment (Alk40, sample 4).

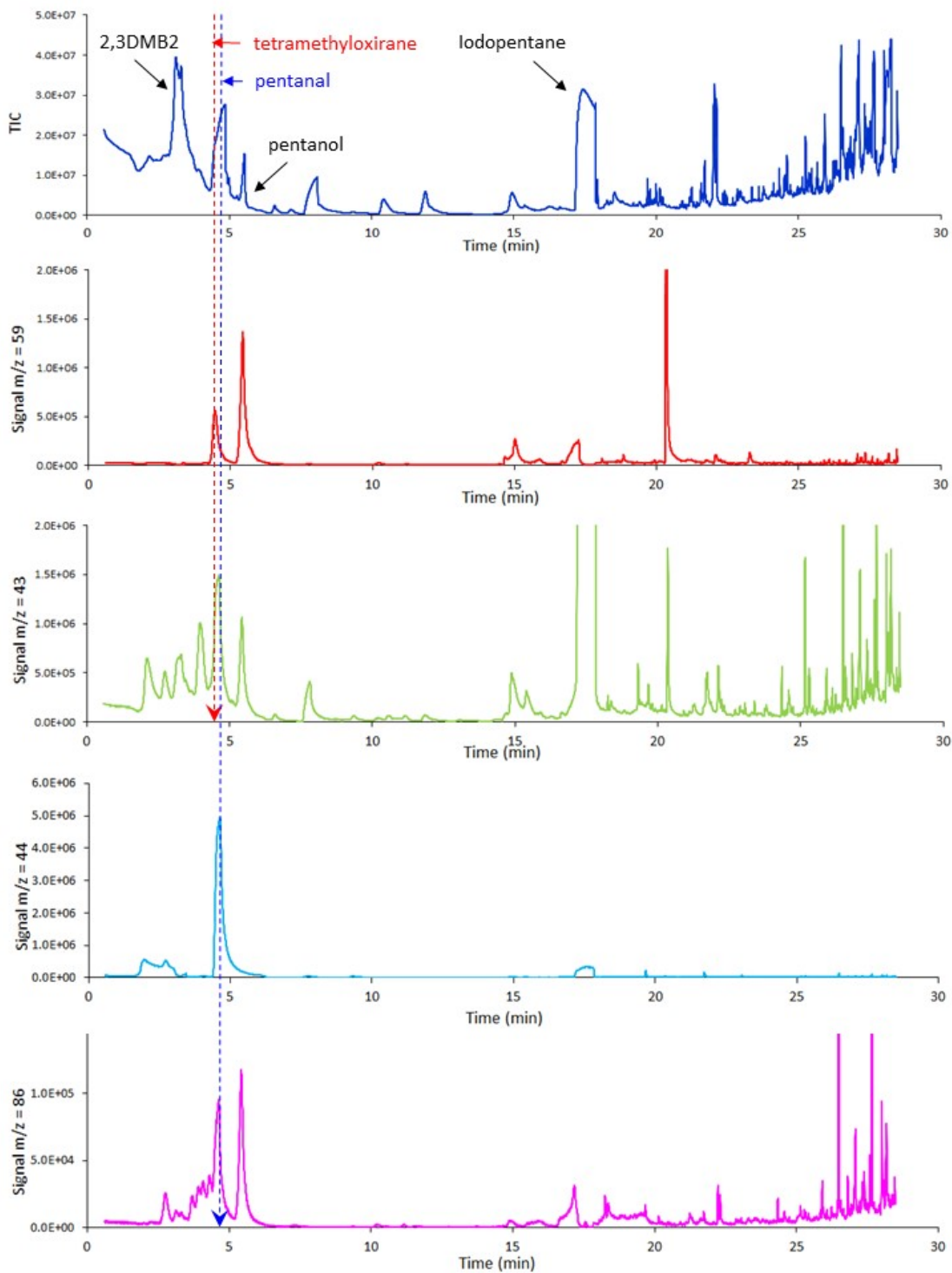
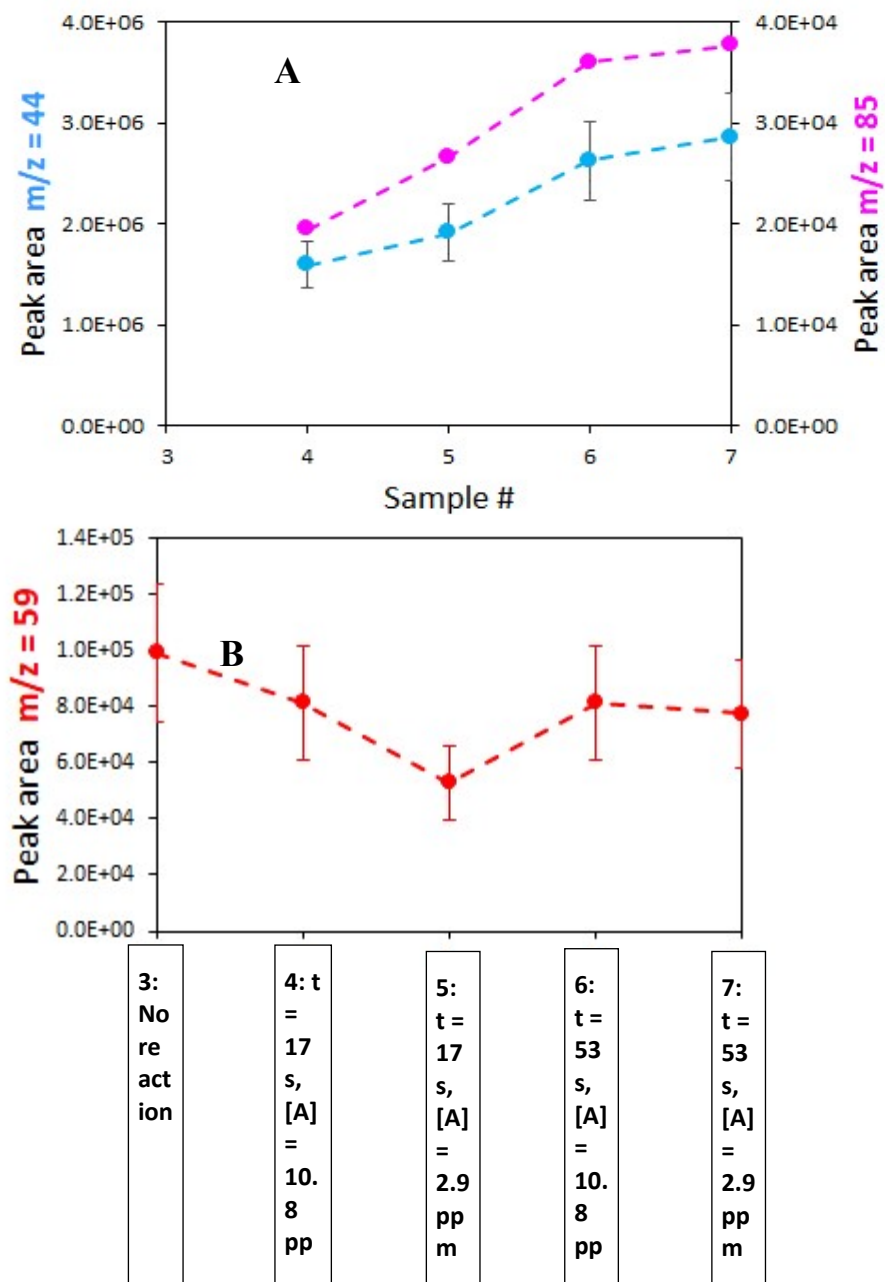


Figure S7: GC/MS analysis: Evolution of the concentration of 1-pentanal and tetramethyloxirane.

A) Pentanal at $m/z = 44$ and 85. B) tetramethyl oxirane at $m/z = 59$. Data are averaged between Alk39 and Alk40 and error bars represent the dispersion between the results. [A] = alkene concentration.



Section S8: Kinetic simulations

Kinetic simulations were performed to determine the amount of epoxide expected if RO2+alkene proceeded entirely by the epoxide channel, as suggested in the literature. As in our previous study, ChemSimul V3.90 was used and with the rate coefficients summarized in Table S8.1. The results are presented in Table S8.2, where $\Delta[\text{alkene}]$ is the amount of alkene consumed and “HOOQO₂” the sum of the autoxidation products for C₅H₁₁O₂.

Estimation of the detection sensitivity for the epoxides: The detection sensitivity for the epoxides, S_0 (cps/ppb) was estimated by considering the background concentration of tetramethyloxirane in Alk38 before reaction. This background signal was $S \sim 100000$ cps (Fig. 3 and above) for a concentration of tetramethyloxirane of 0.2 % $\times 2.7 \times 10^{14} = 5.4 \times 10^{11}$ cm⁻³ (22 ppb). Thus, $S_0 \sim 4630$ cps/ppb, which can be rounded up to 5000 cps/ppb and is typical for oxygenated compounds detected by PTR-MS.

Table S8.1: Rate coefficients used in the simulations

Rate coefficients	HO ₂	CH ₃ O ₂	C ₅ H ₁₁ O ₂
k_{self} (cm ³ s ⁻¹)	1.6×10^{-12}	3.5×10^{-13}	4.0×10^{-13}
k_{HO_2} (cm ³ s ⁻¹)	/	5.2×10^{-12}	1×10^{-11}
k_{iso} (s ⁻¹)	/	/	2.4×10^{-3}
k_{wall} (s ⁻¹)	3×10^{-3}	3×10^{-3}	3×10^{-3}
k_{alk} (cm ³ s ⁻¹) isoprene	1.7×10^{-19}	/	8.0×10^{-18}
k_{alk} (cm ³ s ⁻¹) 2,3-dimethyl-2-butene	3.7×10^{-19}	6.7×10^{-18}	1.6×10^{-16}

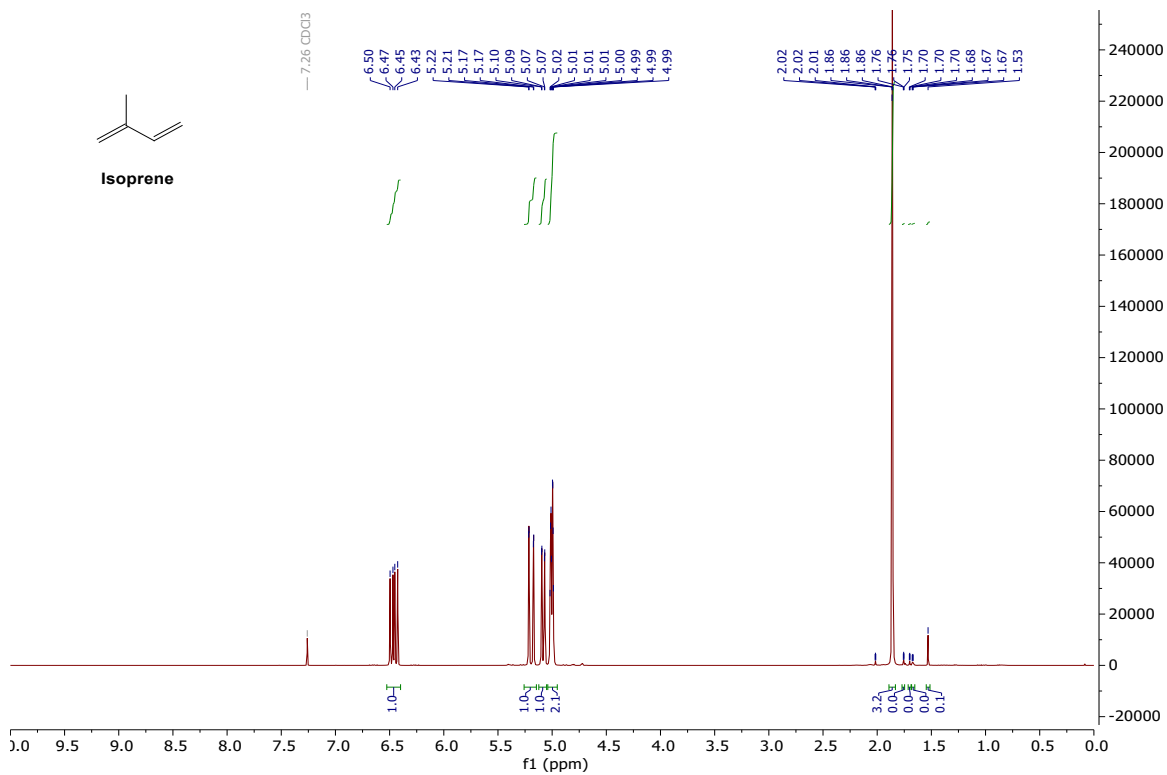
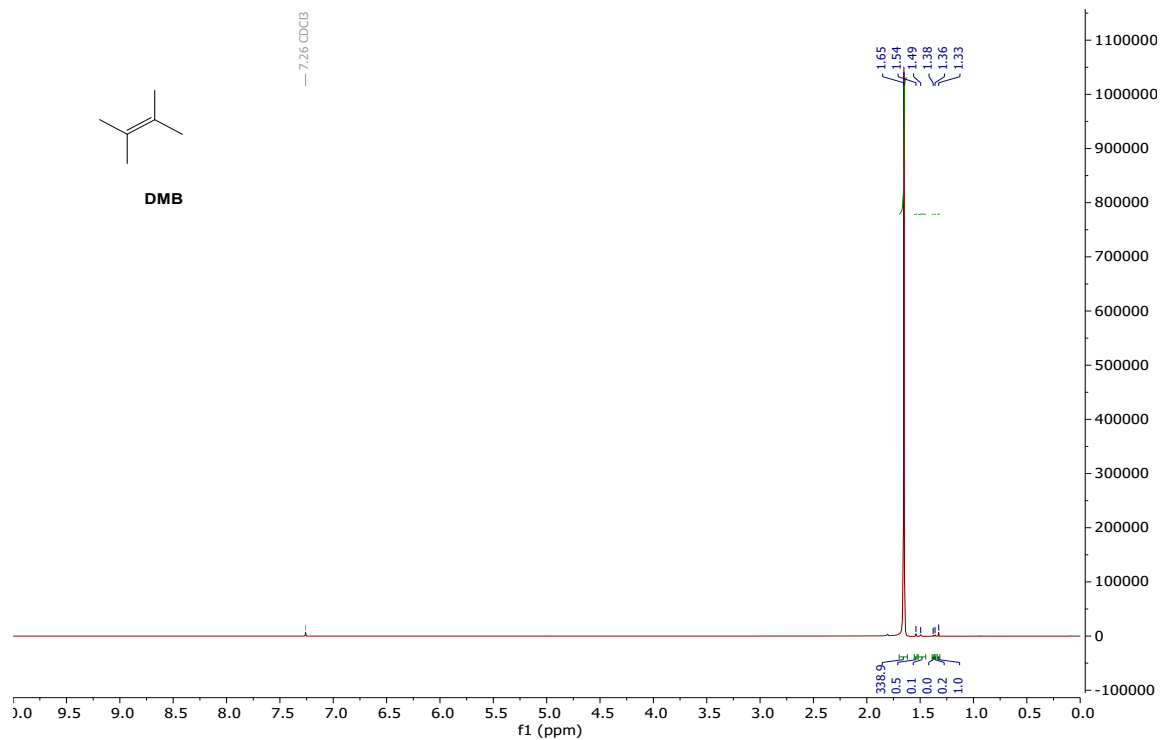
Table S8.2: Results of the kinetic simulations

All concentrations are in cm⁻³. The data highlighted in yellow correspond to reaction times close to those studied in the experiments.

C ₅ H ₁₁ O ₂ + 2,3DM2B (Alk38)							
Time (s)	[C ₅ H ₁₁ O ₂]	[1-pentanal]	[HO ₂]	[HOOQO ₂]	[Epoxide]	[Alkene]	$\Delta[\text{alkene}]$
0	2.50E+12	0.00E+00	0.00E+00	0.00E+00	0.00E+00	3.00E+14	
6	9.69E+10	1.21E+12	9.58E+09	5.55E+09	1.11E+11	3.00E+14	1.10E+11
12	3.51E+10	1.24E+12	6.59E+09	6.39E+09	1.28E+11	3.00E+14	1.30E+11
18	1.63E+10	1.25E+12	5.58E+09	6.74E+09	1.35E+11	3.00E+14	1.30E+11
24	8.37E+09	1.25E+12	5.04E+09	6.91E+09	1.38E+11	3.00E+14	1.40E+11
30	4.51E+09	1.26E+12	4.66E+09	7.00E+09	1.40E+11	3.00E+14	1.40E+11
36	2.51E+09	1.26E+12	4.35E+09	7.05E+09	1.41E+11	3.00E+14	1.40E+11
42	1.43E+09	1.26E+12	4.08E+09	7.08E+09	1.42E+11	3.00E+14	1.40E+11
48	8.28E+08	1.26E+12	3.84E+09	7.10E+09	1.42E+11	3.00E+14	1.40E+11
54	4.88E+08	1.26E+12	3.61E+09	7.10E+09	1.42E+11	3.00E+14	1.40E+11
60	2.92E+08	1.26E+12	3.40E+09	7.11E+09	1.42E+11	3.00E+14	1.40E+11

C ₅ H ₁₁ O ₂ + isoprene (Alk44)							
Time (s)	[C ₅ H ₁₁ O ₂]	[1-pentanal]	[HO ₂]	[HOOQO ₂]	[Epoxide]	[Alkene]	Δ[Alkene]
0	2.50E+12	0.00E+00	0.00E+00	0.00E+00	0.00E+00	9.00E+13	
6	1.27E+11	1.19E+12	6.89E+09	5.98E+09	2.24E+10	9.00E+13	2.20E+10
12	6.09E+10	1.22E+12	3.81E+09	7.23E+09	2.71E+10	9.00E+13	2.70E+10
18	3.83E+10	1.23E+12	2.75E+09	7.92E+09	2.97E+10	9.00E+13	3.00E+10
24	2.70E+10	1.24E+12	2.22E+09	8.38E+09	3.14E+10	9.00E+13	3.10E+10
30	2.02E+10	1.24E+12	1.90E+09	8.72E+09	3.27E+10	9.00E+13	3.30E+10
36	1.57E+10	1.25E+12	1.69E+09	8.97E+09	3.36E+10	9.00E+13	3.40E+10
42	1.26E+10	1.25E+12	1.54E+09	9.18E+09	3.44E+10	9.00E+13	3.40E+10
48	1.02E+10	1.25E+12	1.43E+09	9.34E+09	3.50E+10	9.00E+13	3.50E+10
54	8.46E+09	1.25E+12	1.34E+09	9.47E+09	3.55E+10	9.00E+13	3.60E+10
60	7.08E+09	1.25E+12	1.27E+09	9.59E+09	3.59E+10	9.00E+13	3.60E+10
CH ₃ O ₂ + 2,3DMB (Alk46)							
Time (s)	[CH ₃ O ₂]	[HCHO]	[HO ₂]		[Epoxide]	[Alkene]	Δ[Alkene]
0	5.00E+12	0.00E+00	0.00E+00		0.00E+00	3.50E+14	
6	1.28E+11	2.47E+12	1.27E+10		3.74E+10	3.50E+14	4.00E+10
12	6.17E+10	2.49E+12	6.24E+09		4.38E+10	3.50E+14	4.00E+10
18	3.92E+10	2.50E+12	4.05E+09		4.74E+10	3.50E+14	5.00E+10
24	2.80E+10	2.50E+12	2.95E+09		4.99E+10	3.50E+14	5.00E+10
30	2.12E+10	2.51E+12	2.29E+09		5.17E+10	3.50E+14	5.00E+10
36	1.68E+10	2.51E+12	1.86E+09		5.30E+10	3.50E+14	5.00E+10
42	1.36E+10	2.51E+12	1.55E+09		5.42E+10	3.50E+14	5.00E+10
48	1.13E+10	2.51E+12	1.32E+09		5.51E+10	3.50E+14	6.00E+10
54	9.51E+09	2.51E+12	1.14E+09		5.58E+10	3.50E+14	6.00E+10
60	8.09E+09	2.51E+12	1.00E+09		5.65E+10	3.50E+14	6.00E+10

Figure S9: NMR spectra for the 2,3DM2B and isoprene samples.



Section S10: Kinetic analyses of the ion signals in the reactions RO₂ + alkene.

A) Kinetic analyses

First-order kinetic analyses were applied to the most intense ion signals attributed to specific RO₂ + Alkene reactions (cf. Tables S2-S4 and discussion in the text). For this, the signal variations in the Light ON / Light OFF cycle (ΔS) were measured at the two reaction times explored ($t_1 = 17$ s, achieved with a flow of 3 sLm and $t_2 = 53$ s, achieved with a flow of 1 sLm) and for each alkene concentration. The rate coefficient for the formation of the corresponding product, k^{II} (cm³ s⁻¹), was then obtained by applying the equation:

$$\ln\left(1 - \frac{\Delta S_1}{\Delta S_2}\right) = k^{\text{II}} \times [\text{Alkene}] \times (t_2 - t_1) \quad (12).$$

Thus k^{II} was obtained from the slope of $\ln(1 - \Delta S_1/\Delta S_2)$ as function of [alkene]. In the analyses of the experimental profiles ΔS is measured from the relative baseline. The error bars reported in the plots below represent the uncertainties in measuring ΔS_1 and ΔS_2 .

B) Results

Figure S10B1: Evolution of the ion $m/z = 127.112$ in C₅H₁₁O₂ + 2,3DM2B experiment (Alk38).

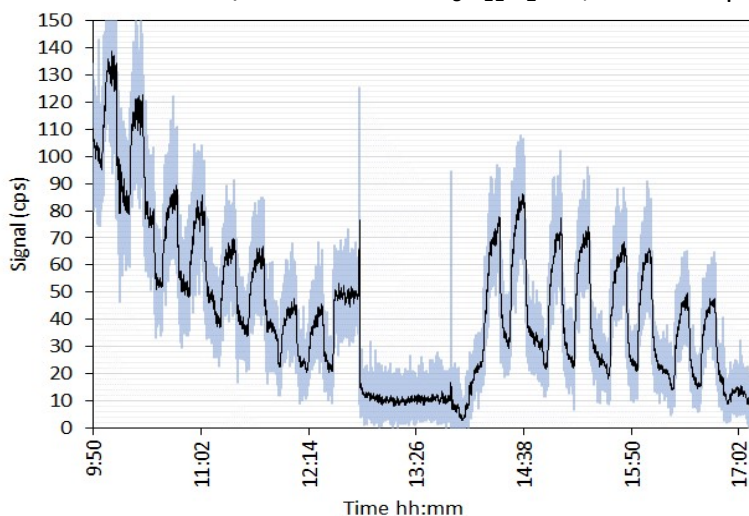


Figure S10B2: Kinetic plot for Fig. S10B1

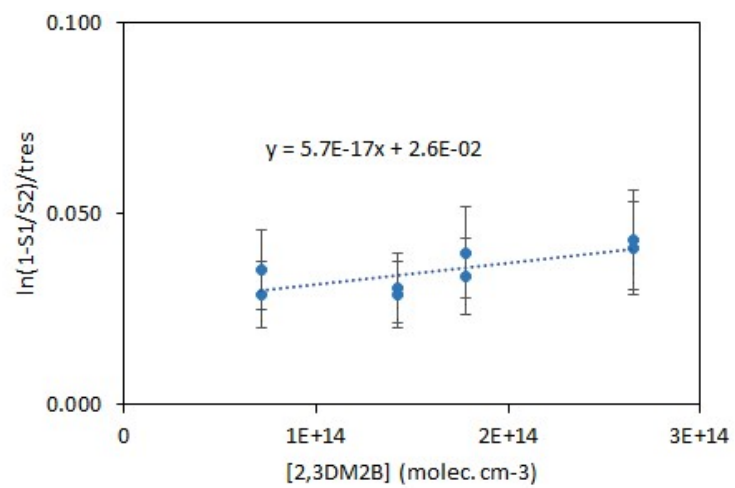


Figure S10B3: Evolution of the ion $m/z = 119.034$ in $C_5H_{11}O_2$ + isoprene experiment (Alk44).

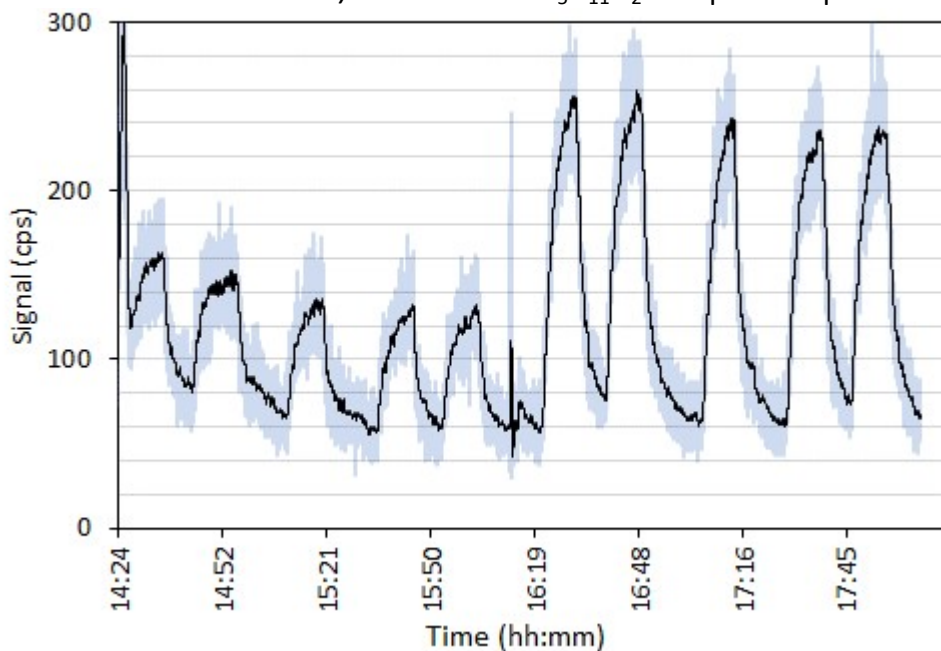


Figure S10B4: Kinetic plot for Fig. S10B3.

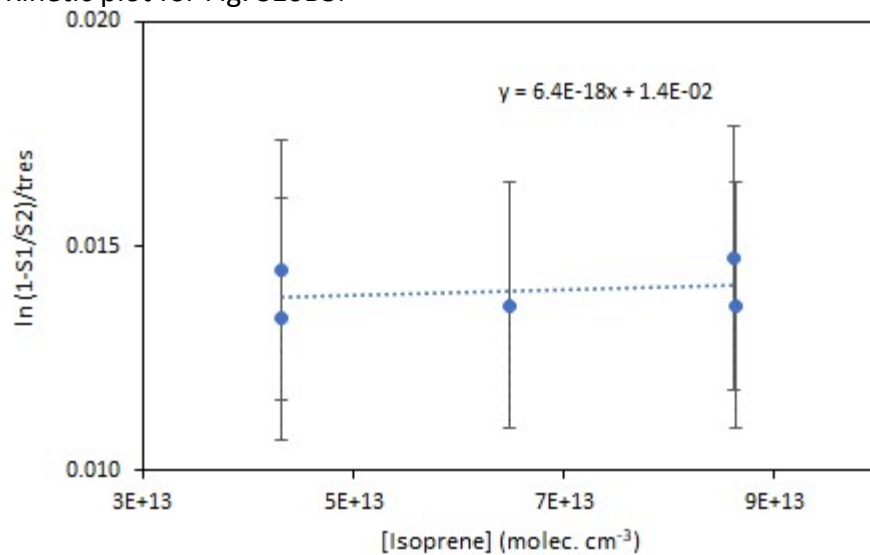


Figure S10B5: Evolution of the ion $m/z = 85.065$ in $\text{CH}_3\text{O}_2 + 2,3\text{DM2B}$ experiment (Alk46).

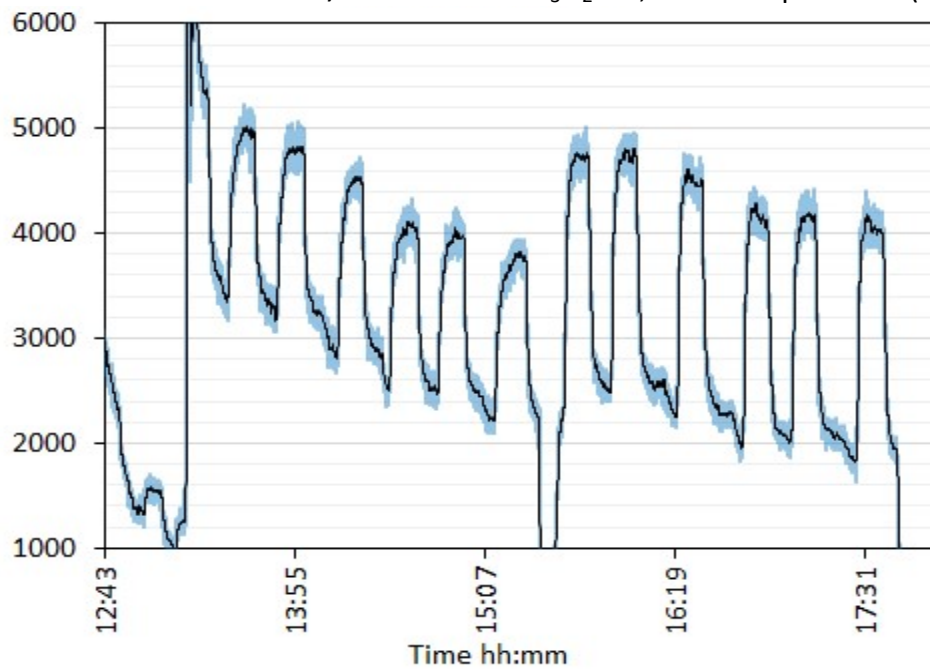


Figure S10B6: Kinetic plot for Fig. S10B5.

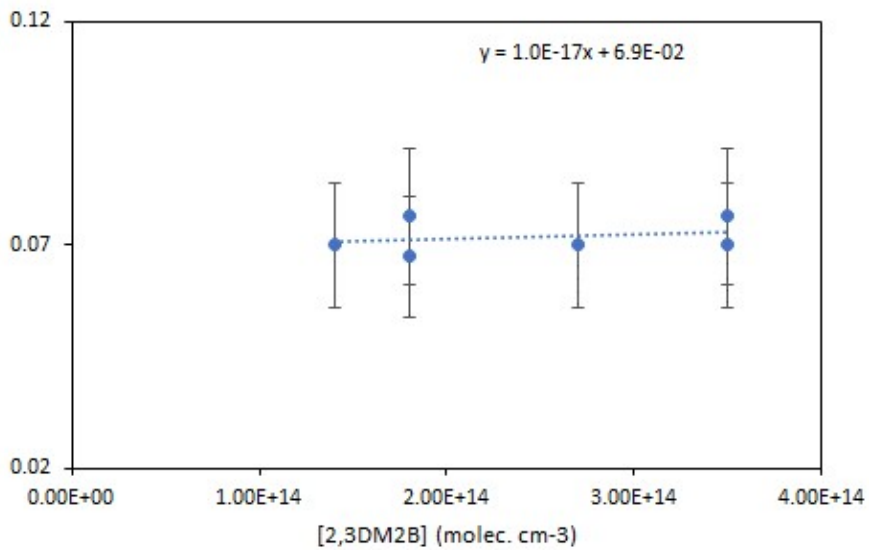
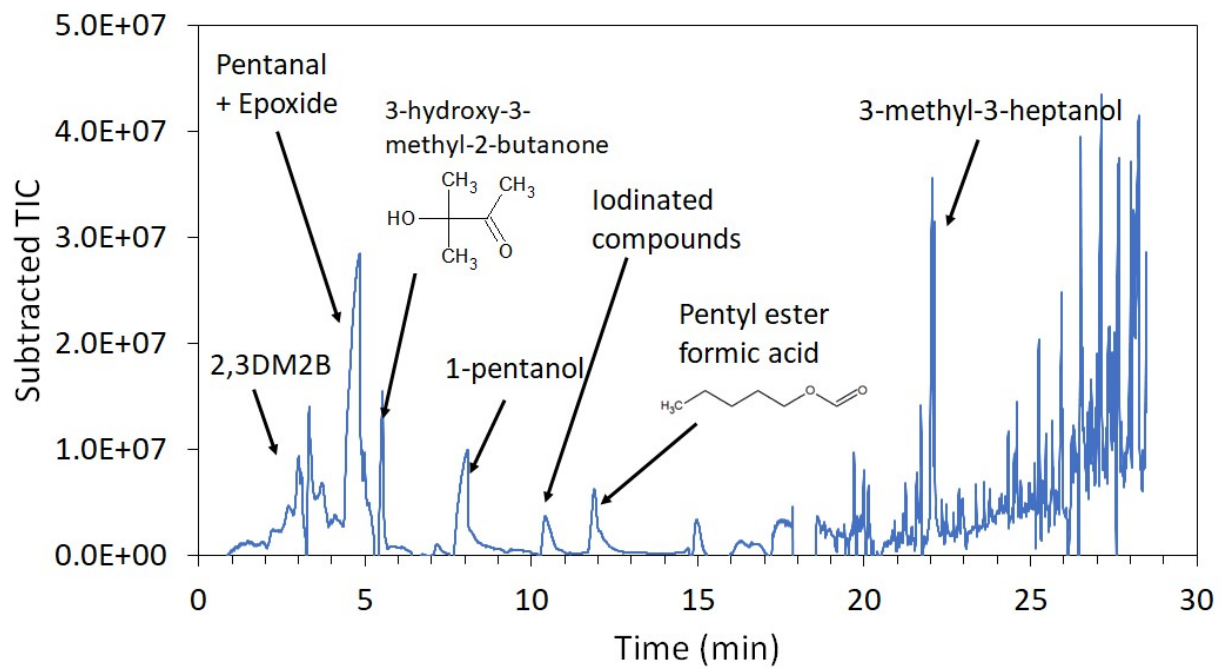


Figure S11: Chromatograms of potential reaction products.



Section S12: Potential effects of RO₂+alkene reactions in chamber experiments (kinetic simulations)

The potential impacts of RO₂+alkene reactions in chamber experiments were examined by using the experiments of ref. 14 (oxidation of isoprene by OH under low NO_x conditions) as an example. Simple kinetic simulations were performed using ChemSimul V3.90 and the reactions presented in Table S12.1. The kinetic system was run over 2h-cycles, mimicking the experiments of ref. 14, and kept as simple as possible to examine mostly the effects on the concentration of isoprene-RO₂ ("IsopRO₂"), the total RO₂, ΣRO₂, and OH recycling. To determine a lower limit for the impact of RO₂+isoprene, only one isoprene-RO₂ was considered, Z-δ-RO₂-I, which has the fastest monomolecular sink rate ($r_{mono} = 0.1$ or 0.4 s^{-1} , see justifications in ref. 14). The initial isoprene concentrations was set to 5 ppb, as in ref. 14 and the rate of photolytic production of OH was adjusted in the simulations to obtain OH concentrations comparable to those reported in ref. 14.

Table S12.1: Reactions and rate coefficients included in the simulations.

Reaction	Rate coefficients	Comment
(1) Precursor → OH	$8 \times 10^5 \text{ cm}^{-3} \text{ s}^{-1}$	Photolytic source for OH. Adjusted to fit [OH] to ref. 14
(2) Isoprene + OH → IsopOH	$1.0 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$	
(3) IsopOH + O ₂ → IsopRO ₂	$8.0 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$	
(4) IsopRO ₂ → DHP-MVK + OH + CO	0.1 to 0.4 s^{-1}	Rates from ref. 14.
(5) IsopRO ₂ + IsopRO ₂ → 2 MVK + 2 HCHO + 2 HO ₂	$3.0 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$	Source for HO ₂
(6) IsopRO ₂ + HO ₂ → ISOPOOH + O ₂	$1.0 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$	Main sink for HO ₂
(7) IsopRO ₂ + isoprene → C10RO ₂	0 to $1.0 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$	Varied to study the impact of RO ₂ +isoprene
(8) C10RO ₂ → products	$1.0 \times 10^{-2} \text{ s}^{-1}$	Lumped sink rate assumed for the R'O ₂ from RO ₂ +isoprene

Figure S12.2: Results of the simulations: concentrations profiles for isoprene-RO₂ (“IsopRO2”), ΣRO₂, and OH, for two different sink rates for the radical Z-δ-RO₂-I.

