

Electronic Supplementary Information for the manuscript
“Reactions of organic peroxy radicals, RO₂, with substituted and biogenic alkenes at room temperature: unsuspected sinks for some RO₂ in the atmosphere ?”

By B. Nozière, and F. Fache

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Table S1: List of experiments

Expt. n°	Radical precursors	Alkene
	Concentrations in molec. cm ⁻³	Concentrations in molec. cm ⁻³
CH₃O₂ , [CH ₄] = (1 - 2) x 10 ¹⁶ molec. cm ⁻³ ; [CH ₃] = 8 x 10 ¹⁶ molec. cm ⁻³ where used [Cl ₂] = 2 x 10 ¹⁵ molec. cm ⁻³		
Alk01	CH ₄ + Cl ₂	Isoprene, (1.2 – 1.8) x 10 ¹⁶
Alk02	CH ₄ + Cl ₂	Isoprene, (1.1 – 2.2) x 10 ¹⁶
Alk03	CH ₄ + Cl ₂	Isoprene, 3.9 x 10 ¹⁵ – 2.2 x 10 ¹⁶
Alk04	CH ₄ + Cl ₂	Isoprene, 5.4 x 10 ¹⁵ – 2.2 x 10 ¹⁶
Alk05	CH ₃ I	Isoprene, 4.6 x 10 ¹⁵ – 2.3 x 10 ¹⁶
Alk06	CH ₄ + Cl ₂	*2M2B, 3.6 x 10 ¹⁵ – 3.6 x 10 ¹⁶
Alk07	CH ₄ + Cl ₂	*2M2B, 7.2 x 10 ¹⁵ – 7.2 x 10 ¹⁶
Alk08	CH ₄ + Cl ₂	*2M2B, 3.6 x 10 ¹⁵ – 3.6 x 10 ¹⁶
Alk09	CH ₃ I	*2M2B, 3.9 x 10 ¹⁵
Alk10	CH ₃ I	*2M2B, 2.5 x 10 ¹⁵
Alk11	CH ₄ + Cl ₂	α-pinene, 3.6 x 10 ¹⁵
Alk12	CH ₄ + Cl ₂	α-pinene, 1.1 x 10 ¹⁴ – 3.6 x 10 ¹⁵
Alk13	CH ₄ + Cl ₂	Limonene, 2.6 x 10 ¹⁴ – 1.3 x 10 ¹⁵
Alk14	CH ₄ + Cl ₂	Limonene, 1.3 x 10 ¹⁵
Alk15	CH ₃ I	Limonene, 6.5 x 10 ¹⁴
Alk16	CH ₃ I	Limonene, (3.2 – 7.1) x 10 ¹⁴
Alk17	CH ₄ + Cl ₂	**2,3DM2B, 9.4 x 10 ¹³ – 1.9 x 10 ¹⁵
Alk18	CH ₄ + Cl ₂	**2,3DM2B, 8.6 x 10 ¹³ – 1.9 x 10 ¹⁴
Alk19	CH ₄ + Cl ₂	**2,3DM2B, 4.7 x 10 ¹³ – 3.2 x 10 ¹⁴
Alk20	CH ₄ + Cl ₂	**2,3DM2B, 4.6 x 10 ¹⁵ – 2.8 x 10 ¹⁶
Alk21	CH ₄ + Cl ₂	**2,3DM2B, (4.8 – 9.5) x 10 ¹⁵
Alk22	CH ₃ I	**2,3DM2B, 5.0 x 10 ¹⁴ – 2.5 x 10 ¹⁵
Alk23	CH ₃ I	**2,3DM2B, 2.5 x 10 ¹⁵
C₅H₁₁O₂ , [C ₅ H ₁₁ I] = 2 x 10 ¹⁶ molec. cm ⁻³		
Alk24	C ₅ H ₁₁ I	Isoprene, (1.8 – 9.2) x 10 ¹⁶
Alk25	C ₅ H ₁₁ I	*2M2B, 3.6 x 10 ¹⁵ – 3.6 x 10 ¹⁶
Alk26	C ₅ H ₁₁ I	*2M2B, (3.6 – 9) x 10 ¹⁵
Alk27	C ₅ H ₁₁ I	Limonene, 8.1 x 10 ¹⁴
Alk28	C ₅ H ₁₁ I	**2,3DM2B, 1.0 x 10 ¹⁶
Alk29	C ₅ H ₁₁ I	**2,3DM2B, 1.0 x 10 ¹⁶
Alk30	C ₅ H ₁₁ I	**2,3DM2B, 4.7 x 10 ¹⁴ – 4.7 x 10 ¹⁵
CH₃C(O)O₂ , [CH ₃ CHO] = 6 x 10 ¹⁴ molec. cm ⁻³ ; [Cl ₂] = 2 x 10 ¹⁵ molec. cm ⁻³		
Alk31	CH ₃ CHO + Cl ₂	Isoprene, 3.8 x 10 ¹³
Alk32	CH ₃ CHO + Cl ₂	*2M2B, 3.0 x 10 ¹³
Alk33	CH ₃ CHO + Cl ₂	**2,3DM2B, 3.4 x 10 ¹²

*2M2B = 2-methyl-2-butene; **2,3DM2B = 2,3-dimethyl-2-butene

Table S2: Vapor pressure, $P_v(298\text{ K})$ (molec. cm^{-3}), used to determine the gas concentration of the liquid reagents used in this study

	CH ₃ I	C ₅ H ₁₁ I	isoprene	α -pinene	limonene	*2M2B	**2,3DM2B
$P_v(298\text{K})$	1.3×10^{19}	1.4×10^{17}	1.8×10^{19}	1.6×10^{17}	5.1×10^{16}	1.5×10^{19}	4.0×10^{18}

*2M2B = 2-methyl-2-butene; **2,3DM2B = 2,3-dimethyl-2-butene.

Table S3: List of observed ion masses

Compound, MW (g mol ⁻¹)	Observed ion mass (m/z)
RO ₂	
CH ₃ O ₂ , 47	66, 84
C ₅ H ₁₁ O ₂ , 103	122, 140, 158
CH ₃ C(O)O ₂ , 75	76, 94
Alkenes	
Isoprene, C ₅ H ₈ , 68	69, 87, 105
2-methyl-2-butene, C ₅ H ₁₀ , 70	71, 89, 107
α-pinene, C ₁₀ H ₁₆ , 136	137, 155
Limonene, C ₁₀ H ₁₆ , 136	137, 155
2,3-dimethyl-2-butene, C ₆ H ₁₂ , 84	85, 103, 121
Reaction product	
Isoprene epoxy, C ₅ H ₈ O, 84	85, 103, 121
2-methyl-2-butene epoxy, C ₅ H ₁₀ O, 86	87, 105, 123
α-pinene epoxy, C ₁₀ H ₁₆ O, 152	153, 171
Limonene epoxy, C ₁₀ H ₁₆ O, 152	153, 171
2,3-dimethyl-2-butene epoxy, C ₆ H ₁₂ O, 100	101, 119, 137
Other (RO ₂ precursor)	
CH ₃ CHO, 44	63, 81, 99

S4: Kinetic simulations

The kinetic analysis applied to the experimental data to determine the rate coefficients k^{\parallel} for RO_2 +alkene was validated by series of simulations using Chemsimul (V3.90, 2018). These simulations had for objective, in particular, to quantify the corrections factors to apply to Eq. (13b).

For this, the concentration profiles for the RO_2 and other compounds in the reactor were calculated from different sets of kinetic equations presented below, using the rate coefficients listed in Table S4, and using for k^{\parallel} a “reference” value, $k^{\text{ref}}_{\text{alk}}$. These simulations were kept as close as possible from the actual experimental conditions by constraining $[\text{RO}_2]_o$ to the values obtained from the experimental signals and using the detection sensitivities determined for these radicals in previous works: $S^\circ(\text{CH}_3\text{O}_2) = 5000 \text{ Hz/ppb}$,^{10,11} $S^\circ(\text{C}_5\text{H}_{11}\text{O}_2) = 200 \text{ Hz/ppb}$,¹⁰ and $S^\circ(\text{CH}_3\text{C}(\text{O})\text{O}_2) = 2000 \text{ Hz/ppb}$.¹¹ A first set of simulations was run with constraining $[\text{RO}_2]_o$ to the experimental value and $[\text{alkene}] = 0$ to determine either the RO_2 concentration at mid-reactor ($t = 0 \text{ s}$), $[\text{RO}_2]_i$, for CH_3O_2 or the photolytic source term S ($\text{molec. cm}^{-3} \text{ s}^{-1}$) for $\text{C}_5\text{H}_{11}\text{O}_2$ and $\text{CH}_3\text{C}(\text{O})\text{O}_2$. Once these parameters were determined, a second set of simulations was run with an alkene concentrations typical of the experiments to determine $[\text{RO}_2]_a$. The RO_2 concentrations calculated in the absence and in the presence of alkene were then used to calculate k^{\parallel} from Eq.(13b). The value of k^{\parallel} thus obtained at $t = 17 \text{ s}$ (the experimental point of measurement) was then compared to $k^{\text{ref}}_{\text{alk}}$ to determine the correction factor to apply to Eq.(13b) in the analyses. These simulations are illustrated below for each radical and for alkene = isoprene and 2,3-dimethyl-2-butene.

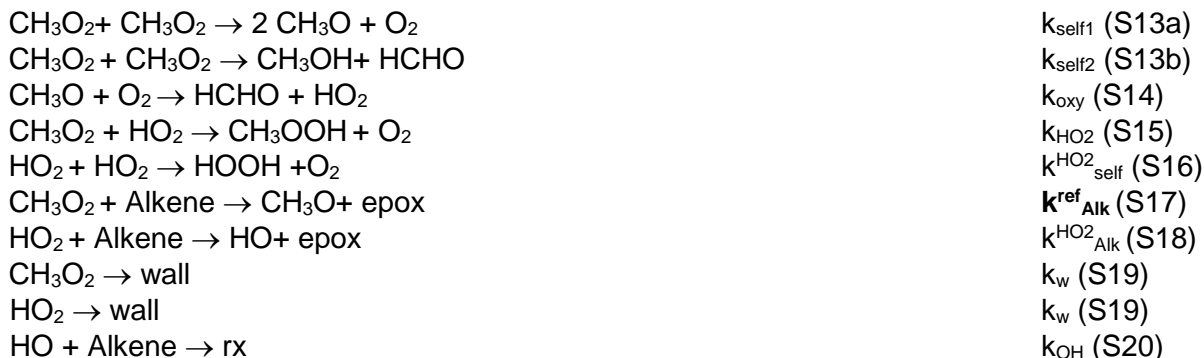
Table S4: Rate coefficients used in the simulations

Rate coefficients (reaction #)	HO ₂	CH ₃ O ₂	C ₅ H ₁₁ O ₂	CH ₃ C(O)O ₂
k _{self} (molec ⁻¹ cm ³ s ⁻¹) (S13)		3.5 × 10 ^{-13b}	4.0 × 10 ^{-13c}	1.6 × 10 ^{-11b}
k _{oxy} (molec ⁻¹ cm ³ s ⁻¹) (S14)	/	1.9 × 10 ^{-15d}	1 × 10 ^{-14d}	> 10 ⁴ s ⁻¹ Decomp. (S24)
k _{HO2} (molec ⁻¹ cm ³ s ⁻¹) (S15)	1.6 × 10 ^{-12a} k ^{HO2} _{self} (S16)	5.2 × 10 ^{-12b}	1 × 10 ^{-11c}	2.0 × 10 ⁻¹¹ⁱ
k _{iso} (s ⁻¹) (S22)	/	/	2.4 × 10 ^{-3(e)}	/
k _{CH3O2} (molec ⁻¹ cm ³ s ⁻¹) (S25)	/	/	/	1.1 × 10 ^{-11b}
k _w (s ⁻¹) (S19)	3 × 10 ^{-3f}	3 × 10 ^{-3f}	3 × 10 ^{-3f}	3 × 10 ^{-3f}
k ^{ref} _{alk} (molec ⁻¹ cm ³ s ⁻¹) (S17) isoprene	1.7 × 10 ^{-19g} k ^{HO2} _{alk} (S18)	2.6 × 10 ^{-18h}	1.0 × 10 ^{-17h}	1.8 × 10 ^{-14h}
k ^{ref} _{alk} (molec ⁻¹ cm ³ s ⁻¹) (S17) 2,3-dimethyl-2-butene	3.7 × 10 ^{-19g} k ^{HO2} _{alk} (S18)	9.0 × 10 ^{-18h}	1.8 × 10 ^{-16h}	1.1 × 10 ^{-13h}
F (molec ⁻¹ cm ³ s ⁻¹) (S21)	/	/	3 × 10 ^{-25h}	10 ^{-20h}
	Alkene	CH ₃ CHO		
k _{OH} (molec ⁻¹ cm ³ s ⁻¹) (S20)	1 × 10 ^{-10d}			
k _{Cl} (molec ⁻¹ cm ³ s ⁻¹) (S23)	4.0 × 10 ^{-10j}	8 × 10 ^{-11d}		

^aref.²⁰; ^bref.²¹; ^cref.²²; ^dref.²³; ^eref.¹⁰; ^fref.¹¹; ^gextrapolated to 298 K from Ref.⁷; ^hdetermined in this work; ⁱIUPAC recommendation, <https://iupac-aeris.ipsl.fr/>; ^jref.²⁴.

1) Reactions of CH_3O_2

The reactions of CH_3O_2 were simulated with the following set of equations:



- CH_3O_2 + isoprene (experiment Alk05)

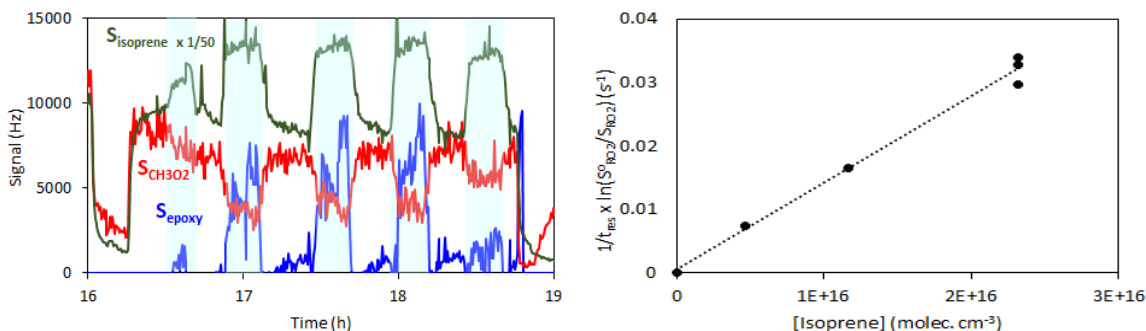


Fig. S1: left: Evolution of the signals during isoprene ON/isoprene OFF cycles measured at the residence time $t = 17$ s by the CIMS in the experiment ALK05: (CH_3O_2 , red line), isoprene (green line), and epoxy (blue line); Right: kinetic analysis of these CH_3O_2 signals with Eq.(13b) providing the rate coefficient k^{II} .

In these simulations $[\text{CH}_3\text{O}_2]_0$ was constrained by the signal $S^{\text{O}}_{\text{CH}_3\text{O}_2} = 7200$ Hz, corresponding to $[\text{CH}_3\text{O}_2]_0 = 3.6 \times 10^{10}$ molec. cm^{-3} , measured with the CIMS at $t = 17$ s. Running the model with $[\text{isoprene}] = 0$ and adjusting the value of $[\text{CH}_3\text{O}_2]_i$ to obtain the above value for $[\text{CH}_3\text{O}_2]_0$ at $t = 17$ s led to $[\text{CH}_3\text{O}_2]_i = 1 \times 10^{11}$ molec. cm^{-3} and the concentration profiles shown in Table S4.1 (columns 2-3) and Fig. S2 (continuous lines for the radicals). Running the model again with this value of $[\text{CH}_3\text{O}_2]_i$, $[\text{isoprene}] = 2.3 \times 10^{16}$ molec. cm^{-3} and $k_{\text{Alk}}^{\text{ref}} = 2.6 \times 10^{-18}$ molec. $^{-1}$ cm^3 s^{-1} (Table S4) gave a new set of profiles (columns 7 - 10 in Table S4.1 and dashed lines for the radicals in Fig. S2). Applying Eq.(13b) (Table S4.1, last column) thus gave $k^{\text{II}} = 3.4 \times 10^{-18}$ molec. $^{-1}$ cm^3 s^{-1} at $t = 17$ s, which compared to $k_{\text{Alk}}^{\text{ref}}$ gave a correction factor of $\times 0.75$ to be applied to Eq.(13b) in the analysis.

This correction factor compensates for the overall effects of neglecting the self-reaction of CH_3O_2 (mostly, in the absence of isoprene, Table S4.1, columns 5 and 12), for the increase of the first

order sinks other than isoprene (k_I and k'_I) in the presence of isoprene (columns 4 and 11) and for the fact that the reaction with isoprene contributed only for 60 % of the observed CH_3O_2 decay. Reaction S20 was added to the simulations to determine the concentration of other organic radicals, "rx", produced by the reaction of OH from reaction S18 with isoprene and their potential impact on the CH_3O_2 concentration. As shown in Table S4.1, column 10, even when lumping these radicals into a single species, their overall concentrations is less than 1/10 of the HO_2 concentration. Since HO_2 contributes to 35 - 40 % of the CH_3O_2 sink in the presence of isoprene (column 13), these radicals would contribute in total to less than 3.6 - 4 %, assuming rate coefficients for their cross-reaction with CH_3O_2 similar to that for $\text{CH}_3\text{O}_2 + \text{HO}_2$. In practice, each individual radical would contribute to even less, having smaller concentration than indicated in column 13, thus have negligible contributions to the CH_3O_2 sinks.

Applying Eq.(13b) with the correction factor of 0.75 found above to the experimental profiles led to $k'' = 1.9 \times 10^{-18} \text{ molec.}^{-1} \text{ cm}^3 \text{ s}^{-1}$ (Table S5).

Table S4.1: Numeric simulation of the CH₃O₂ + isoprene system (experiment Alk05).

t(s)	Isoprene = 0 ^(a)			% sink ^(c)		isoprene= 2.3e16 ^(a)					% sink ^(c)			k ^{II(d)}
	CH ₃ O _{2o} ^(a)	HO _{2o} ^(a)	k ^{l(b)}	Self	HO ₂	CH ₃ O _{2a} ^(a)	HO _{2a} ^(a)	epox ^(a)	rx ^(a)	k ^{l(b)}	Self	HO ₂	Alkene	
0	1.3E+11	0.0E+00		0.94	0.00	1.3E+11	0.0E+00	0.0E+00	0.0E+00		0.34	0.00		
2	1.0E+11	6.4E+09	0.04	0.50	0.46	9.0E+10	1.3E+10	1.3E+10	6.8E+07	0.07	0.17	0.36	0.45	3.4E-18
4	8.5E+10	6.9E+09	0.04	0.43	0.52	6.2E+10	1.4E+10	2.2E+10	1.8E+08	0.08	0.12	0.40	0.46	3.5E-18
6	7.1E+10	6.3E+09	0.04	0.41	0.54	4.4E+10	1.4E+10	2.9E+10	2.9E+08	0.07	0.09	0.41	0.49	3.5E-18
8	6.0E+10	5.6E+09	0.03	0.40	0.55	3.2E+10	1.3E+10	3.3E+10	3.9E+08	0.07	0.07	0.40	0.51	3.5E-18
10	5.3E+10	5.0E+09	0.03	0.39	0.55	2.4E+10	1.2E+10	3.6E+10	4.9E+08	0.06	0.05	0.39	0.54	3.5E-18
12	4.6E+10	4.4E+09	0.03	0.38	0.54	1.8E+10	1.1E+10	3.9E+10	5.8E+08	0.06	0.04	0.38	0.56	3.4E-18
14	4.2E+10	4.0E+09	0.02	0.38	0.54	1.4E+10	1.1E+10	4.1E+10	6.7E+08	0.06	0.03	0.37	0.57	3.4E-18
16	3.8E+10	3.6E+09	0.02	0.38	0.54	1.1E+10	1.0E+10	4.3E+10	7.5E+08	0.05	0.03	0.36	0.59	3.4E-18
18	3.4E+10	3.3E+09	0.02	0.37	0.53	8.4E+09	9.6E+09	4.4E+10	8.3E+08	0.05	0.02	0.35	0.61	3.4E-18
20	3.1E+10	3.0E+09	0.02	0.37	0.53	6.7E+09	9.1E+09	4.5E+10	9.0E+08	0.05	0.02	0.34	0.62	3.4E-18
k ^{ref} _{Alk} = 2.6e-18 ⇒ corr. factor=														0.76

^(a)All concentrations are in molec. cm⁻³; ^(b)First-order sinks other than alkene (s⁻¹) = wall losses + k_{HO₂} × [HO₂]; ^(c)% of the total CH₃O₂ sinks; ^(d)k^{II} in molec.⁻¹ cm³ s⁻¹ calculated from Eq.(13b).

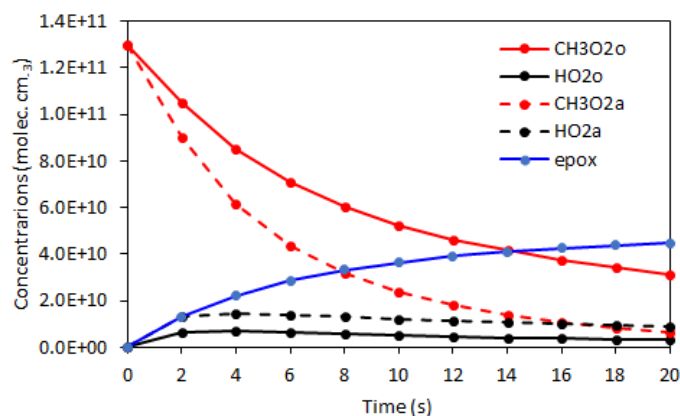


Fig. S2: Concentration profiles in the reactors in the CH₃O₂ + isoprene system (experiment Alk05) corresponding to Table S4.1. CH₃O₂ = red lines, HO₂ = black lines, for both radicals, solid lines = in absence of alkene; dashed lines = in presence of alkene. Blue solid line (“epox”) = concentration of alkene epoxy. The CIMS measurements are performed at t ~ 17 s.

Reaction $\text{CH}_3\text{O}_2 + 2,3\text{-dimethyl-2-butene}$ (experiment Alk22)

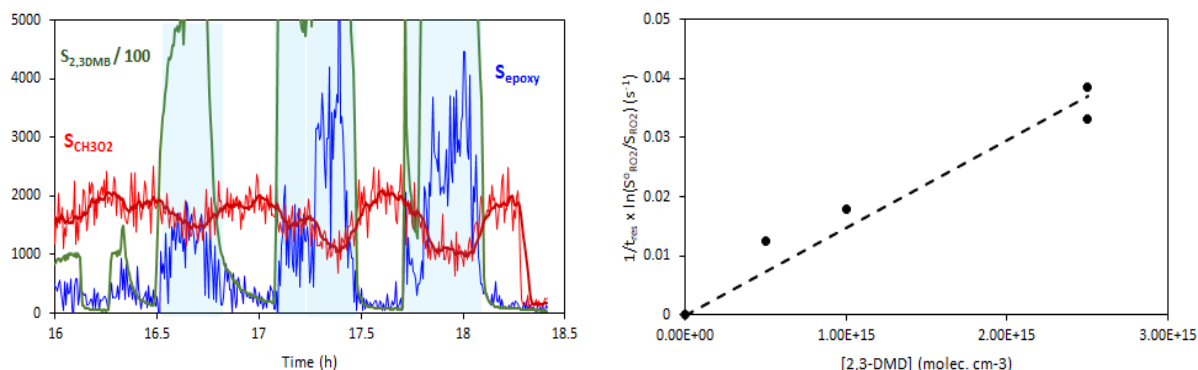


Fig. S3: left: Evolution of the signals during alkene ON/alkene OFF cycles measured at the residence time $t = 17$ s by the CIMS in experiment ALK22: (CH_3O_2 , red line), 2,3-dimethyl-2-butene (green line), epoxy (blue line); Right: kinetic analysis of the CH_3O_2 signals with Eq.(13b) providing the rate coefficient k^{II} .

In the experiments with 2,3-dimethyl-2-butene, CH_3O_2 could not be monitored at $m/z = 84$ as this mass overlapped with the main ion for 2,3-dimethyl-2-butene ($m/z = 85$, Table S3). CH_3O_2 was thus monitored at $m/z = 66$, for which the detection sensitivity was estimated to $S^0(\text{CH}_3\text{O}_2) = 2500$ Hz/ppb. In the absence of 2,3-dimethylbutene, the CH_3O_2 signal observed at the bottom of the reactor, $S_{\text{CH}_3\text{O}_2} = 2500$ Hz, corresponded to $[\text{CH}_3\text{O}_2]_0 = 2.5 \times 10^{10}$ molec. cm^{-3} . Adjusting $[\text{CH}_3\text{O}_2]_i$ in the simulations to match this value of $[\text{CH}_3\text{O}_2]_0$ gave $[\text{CH}_3\text{O}_2]_i \sim 5 \times 10^{10}$ molec. cm^{-3} and the profiles in Table S4.2 (columns 2-3) and Fig. S4 (continuous lines for the radicals). Then adding $[2,3\text{-dimethyl-2-butene}] = 2.5 \times 10^{15}$ molec. cm^{-3} and using $k^{\text{ref}}_{\text{Alk}} = 9.0 \times 10^{-18}$ molec. $^{-1}$ cm^3 s^{-1} (Table S4) gave a new set of profiles (columns 7-8 in Table S4.2 and dashed lines for radicals in Fig.S4). Applying Eq.(13b) to these results (last column of Table S4.2) gave $k^{\text{II}} = 1.2 \times 10^{-17}$ at $t = 17$ s, which, compared with $k^{\text{ref}}_{\text{Alk}}$, gave the correction factor 0.75, identical to the one for the isoprene experiments. This correction factor compensates mostly for the increase of the first-order sink for CH_3O_2 other than alkene, k^{I} , in the presence of 2,3-dimethyl-2-butene (columns 4 and 11) and the fact that the reaction with 2,3-dimethyl-2-butene contributed for only 40 % of the observed CH_3O_2 decays.

Reaction S20 was also added to quantify the concentration of other radicals, “rx”, produced by the reaction of OH from reaction S18 with 2,3-dimethyl-2-butene and their contribution to the CH_3O_2 sinks. Table S4.2 (column 10) shows that their lumped concentration was about 1/70 that of HO_2 , thus that they should have a negligible impact on the CH_3O_2 sinks.

Applying Eq.(13b) with the correction factor 0.75 to the experimental profiles led to $k^{\text{II}} = 6.8 \times 10^{-18}$ molec. $^{-1}$ cm^3 s^{-1} (Table S5).

Table S4.2: Numeric simulation of the CH₃O₂ + 2,3-dimethyl-2-butene system (experiment Alk22).

t(s)	2,3-dimethyl-2-butene = 0 ^(a)			% sink ^(c)		2,3-dimethyl-2-butene= 2.5e15 ^(a)					% sink ^(c)			k ^{II(d)}
	CH ₃ O _{2o} ^(a)	HO _{2o} ^(a)	k ^{I(b)}	Self	HO ₂	CH ₃ O _{2a} ^(a)	HO _{2a} ^(a)	epox ^(a)	rx ^(a)	k ^{I(b)}	Self	HO ₂	Alkene	
0	5.0E+10	0.0E+00		0.85	0.00	5.0E+10	0.0E+00	0.0E+00	0.0E+00		0.41	0.00	0.52	
2	4.6E+10	1.5E+09	0.01	0.60	0.29	4.4E+10	3.1E+09	2.1E+09	3.2E+06	0.02	0.27	0.28	0.40	1.1E-17
4	4.2E+10	2.2E+09	0.01	0.50	0.40	3.8E+10	4.5E+09	3.9E+09	1.0E+07	0.03	0.21	0.38	0.36	1.1E-17
6	3.9E+10	2.5E+09	0.02	0.45	0.44	3.2E+10	5.2E+09	5.5E+09	1.9E+07	0.03	0.18	0.42	0.35	1.2E-17
8	3.6E+10	2.6E+09	0.02	0.43	0.47	2.8E+10	5.4E+09	6.9E+09	2.9E+07	0.03	0.15	0.44	0.36	1.2E-17
10	3.3E+10	2.6E+09	0.02	0.41	0.48	2.4E+10	5.4E+09	8.1E+09	3.9E+07	0.03	0.14	0.45	0.36	1.2E-17
12	3.0E+10	2.5E+09	0.02	0.40	0.49	2.1E+10	5.4E+09	9.1E+09	4.9E+07	0.03	0.12	0.46	0.37	1.2E-17
14	2.8E+10	2.4E+09	0.02	0.39	0.50	1.8E+10	5.3E+09	1.0E+10	5.9E+07	0.03	0.11	0.46	0.38	1.2E-17
16	2.6E+10	2.3E+09	0.01	0.38	0.50	1.6E+10	5.2E+09	1.1E+10	6.9E+07	0.03	0.10	0.46	0.39	1.2E-17
18	2.5E+10	2.2E+09	0.01	0.37	0.50	1.4E+10	5.0E+09	1.1E+10	7.8E+07	0.03	0.09	0.46	0.40	1.2E-17
20	2.3E+10	2.1E+09	0.01	0.37	0.50	1.3E+10	4.9E+09	1.2E+10	8.7E+07	0.03	0.08	0.46	0.41	1.2E-17
k ^{ref} _{Alk} = 9e-18 ⇒ correction factor =														0.75

^(a)All concentrations are in molec. cm⁻³; ^(b)First-order sinks other than alkene (s⁻¹) = wall losses + k_{HO2} x [HO₂]; ^(c)% of the total CH₃O₂ sinks; ^(d)k^{II} in molec.⁻¹ cm³ s⁻¹ calculated from Eq.(13b).

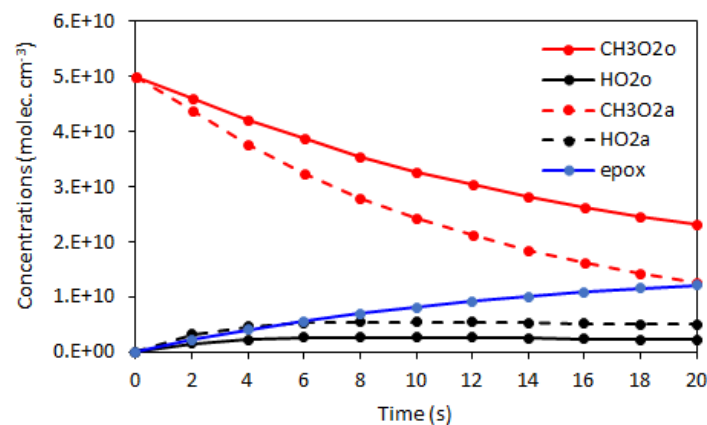
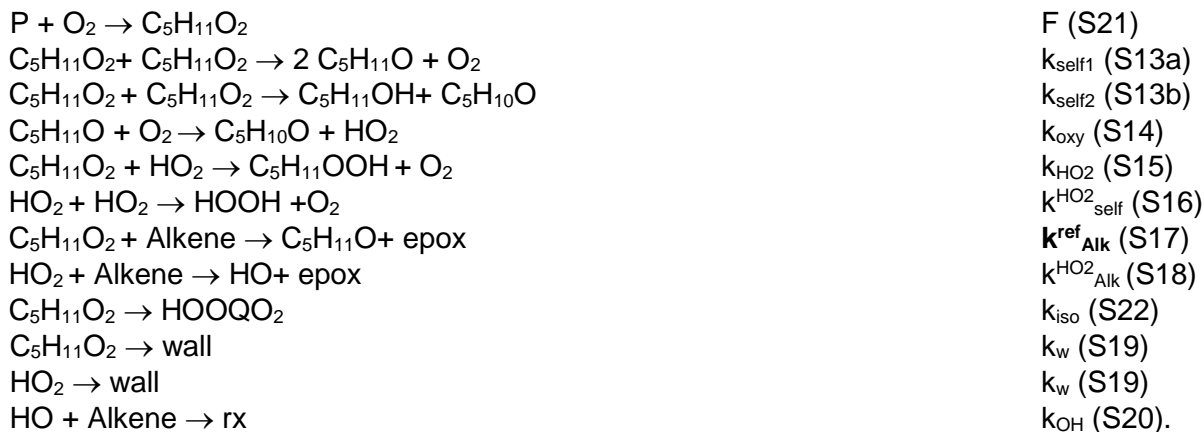


Fig. S4: Concentration profiles in the reactors in the CH₃O₂ + 2,3-dimethyl-2-butene system (experiment Alk22) corresponding to Table S4.2. CH₃O₂ = red lines, HO₂ = black lines, for both radicals, solid lines = in absence of alkene; dashed lines = in presence of alkene. Blue solid line (“epox”) = concentration of alkene epoxy. The CIMS measurements are performed at t ~ 17 s.

2) reactions of C₅H₁₁O₂

The reactions of C₅H₁₁O₂ were simulated with the following set of equations:



Unlike CH₃O₂, C₅H₁₁O₂ and CH₃C(O)O₂ were produced throughout the lower half of the reactor photolytically, which was represented by reaction S21 in the simulations, where P is the precursor (iodopentane). The photolytic formation rate for C₅H₁₁O₂, J (s⁻¹) = F x [O₂], and/or P were adjusted in the simulations to match the [C₅H₁₁O₂]₀ observed at t = 17 s in the experiments thus providing the source S (molec. cm⁻³. s⁻¹) = F x [O₂] x [P]. C₅H₁₁O₂ also undergoes isomerization by H-migration (autoxidation), which was represented by reaction S22 and the rate coefficient k_{iso} = 2.4 x 10⁻³ s⁻¹ (Table S4).¹⁰

- C₅H₁₁O₂ + isoprene (experiment Alk24)

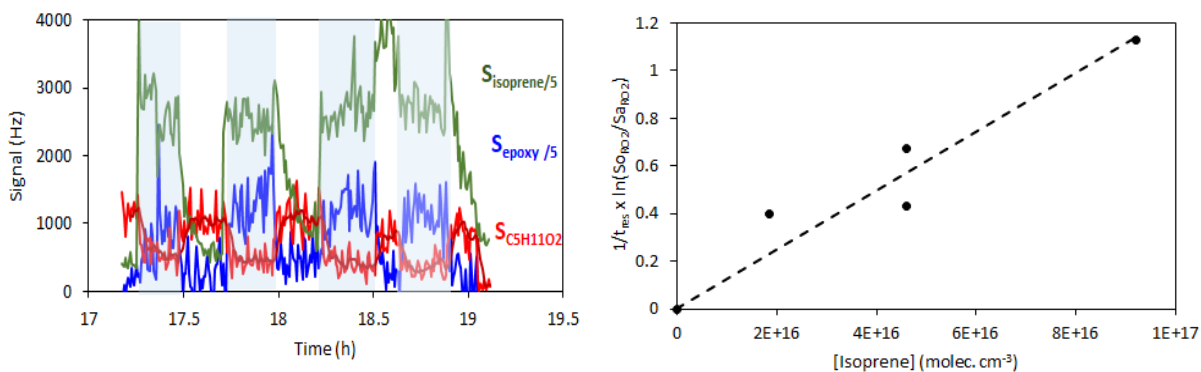


Fig. S5: left: Evolution of the signals during isoprene ON/isoprene OFF cycles measured at the residence time t = 17 s by the CIMS in the experiment ALK24: (C₅H₁₁O₂, red line), isoprene (green line), and epoxy (blue line); Right: kinetic analysis of the C₅H₁₁O₂ signals with Eq.(13b) providing the rate coefficient k^{II}.

In experiment ALK24, the observed S⁰_{RO2} ~ 1200 Hz at the bottom of the reactor, corresponding to [C₅H₁₁O₂]₀ = 1.5 x 10¹¹ molec.cm⁻³ at t = 17 s, was used to determine the source term for C₅H₁₁O₂. Adjusting the concentration P to match this concentration in the absence of alkene led

to a photolytic formation rate $J = 1.5 \times 10^{-6} \text{ s}^{-1}$ and source term $S = 3.0 \times 10^{10} \text{ molec. cm}^{-3} \text{ s}^{-1}$ and to the concentration profiles given in Table S4.3 (columns 2-3) and shown in Fig. S6 (continuous lines for the radicals). Using this source term and adding $[\text{isoprene}] = 4.6 \times 10^{16} \text{ molec. cm}^{-3}$ and $k^{\text{ref}}_{\text{Alk}} = 1.4 \times 10^{-18} \text{ molec}^{-1} \text{ cm}^3 \text{ s}^{-1}$ (Table S4) led to new concentration profiles (columns 8-11 in Table S4.3 and dashed lines for the radicals in Fig. S6). Applying Eq.(13b) to these results gave k^{II} (last column of Table S4.3). At $t = 17 \text{ s}$, $k^{\text{II}} = 1.9 \times 10^{-18} \text{ molec}^{-1} \text{ cm}^3 \text{ s}^{-1}$ was compared to $k^{\text{ref}}_{\text{Alk}} = 1.0 \times 10^{-17} \text{ molec}^{-1} \text{ cm}^3 \text{ s}^{-1}$ (Table S4) and gave the correction factor 5.4. This factor compensates mostly for neglecting the self-reaction of $\text{C}_5\text{H}_{11}\text{O}_2$ in the absence of isoprene (Table S4.3, columns 5 and 13), for the increase of the first-order sinks for $\text{C}_5\text{H}_{11}\text{O}_2$ other than isoprene, k^{I} (columns 4 and 12) in the presence of isoprene and for the fact that the reaction with isoprene contributed to only 55 % of the observed radical decays.

Reaction S20 was added to the system to quantify the formation of other radicals, "rx", from the reactions of OH from reaction S18 with isoprene and determine if they could significantly contribute to the $\text{C}_5\text{H}_{11}\text{O}_2$ sinks. Table S4.3, column 11 shows that the lumped concentration for these radicals is about 1/10 that of HO_2 , thus should have individually negligible impacts on the $\text{C}_5\text{H}_{11}\text{O}_2$ sinks.

Applying Eq.(13b) with the above correction factor to the experimental data gave $k^{\text{II}} = 7.8 \times 10^{-18} \text{ molec}^{-1} \text{ cm}^3 \text{ s}^{-1}$ (Table S5).

Table S4.3: Numeric simulation of the $C_5H_{11}O_2$ + isoprene system (experiment Alk24).

t(s)	isoprene = 0 ^(a)			% sink ^(c)			isoprene= 4.6e16 ^(a)					% sink ^(c)				k ^{II} (d)
	C ₅ H ₁₁ O _{2o} ^(a)	HO _{2o} ^(a)	k ^I (b)	Self	HO ₂	iso	C ₅ H ₁₁ O _{2a} ^(a)	HO _{2a} ^(a)	epox ^(a)	rx ^(a)	k ^{II} (b)	Self	HO ₂	iso	Alkene	
0	0.0E+00	0.0E+00		0.00	0.00		0.0E+00	0.0E+00	0.0E+00	0.0E+00		0.00	0.00			
2	5.8E+10	9.5E+08	0.01	0.61	0.25	0.06	3.5E+10	1.6E+10	2.0E+10	1.0E+08	0.17	0.02	0.25	0.0	0.72	
4	1.0E+11	3.9E+09	0.04	0.48	0.46	0.03	3.9E+10	3.0E+10	5.6E+10	4.8E+08	0.30	0.02	0.38	0.0	0.59	
6	1.3E+11	6.0E+09	0.06	0.44	0.51	0.02	3.7E+10	3.4E+10	9.1E+10	9.9E+08	0.35	0.02	0.42	0.0	0.56	
8	1.4E+11	6.9E+09	0.07	0.43	0.53	0.02	3.6E+10	3.5E+10	1.2E+11	1.5E+09	0.36	0.02	0.42	0.0	0.55	
10	1.5E+11	7.3E+09	0.08	0.42	0.54	0.02	3.5E+10	3.5E+10	1.6E+11	2.1E+09	0.36	0.02	0.42	0.0	0.55	
12	1.5E+11	7.5E+09	0.08	0.42	0.54	0.02	3.5E+10	3.5E+10	1.9E+11	2.6E+09	0.36	0.02	0.42	0.0	0.55	
14	1.5E+11	7.6E+09	0.08	0.42	0.54	0.02	3.5E+10	3.5E+10	2.2E+11	3.2E+09	0.36	0.02	0.42	0.0	0.55	
16	1.5E+11	7.6E+09	0.08	0.42	0.54	0.02	3.5E+10	3.5E+10	2.6E+11	3.8E+09	0.36	0.02	0.42	0.0	0.55	
18	1.5E+11	7.6E+09	0.08	0.42	0.54	0.02	3.5E+10	3.5E+10	2.9E+11	4.3E+09	0.36	0.02	0.42	0.0	0.55	
20	1.5E+11	7.6E+09	0.08	0.42	0.54	0.02	3.5E+10	3.5E+10	3.2E+11	4.9E+09	0.36	0.02	0.42	0.0	0.55	
k ^{ref} _{Alk} = 1e-17 ⇒ correction factor =															5.4	

^(a)All concentrations are in molec. cm⁻³; ^(b)First-order sinks other than alkene (s⁻¹) = wall losses + isomerisation+ k_{HO2} × [HO₂]; ^(c)% of the total CH₃O₂ sinks; ^(d)k^{II} in molec.⁻¹ cm³ s⁻¹ calculated from Eq.(13b).

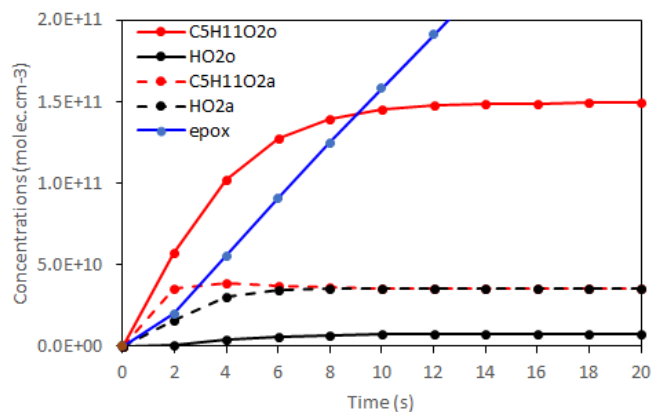


Fig. S6: Concentration profiles in the reactors in the $C_5H_{11}O_2$ + isoprene system (experiment Alk24) corresponding to Table S4.3. $C_5H_{11}O_2$ = red lines, HO_2 = black lines, for both radicals, solid lines = in absence of alkene; dashed lines = in presence of alkene. Blue solid line (“epox”) = concentration of alkene epoxy. The CIMS measurements are performed at t ~ 17 s.

- $C_5H_{11}O_2$ + 2,3-dimethyl-2-butene (experiments Alk30)

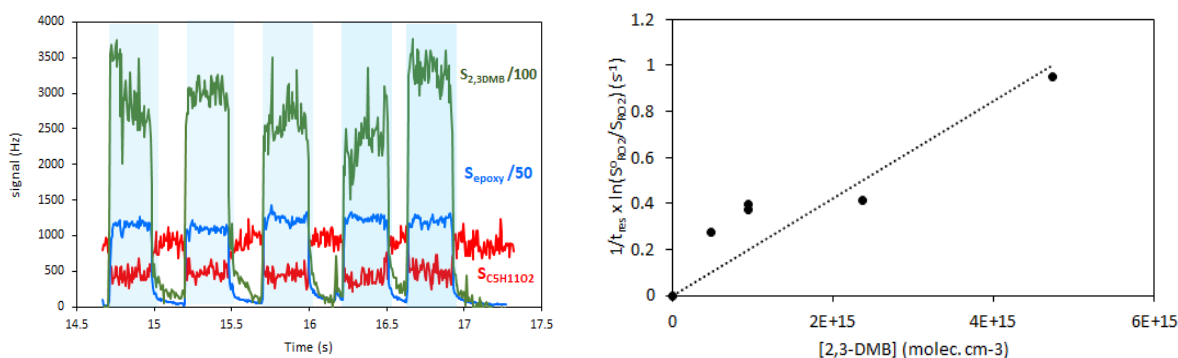


Fig. S7: left: Evolution of the signals during alkene ON/alkene OFF cycles measured at the residence time $t = 17$ s by the CIMS in experiment ALK30: ($C_5H_{11}O_2$, red line), 2,3-dimethyl-2-butene (green line), epoxy (blue line); Right: kinetic analysis of the $C_5H_{11}O_2$ signals with Eq.(13b) providing the rate coefficient k^{II} .

In experiment ALK30, the observed $S_{RO_2}^0 \sim 900$ Hz in the absence of alkene at the bottom of the reactor, corresponding to $[C_5H_{11}O_2]_0 = 1.1 \times 10^{11}$ molec. cm^{-3} , led to a source term $S = 1.8 \times 10^{10}$ molec. $cm^{-3} s^{-1}$ and to the profiles in Table S4.4 (columns 2 -3) and Fig. S8 (continuous lines for the radicals). With this source term, adding $[2,3\text{-dimethyl-2-butene}] = 2.36 \times 10^{15}$ molec. cm^{-3} and $k_{Alk}^{ref} = 1.8 \times 10^{-16}$ molec. $^{-1} cm^3 s^{-1}$ (Table S4) gave a new set of concentration profiles (table S4.4, columns 8 - 11) and Fig. S8 (dashed lines for the radicals). Eq.(13b) was then applied to these results to determine k^{II} (last column of Table S4.4). At $t = 17$ s, $k^{II} = 3.9 \times 10^{-17}$ molec. $^{-1} cm^3 s^{-1}$ was compared to k_{Alk}^{ref} (Table S4) and gave the correction factor 4.6, thus within 15 % of the one in the isoprene experiment. This factor compensated for neglecting the self-reaction of $C_5H_{11}O_2$ in the absence of with 2,3-dimethyl-2-butene, (Table S4.4, columns 5 and 13), for the increase in the first-order sinks other than alkene (k_I and k'_I , columns 4 and 12), and for the fact that the reaction with 2,3-dimethyl-2-butene contributed only to 60 % of the observed decay for $C_5H_{11}O_2$.

In reaction S20 the formation of other radicals, "rx", from the reactions of OH with 2,3-dimethyl-2-butene was quantified. Column 11 shows that the lumped concentration for these radicals is about 1/100 that of HO_2 , thus should have negligible impacts on the $C_5H_{11}O_2$ sinks.

Applying Eq.(13b) with the above correction factor to the experimental data gave $k^{II} = 1.6 \times 10^{-16}$ molec. $^{-1} cm^3 s^{-1}$ (Table S5).

Table S4.4: Numeric simulation of the $C_5H_{11}O_2 + 2,3\text{dimethyl-2-butene}$ system (experiment Alk30).

t(s)	2,3-dimethyl-2-butene = 0 ^(a)			% sink ^(c)			2,3-dimethyl-2-butene = 2.36e15 ^(a)					% sink ^(c)				k ^{II} (d)
	C ₅ H ₁₁ O _{2o} ^(a)	HO _{2o} ^(a)	k ^I (b)	Self	HO ₂	iso	C ₅ H ₁₁ O _{2a} ^(a)	HO _{2a} ^(a)	epox ^(a)	rx ^(a)	k ^I (b)	Self	HO ₂	iso	Alkene	
0	0.0E+00	0.0E+00	0.01	0.00	0.00		0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.01	0.00	0.00			
2	3.5E+10	3.8E+08	0.01	0.60	0.16	0.10	2.3E+10	1.0E+10	1.1E+10	6.7E+06	0.11	0.02	0.19	0.00	0.79	
4	6.5E+10	1.9E+09	0.02	0.51	0.38	0.05	2.7E+10	2.2E+10	3.3E+10	3.6E+07	0.23	0.02	0.32	0.00	0.66	
6	8.6E+10	3.6E+09	0.04	0.45	0.48	0.03	2.6E+10	2.8E+10	5.6E+10	8.0E+07	0.28	0.01	0.37	0.00	0.61	
8	9.9E+10	4.7E+09	0.05	0.43	0.51	0.03	2.5E+10	3.0E+10	7.7E+10	1.3E+08	0.30	0.01	0.39	0.00	0.60	
10	1.1E+11	5.3E+09	0.06	0.42	0.52	0.02	2.4E+10	3.0E+10	9.8E+10	1.8E+08	0.31	0.01	0.39	0.00	0.59	
12	1.1E+11	5.6E+09	0.06	0.42	0.53	0.02	2.4E+10	3.1E+10	1.2E+11	2.4E+08	0.31	0.01	0.39	0.00	0.59	
14	1.1E+11	5.7E+09	0.06	0.42	0.53	0.02	2.4E+10	3.1E+10	1.4E+11	2.9E+08	0.31	0.01	0.39	0.00	0.59	
16	1.1E+11	5.8E+09	0.06	0.42	0.53	0.02	2.4E+10	3.1E+10	1.6E+11	3.4E+08	0.31	0.01	0.39	0.00	0.59	
18	1.1E+11	5.8E+09	0.06	0.42	0.53	0.02	2.4E+10	3.1E+10	1.8E+11	4.0E+08	0.31	0.01	0.39	0.00	0.59	
20	1.1E+11	5.9E+09	0.06	0.42	0.53	0.02	2.4E+10	3.1E+10	2.0E+11	4.5E+08	0.31	0.01	0.39	0.00	0.59	
k ^{ref} _{Alk} = 1.8e-16 ⇒ correction factor =															4.6	

^(a)All concentrations are in molec. cm⁻³; ^(b)First-order sinks other than alkene (s⁻¹) = wall losses + isomerisation + k_{HO2} × [HO₂]; ^(c)% of the total CH₃O₂ sinks; ^(d)k^{II} in molec.⁻¹ cm³ s⁻¹ calculated from Eq.(13b).

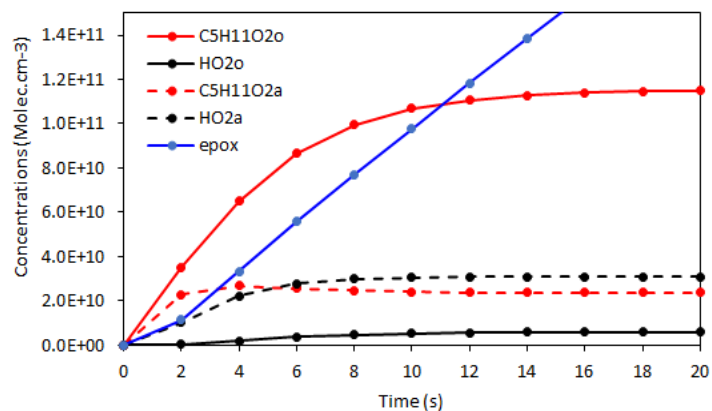
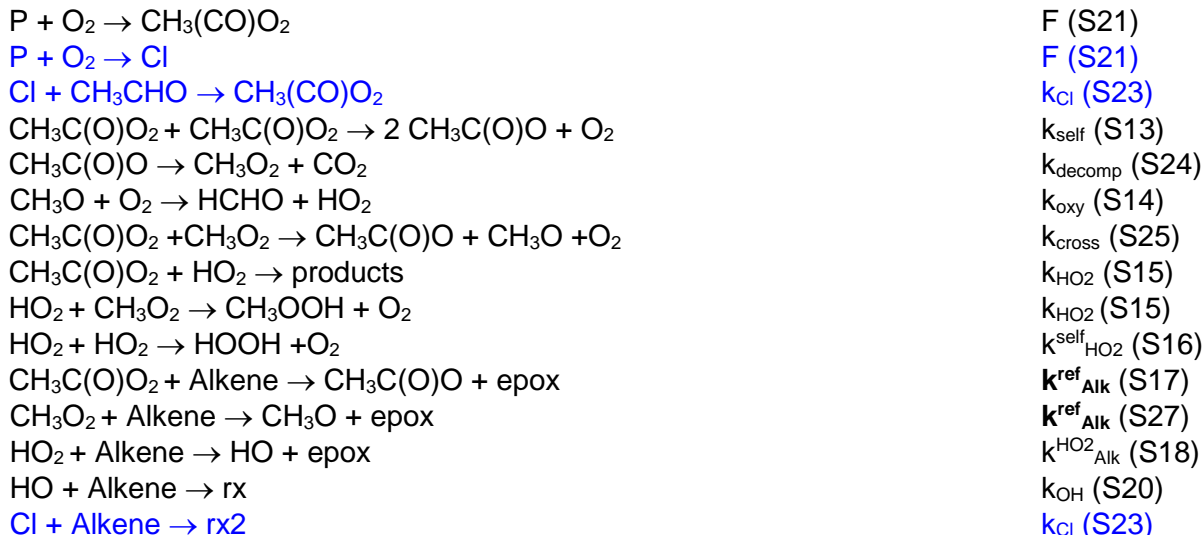


Fig. S8: Concentration profiles in the reactors in the $C_5H_{11}O_2 + 2,3\text{dimethyl-2-butene}$ system (experiment Alk30) corresponding to Table S4.4. $C_5H_{11}O_2$ = red lines, HO_2 = black lines, for both radicals, solid lines = in absence of alkene; dashed lines = in presence of alkene. Blue solid line (“epox”) = concentration of alkene epoxy. The CIMS measurements are performed at $t \sim 17$ s.

3) Reactions of $\text{CH}_3\text{C}(\text{O})\text{O}_2$

The reactions of $\text{CH}_3\text{C}(\text{O})\text{O}_2$ were simulated with the following set of equations:



As for $\text{C}_5\text{H}_{11}\text{O}_2$, $\text{CH}_3\text{C}(\text{O})\text{O}_2$ is produced by a photolytic source throughout the lower part of the reactor, represented by reaction S21. A first set of simulations was thus performed identically as for the $\text{C}_5\text{H}_{11}\text{O}_2$ systems to determine k^{II} . However, to estimate how much reactions Cl + alkene could be in competition with Cl + CH_3CHO , for some experiments a second set of simulations was performed where S21 was replaced by reactions S21/S23 in blue above. Reaction S20 was also included in the simulation to determine the potential impact of organic radicals produced by OH+ Alkene.

- $\text{CH}_3\text{C}(\text{O})\text{O}_2$ + isoprene (experiment Alk31).

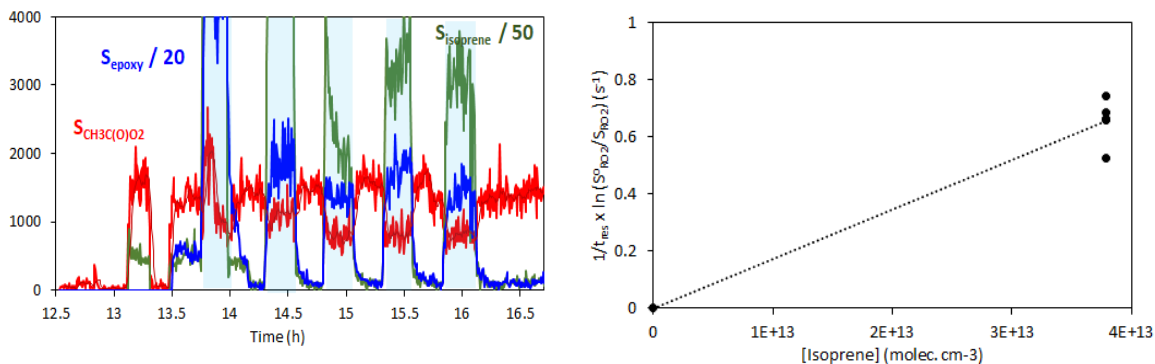


Fig. S9: left: Evolution of the signals in isoprene ON/isoprene OFF cycles measured at the residence time $t = 17$ s by the CIMS in the experiment ALK31: ($\text{CH}_3\text{C}(\text{O})\text{O}_2$, red line), isoprene (green line), and epoxy (blue line); Right: kinetic analysis of the $\text{C}_5\text{H}_{11}\text{O}_2$ signals with Eq.(13b) providing the rate coefficient k^{II} .

A first series of simulations of experiment ALK31 was performed using the set of equations in black above. $[\text{CH}_3\text{C}(\text{O})\text{O}_2]_0$ was constrained by the signal $S_{\text{RO}_2}^0 = 1050$ Hz measured at the bottom

of the reactor, corresponding to $[\text{CH}_3\text{C}(\text{O})\text{O}_2]_o = 1.3 \times 10^{10} \text{ molec. cm}^{-3}$, led to a source term $S = 5 \times 10^{10} \text{ molec. cm}^{-3} \text{ s}^{-1}$ and to $[\text{CH}_3\text{C}(\text{O})\text{O}_2]_o = 1.3 \times 10^{10}$, $[\text{CH}_3\text{O}_2]_o = 7.4 \times 10^{10}$, and $[\text{HO}_2]_o = 1.9 \times 10^{10} \text{ molec. cm}^{-3}$ at $t = 17 \text{ s}$. Then, adding $[\text{isoprene}] = 3.8 \times 10^{13} \text{ molec. cm}^{-3}$ and $k^{\text{ref}}_{\text{Alk}} = 1.8 \times 10^{-14} \text{ molec}^{-1} \text{ cm}^3 \text{ s}^{-1}$ (Table S4) led to a new set of profiles with $[\text{CH}_3\text{C}(\text{O})\text{O}_2]_a = 8.5 \times 10^9$, $[\text{CH}_3\text{O}_2]_a = 1.1 \times 10^{11}$, and $[\text{HO}_2]_a = 1.6 \times 10^{10} \text{ molec. cm}^{-3}$ at $t = 17 \text{ s}$.

The total concentration of radicals produced by OH+isoprene, “rx”, in S20 (Table S4.5, column 13) is 1/10000 that of HO_2 , showing that these radicals did not interfere with the kinetic analysis.

A second set of simulations was then performed to determine if Cl + isoprene could be significantly in competition with Cl + CH_3CHO and, if so, to quantify the corresponding reduction in $\text{CH}_3\text{C}(\text{O})\text{O}_2$ concentrations. For this, reaction S21 was replaced by reactions S21/ S23 in blue above. The total concentration of Cl atoms produced photolytically in the reactor was calculated in the absence of CH_3CHO and alkene as “Cl*” (Table S4.5, column 2). Then, running the simulation in the presence of acetaldehyde but with $[\text{isoprene}] = 0$ gave the profiles in Table S4.5 (columns 3—5) and Fig. S10, which were, as expected, identical to those predicted by the previous simulations. Finally, running the simulations with $[\text{isoprene}] = 3.8 \times 10^{13} \text{ molec. cm}^{-3}$ and $k^{\text{ref}}_{\text{Alk}} = 1.8 \times 10^{-14} \text{ molec}^{-1} \text{ cm}^3 \text{ s}^{-1}$ (Table S4) led to a new set of profiles (Table S4.5 columns 9 -12 and Fig. S10). The fraction of Cl radicals reacting with isoprene was given by the ratio of “rx2” produced by Cl+isoprene over the Cl* concentration, and are given in column 14. Although this fraction was 24 %, as expected, the $\text{CH}_3\text{C}(\text{O})\text{O}_2$ concentrations (column 9) were only reduced by 12 to 17 % compared to not accounting for Cl+ isoprene. This was because reducing the $\text{CH}_3\text{C}(\text{O})\text{O}_2$ concentrations also reduced those of CH_3O_2 , which is the main sink for $\text{CH}_3\text{C}(\text{O})\text{O}_2$ (column 16). Applying Eq.(13b) to these concentrations (last column of Table S4.5) led to $k^{\text{II}} = 9.9 \times 10^{-16} \text{ molec}^{-1} \text{ cm}^3 \text{ s}^{-1}$ at $t = 17 \text{ s}$, which, compared to $k^{\text{ref}}_{\text{Alk}}$ (Table S4) gave the correction factor 18.7. This correction factor compensates for the increase in the first-order sinks, k^{I} , in the presence of isoprene and, mostly, for the fact that the reaction with isoprene represented only about 28 % of the overall decay of $\text{CH}_3\text{C}(\text{O})\text{O}_2$. Applying Eq.(13b) with this correction factor to the experimental data gave $k^{\text{II}} = 1.8 \times 10^{-14} \text{ molec}^{-1} \text{ cm}^3 \text{ s}^{-1}$ (Table S5), which is identical to $k^{\text{ref}}_{\text{Alk}}$ as the later was chosen from the results of several self-consistency iterations in the determination of k^{II} .

Table S4.5: Numeric simulation of the $\text{CH}_3\text{C}(\text{O})\text{O}_2$ + isoprene system (experiment Alk31).

t(s)	Isoprene = 0 ^(a)				% sink ^(b)			Isoprene = 2.3e16 ^(a)					% sink ^(ab)				k ^{II(c)}	
	Cl ^{*(a)}	$\text{CH}_3\text{C}(\text{O})\text{O}_{2o}^{(a)}$	$\text{CH}_3\text{O}_{2o}^{(a)}$	$\text{HO}_{2o}^{(a)}$	Self	CH_3O_2	HO_2	$\text{CH}_3\text{C}(\text{O})\text{O}_{2a}^{(a)}$	$\text{CH}_3\text{O}_{2a}^{(a)}$	$\text{HO}_{2a}^{(a)}$	epox ^(a)	rx ^(a)	Cl	Self	CH_3O_2	HO_2		Alkene
0	0.0E+00	0.0E+00	0.0E+00	0.0E+00				0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00					
2	9.5E+10	3.0E+10	4.7E+10	9.4E+09	0.39	0.46	0.15	1.9E+10	4.2E+10	6.2E+09	2.3E+10	3.7E+04	0.24	0.19	0.35	0.10	0.36	5.7E-15
4	1.8E+11	2.1E+10	7.6E+10	2.1E+10	0.20	0.55	0.25	1.4E+10	7.5E+10	1.5E+10	4.5E+10	2.3E+05	0.24	0.11	0.45	0.15	0.28	2.8E-15
6	2.6E+11	1.9E+10	8.3E+10	2.3E+10	0.17	0.57	0.26	1.2E+10	8.8E+10	1.8E+10	6.3E+10	5.0E+05	0.24	0.08	0.49	0.15	0.27	2.0E-15
8	3.3E+11	1.7E+10	8.3E+10	2.2E+10	0.16	0.58	0.26	1.0E+10	9.4E+10	1.7E+10	7.8E+10	7.7E+05	0.24	0.08	0.50	0.14	0.26	1.6E-15
10	3.9E+11	1.6E+10	8.2E+10	2.2E+10	0.15	0.59	0.26	9.5E+09	9.7E+10	1.7E+10	9.1E+10	1.0E+06	0.24	0.07	0.52	0.13	0.27	1.4E-15
12	4.5E+11	1.5E+10	7.9E+10	2.1E+10	0.15	0.59	0.26	8.7E+09	9.9E+10	1.6E+10	1.0E+11	1.3E+06	0.24	0.06	0.52	0.13	0.27	1.2E-15
14	5.0E+11	1.4E+10	7.7E+10	2.0E+10	0.15	0.59	0.26	8.0E+09	9.9E+10	1.5E+10	1.1E+11	1.5E+06	0.24	0.06	0.53	0.12	0.27	1.1E-15
16	5.5E+11	1.3E+10	7.4E+10	1.9E+10	0.15	0.60	0.26	7.3E+09	9.8E+10	1.4E+10	1.3E+11	1.7E+06	0.24	0.06	0.53	0.11	0.28	1.0E-15
18	5.9E+11	1.3E+10	7.1E+10	1.8E+10	0.14	0.60	0.25	6.8E+09	9.7E+10	1.3E+10	1.3E+11	1.9E+06	0.24	0.05	0.54	0.11	0.28	9.3E-16
20	6.3E+11	1.2E+10	6.8E+10	1.7E+10	0.14	0.60	0.25	6.3E+09	9.6E+10	1.2E+10	1.4E+11	2.1E+06	0.24	0.05	0.54	0.10	0.29	8.7E-16
$k_{\text{Alk}}^{\text{ref}} = 1.8e^{-14} \Rightarrow$ correction factor =																	18.7	

(a)All concentrations are in molec. cm^{-3} ;(b)% of the total CH_3O_2 sinks;(c)k^{II} in molec.⁻¹ $\text{cm}^3 \text{ s}^{-1}$ calculated from Eq.(13b).

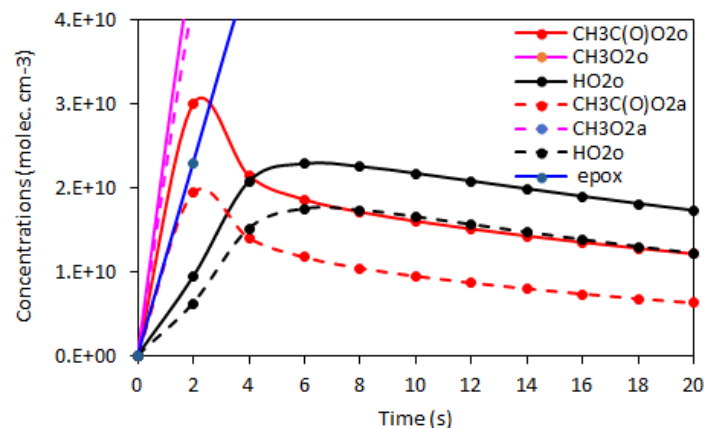


Fig. S10: Concentration profiles in the reactors in the $\text{CH}_3\text{C}(\text{O})\text{O}_2$ + isoprene system (experiment Alk31) corresponding to Table S4.5. $\text{CH}_3\text{C}(\text{O})\text{O}_2$ = red lines, CH_3CO_2 = pink lines, HO_2 = black lines, for all radicals, solid lines = in absence of alkene; dashed lines = in presence of alkene. Blue solid line (“epox”) = concentration of alkene epoxy. The CIMS measurements are performed at $t \sim 17$ s.

- $\text{CH}_3\text{C}(\text{O})\text{O}_2$ + 2,3-dimethyl-2-butene (experiment Alk33)

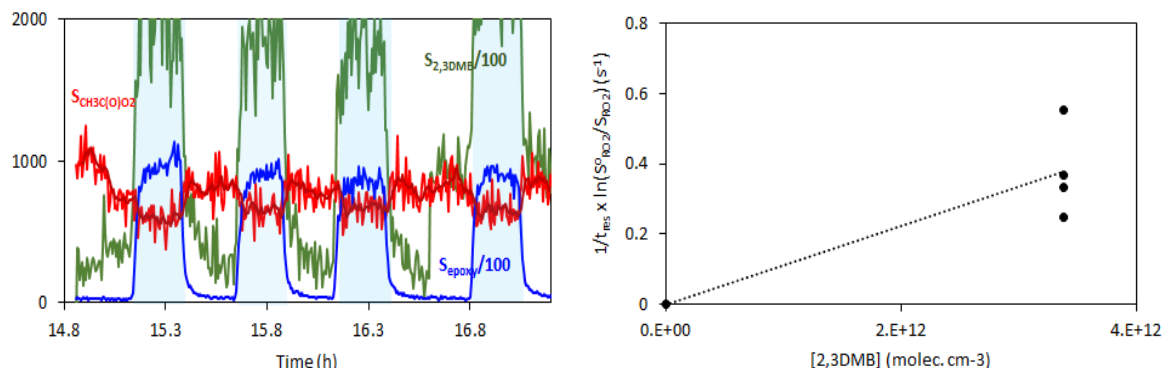


Fig. S11: left: experimental profile for experiment ALK33, showing the evolution of the $\text{CH}_3\text{C}(\text{O})\text{O}_2$ signal (red lines), 2,3-DMB (green line), and epoxy (blue line) during the alkene ON/alkene OFF cycles; Right: corresponding kinetic plot providing the rate coefficient.

In experiment ALK33, $S_{\text{RO}_2}^0 = 800 \text{ Hz}$ measured at the bottom of the reactor, corresponding to $[\text{CH}_3\text{C}(\text{O})\text{O}_2]_0 = 1 \times 10^{10} \text{ molec. cm}^{-3}$, was used to determine the photolytic source term, which was found to be $S = 2.5 \times 10^{10} \text{ molec. cm}^{-3} \text{ s}^{-1}$. Running the simulations with this source term and $[\text{2,3-dimethyl-2-butene}] = 0$ gave the concentrations profiles given in Table S4.6, columns 2-4, and Fig.S12 (continuous lines for the radicals). Then, adding $[\text{2,3-dimethyl-2-butene}] = 3.4 \times 10^{12} \text{ molec. cm}^{-3}$ and $k_{\text{Alk}}^{\text{ref}} = 1.1 \times 10^{-13} \text{ molec}^{-1} \text{ cm}^3 \text{ s}^{-1}$ (Table S4) led a new set of profiles (columns 9 - 12). Applying Eq.(13b) to the results gave k^{II} (last column). The value obtained at $t = 17\text{s}$, $k^{\text{II}} = 5.7 \times 10^{-15} \text{ molec}^{-1} \text{ cm}^3 \text{ s}^{-1}$, was compared to $k_{\text{Alk}}^{\text{ref}}$ (Table S4) which gave the correction factor of 19.3, thus within 3 % of the one obtained in the isoprene experiments.

Calculations of the concentration of radicals from $\text{OH} + \text{2,3-dimethyl-2-butene}$ in S20, “rx” (column 13) shows that these concentrations are very small, thus that these radicals do not contribute to the kinetics.

In these experiments, $\text{Cl} + \text{2,3-dimethyl-2-butene}$ was expected to be less than 6 % of $\text{Cl} + \text{CH}_3\text{CHO}$, thus not to affect the production of $\text{CH}_3\text{C}(\text{O})\text{O}_2$.

Applying Eq. (13b) with the above correction factor to the experimental data gave $k^{\text{II}} = 1.2 \times 10^{-13} \text{ molec}^{-1} \text{ cm}^3 \text{ s}^{-1}$ (Table S5), thus nearly identical to the assumed value of $k_{\text{Alk}}^{\text{ref}}$, as the later was chosen from the results of several self-consistency iterations in the determination of k^{II} .

Table S4.6: Numeric simulation of the $\text{CH}_3\text{C}(\text{O})\text{O}_2 + 2,3\text{-dimethyl-2-butene}$ system (experiment Alk33).

t(s)	2,3-dimethylbutene = 0 ^(a)				% sink ^(c)			2,3-dimethylbutene= 3.4e12 ^(a)					% sink ^(c)				k ^{II(d)}	
	$\text{CH}_3\text{C}(\text{O})\text{O}_{20}$ ^(a)	CH_3O_{20} ^(a)	HO_{20} ^(a)	k ^{I(b)}	Self	CH_3O_2	HO_2	$\text{CH}_3\text{C}(\text{O})\text{O}_{2a}$ ^(a)	CH_3O_{2a} ^(a)	HO_{2a} ^(a)	epox ^(a)	rx ^(a)	k ^{I(b)}	Self	CH_3O_2	HO_2		Alkene
0	0.0E+00	0.0E+00	0.0E+00					0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00						
2	2.3E+10	2.0E+10	2.9E+09	0.30	0.55	0.37	0.09	1.8E+10	2.5E+10	3.1E+09	1.0E+10	2.0E+03	0.53	0.29	0.29	0.06	0.36	3.3E-14
4	1.7E+10	4.4E+10	1.1E+10	0.75	0.27	0.52	0.21	1.4E+10	5.0E+10	1.0E+10	2.2E+10	2.0E+04	1.13	0.16	0.43	0.15	0.27	1.8E-14
6	1.4E+10	5.3E+10	1.5E+10	0.93	0.20	0.55	0.25	1.1E+10	6.2E+10	1.4E+10	3.1E+10	5.1E+04	1.40	0.11	0.47	0.18	0.24	1.2E-14
8	1.3E+10	5.6E+10	1.5E+10	0.98	0.17	0.57	0.26	9.8E+09	6.7E+10	1.4E+10	3.9E+10	8.6E+04	1.51	0.10	0.49	0.18	0.23	9.3E-15
10	1.2E+10	5.6E+10	1.5E+10	0.98	0.16	0.58	0.26	8.8E+09	6.9E+10	1.4E+10	4.6E+10	1.2E+05	1.55	0.09	0.51	0.17	0.23	7.9E-15
12	1.1E+10	5.5E+10	1.5E+10	0.96	0.15	0.59	0.26	8.1E+09	7.0E+10	1.4E+10	5.2E+10	1.6E+05	1.56	0.08	0.52	0.17	0.23	7.0E-15
14	1.0E+10	5.4E+10	1.4E+10	0.94	0.15	0.59	0.26	7.5E+09	7.0E+10	1.3E+10	5.8E+10	1.9E+05	1.55	0.08	0.53	0.16	0.24	6.4E-15
16	9.5E+09	5.3E+10	1.4E+10	0.91	0.14	0.60	0.26	6.9E+09	6.9E+10	1.2E+10	6.3E+10	2.2E+05	1.54	0.07	0.53	0.16	0.24	5.9E-15
18	9.0E+09	5.1E+10	1.3E+10	0.87	0.14	0.60	0.26	6.4E+09	6.9E+10	1.2E+10	6.8E+10	2.5E+05	1.51	0.07	0.54	0.15	0.24	5.5E-15
20	8.5E+09	4.9E+10	1.2E+10	0.84	0.14	0.61	0.26	5.9E+09	6.8E+10	1.1E+10	7.3E+10	2.8E+05	1.48	0.06	0.54	0.15	0.25	5.3E-15
$k_{\text{Alk}}^{\text{ref}} = 1.1 \times 10^{-13} \Rightarrow \text{correction factor} =$																	19.3	

^(a)All concentrations are in molec. cm^{-3} ; ^(b)First-order sinks other than alkene (s^{-1}) = wall losses + $k_{\text{HO}_2} \times [\text{HO}_2] + k_{\text{CH}_3\text{O}_2} \times [\text{CH}_3\text{O}_2]$; ^(c)% of the total CH_3O_2 sinks; ^(d)k^{II} in $\text{molec.}^{-1} \text{cm}^3 \text{s}^{-1}$ calculated from Eq.(13b).

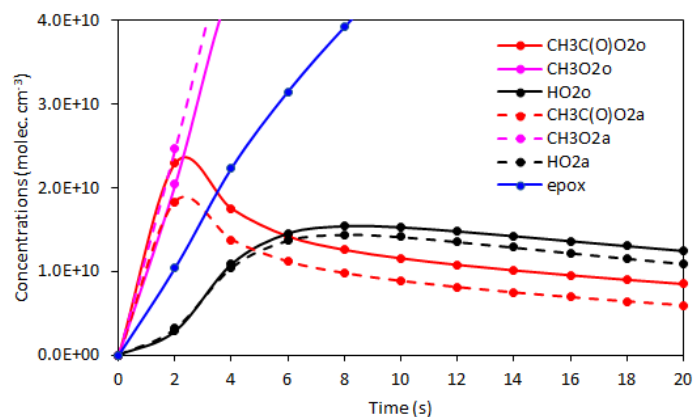


Fig. S12: Concentration profiles in the reactors in the $\text{CH}_3\text{C}(\text{O})\text{O}_2 + 2,3\text{-dimethyl-2-butene}$ system (experiment Alk33) corresponding to Table S4.6: $\text{CH}_3\text{C}(\text{O})\text{O}_2 =$ red lines, $\text{HO}_2 =$ black lines, for both radicals, solid lines = in absence of alkene; dashed lines = in presence of alkene. Blue solid line ("epox") = concentration of alkene epoxy. The CIMS measurements are performed at $t \sim 17$ s.

Table S5: Rate coefficient k^{II} (298 K) obtained for the reactions studied.

Reaction	k^{II} (298 K) (molec. ⁻¹ cm ³ s ⁻¹)
CH ₃ O ₂ + isoprene	1.9 x 10 ⁻¹⁸ x2/2
CH ₃ O ₂ + 2-methyl-2-butene	2.2 x 10 ⁻¹⁸ x2/2
CH ₃ O ₂ + α -pinene	2.7 x 10 ⁻¹⁸ x2/2
CH ₃ O ₂ + limonene	4.9 x 10 ⁻¹⁸ x2/2
CH ₃ O ₂ + 2,3-dimethyl-2-butene	6.7 x 10 ⁻¹⁸ x2/2
C ₅ H ₁₁ O ₂ + Isoprene	7.8 x 10 ⁻¹⁸ x5/5
C ₅ H ₁₁ O ₂ + 2-methyl-2-butene	1.1 x 10 ⁻¹⁷ x5/5
C ₅ H ₁₁ O ₂ + limonene	1.1 x 10 ⁻¹⁶ x5/5
C ₅ H ₁₁ O ₂ + 2,3-dimethyl-2-butene	1.6 x 10 ⁻¹⁶ x5/5
CH ₃ C(O)O ₂ + isoprene	1.8 x 10 ⁻¹⁴ x5/5
CH ₃ C(O)O ₂ + 2-methyl-2-butene	1.7 x 10 ⁻¹⁴ x5/5
CH ₃ C(O)O ₂ + 2,3-dimethyl-2-butene	1.2 x 10 ⁻¹³ x5/5

S6: References

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