

Table S2. Reaction scheme used in the numerical simulation of the temporal profiles of the detected products in the presence of OH-scavenger at 400 Torr

	Reaction	k^a
R1a	$\text{CF}_3\text{CH}_2\text{CHO} + \text{hv}(308 \text{ nm}) \rightarrow \text{CF}_3\text{CH}_2 + \text{HCO}$	see text
R1b	$\rightarrow \text{CF}_3\text{CH}_3 + \text{CO}$	see text
R1c	$\rightarrow \text{CF}_3\text{CH}_2\text{CO} + \text{H}$	see text
R2a	$\text{HCO} + \text{O}_2 \rightarrow \text{HO}_2 + \text{CO}$	see text
R2b	$\rightarrow \text{HC(O)O}_2 (+\text{M}) \rightarrow \text{HO}_2 + \text{CO}$	see text
R3	$\text{CF}_3\text{CH}_2\text{CO} \rightarrow \text{CF}_3\text{CH}_2 + \text{CO}$	$2.95 \times 10^4^b$
R4	$\text{H} + \text{O}_2 (+\text{M}) \rightarrow \text{HO}_2 (+\text{M})$	$6.03 \times 10^{-13}^c$
R5a	$\text{HC(O)O}_2 + \text{HO}_2 \rightarrow \text{HC(O)OH} + \text{O}_3$	$2.10 \times 10^{-12}^{\text{d,e}}$
R5b	$\rightarrow \text{HC(O)OOH} + \text{O}_2$	$5.74 \times 10^{-12}^{\text{d,e}}$
R5c	$\rightarrow \text{HC(O)O} + \text{OH} + \text{O}_2$	$6.16 \times 10^{-12}^{\text{d,e}}$
R6a	$\text{CF}_3\text{CH}_2 + \text{O}_2 (+\text{M}) \rightarrow \text{CF}_3\text{CH}_2\text{O}_2 (+\text{M})$	$6.71 \times 10^{-12}^{\text{d,e}}$
R6b	$\rightarrow \text{CF}_3\text{CH} + \text{HO}_2$	$3.80 \times 10^{-15}^{\text{d,e}}$
R7a	$2 \text{ CF}_3\text{CH}_2\text{O}_2 \rightarrow 2 \text{ CF}_3\text{CH}_2\text{O} + \text{O}_2$	$3.97 \times 10^{-14}^{\text{d,e}}$
R7b	$\rightarrow \text{CF}_3\text{CHO} + \text{CF}_3\text{CH}_2\text{OH} + \text{O}_2$	$1.22 \times 10^{-14}^{\text{d,e}}$
R7c	$\rightarrow \text{CF}_3\text{CH}_2\text{OOCH}_2\text{CF}_3 + \text{O}_2$	$1.22 \times 10^{-14}^{\text{d,e}}$
R8	$\text{CF}_3\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CF}_3\text{CHO} + \text{HO}_2$	$8.06 \times 10^{-15}^{\text{d,e}}$
R9	$\text{CF}_3\text{CHO} + \text{hv}(308 \text{ nm}) \rightarrow \text{CF}_3 + \text{HCO}$	$1.02 \times 10^{-3}^f$
R10	$\text{CF}_3 + \text{O}_2 (+\text{M}) \rightarrow \text{CF}_3\text{O}_2 (+\text{M})$	$2.93 \times 10^{-12}^g$
R11	$2 \text{ CF}_3\text{O}_2 \rightarrow 2 \text{ CF}_3\text{O} + \text{O}_2$	$1.50 \times 10^{-12}^g$
R12	$\text{CF}_3\text{O} + \text{O}_2 \rightarrow \text{F}_2\text{CO} + \text{FO}_2$	$1.00 \times 10^{-18}^g$
R13	$\text{CF}_3\text{CH}_2\text{O} \rightarrow \text{CF}_3 + \text{CH}_2\text{O}$	$8 \times 10^4^h$
R14a	$\text{CF}_3\text{CH}_2\text{CO} + \text{O}_2 \rightarrow \text{CF}_3\text{CH}_2\text{C(O)O}_2 (+\text{M})$	$5.91 \times 10^{-12}^{\text{i,e}}$
R14b	$\rightarrow \text{OH} + \text{Products}$	$5.37 \times 10^{-13}^{\text{i,e}}$
R15a	$\text{CF}_3\text{CH}_2\text{C(O)O}_2 + \text{HO}_2 \rightarrow \text{CF}_3\text{CH}_2\text{C(O)OH} + \text{O}_3$	$2.10 \times 10^{-12}^{\text{d,e}}$
R15b	$\rightarrow \text{CF}_3\text{CH}_2\text{C(O)OOH} + \text{O}_2$	$5.74 \times 10^{-12}^{\text{d,e}}$
R15c	$\rightarrow \text{CF}_3\text{CH}_2\text{C(O)O} + \text{OH} + \text{O}_2$	$6.16 \times 10^{-12}^{\text{d,e}}$
R16a	$\text{CF}_3\text{CH}_2\text{C(O)O}_2 + \text{CF}_3\text{CH}_2\text{O}_2 \rightarrow \text{CF}_3\text{CHO} + \text{CF}_3\text{CH}_2\text{C(O)OH} + \text{O}_2$	$2.40 \times 10^{-12}^{\text{j,e}}$
R16b	$\rightarrow \text{CF}_3\text{CH}_2\text{C(O)O} + \text{CF}_3\text{CH}_2\text{O} + \text{O}_2$	$9.60 \times 10^{-12}^{\text{j,e}}$
R17	$\text{OH} + \text{CF}_3\text{CH}_2\text{CHO} \rightarrow \text{H}_2\text{O} + \text{CF}_3\text{CH}_2\text{CO}$	$2.59 \times 10^{-12}^k$
R18	$\text{OH} + \text{CF}_3\text{CHO} \rightarrow \text{H}_2\text{O} + \text{CF}_3\text{CO}$	$5.70 \times 10^{-13}^g$
R19	$\text{OH} + \text{CF}_3 \rightarrow \text{F}_2\text{CO} + \text{HF}$	$1.50 \times 10^{-11}^l$
R20	$\text{HO}_2 + \text{CH}_2\text{O} \rightarrow \text{HOCH}_2\text{OO}$	$7.9 \times 10^{-14}^d$
R21a	$2 \text{ HOCH}_2\text{OO} \rightarrow \text{HC(O)OH} + \text{CH}_2(\text{OH})_2 + \text{O}_2$	$7.0 \times 10^{-13}^j$
R21b	$\rightarrow 2 \text{ HOCH}_2\text{O} + \text{O}_2$	$5.5 \times 10^{-12}^j$
R22	$\text{OH} + \text{C}_6\text{H}_{12} \rightarrow \text{H}_2\text{O} + \text{C}_6\text{H}_{11}$	$6.97 \times 10^{-12}^m$
R23	$\text{OH} + \text{CF}_3\text{CH}_2\text{OH} \rightarrow \text{H}_2\text{O} + \text{CF}_3\text{CHOH}$	$1.02 \times 10^{-13}^n$

R24	$\text{OH} + \text{HC(O)OH} \rightarrow \text{H}_2\text{O} + \text{HC(O)O}$	4.5×10^{-13} d
R25	$\text{OH} + \text{CH}_2\text{O} \rightarrow \text{H}_2\text{O} + \text{HCO}$	8.5×10^{-12}
R26	$\text{CF}_3\text{CH}_2\text{O}_2 + \text{HO}_2 \rightarrow \text{CF}_3\text{CH}_2\text{OOH} + \text{O}_2$	8.00×10^{-12} j,e
R27	$\text{CF}_3\text{CH}_2\text{C(O)O} \rightarrow \text{CO}_2 + \text{CF}_3\text{CH}_2$	Instantaneous
R28	$\text{CF}_3 + \text{CF}_3\text{CH}_2\text{CHO} \rightarrow \text{CF}_3\text{H} + \text{CF}_3\text{CH}_2\text{CO}$	1.58×10^{-12} o
R29	$2 \text{ HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	1.60×10^{-12} c
R30	$2 \text{ HO}_2 (+\text{M}) \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 (+\text{M})$	6.74×10^{-13} c

^a First order rate coefficients in s⁻¹; second order rate coefficients in cm³ molecule⁻¹ s⁻¹; ^b Maricq *et al.*²⁰; ^c Atkinson *et al.*³⁵; ^d Atkinson *et al.*¹⁵; ^e Data taken from methyl substituted molecules; ^f estimated from Chiappero *et al.*¹⁰; ^g Atkinson *et al.*⁷; ^h Curran³⁶; ⁱ Baeza Romero *et al.*³⁷; ^j IUPAC recommendation²⁸ for CF₃CO; ^k Antiñolo *et al.*⁸; ^l Srinivasan *et al.*³⁸; ^m Atkinson *et al.*³⁹; ⁿ Hurley *et al.*⁵; ^o Loucks *et al.*⁴⁰ for CF₃CHO.

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