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S1 Optimisation of first-generation OH-initiated chemistry

The first generation OH-initiated chemistry, as used in the optimisation procedure, is listed in Table S1. The performance of the mechanism was optimised using reported product yields (summarised in Table S2), with a number of constraints that are described and justified in Sects. 2.1.1–2.1.3 of the main paper. The following subsections give an overview of the optimisation procedure, and associated mechanistic information not presented in the main paper.

S1.1 OH addition ratios

The OH addition ratios were initially estimated using an updated structure activity relationship (SAR) method, based on the widely-applied methods of Peeters et al. (2007) and Kwok and Atkinson (1995)¹. An estimated rate coefficient is thus based on the summation of the partial rate coefficients for OH addition and H atom abstraction for each attack position in a given alkene or polyalkene. The partial rate coefficients were optimized using a set of preferred kinetic data for reactions of OH with 91 alkenes and polyalkenes¹.

The SAR method results in an estimated rate coefficient for the reaction of OH with isoprene of $9.97 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K, in excellent agreement with the IUPAC Task Group recommendation ($1.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)². H atom abstraction is estimated to account for 0.3 % of the reaction, and is therefore not represented in MCM v3.3. The estimated addition branching ratios are 61.4 %, 4.2 %, 4.2 % and 30.2 % at positions 1, 2, 3 and 4 at 298 K, with these varying only weakly with temperature. These branching ratios are consistent with those estimated elsewhere (e.g. McGivern et al., 2000; Lei et al., 2000; Greenwald et al., 2007). The ratios for minor addition to the central carbon atoms (i.e. at positions 2 and 3) are left unchanged from these values in MCM v3.3. The relative attack at positions 1 and 4 was adjusted to optimize the performance of the mechanism, specifically in relation to reported yields of MVK and MACR at the high [NO] limit (see Table S2). This resulted in optimized addition branching ratios of 56.0 % and 35.6 % at positions 1 and 4, respectively.

S1.2 Reactions of CISOPAO and CISOPCO

A number of fates are included for the Z- isomers of the δ -hydroxy oxy radicals, CISOPAO and CISOPCO (as illustrated in Figs. S1 and S2). These are all initiated by a 1,5 H atom shift isomerisation, to produce a resonant C₅ dihydroxy alkenyl radical in each case, which is represented to react three ways:

(i) **Formation of C₅ hydroxycarbonyls:** This occurs via α -hydroxy H atom abstraction, to yield HO₂ and the C₅ unsaturated hydroxyaldehydes HC4CCHO (from CISOPAO) and HC4ACHO (from CISOPCO).

(ii) **Formation of glyoxal/hydroxyacetone and methyl glyoxal/glycolaldehyde:** Addition of O₂ γ - to the OH group, as postulated by Dibble (2004). This initiates sequences of reactions, involving C₅ α -formyl peroxy radicals (C526O2 and C527O2), leading to the ultimate formation of either methyl glyoxal (MGLYOX), glycolaldehyde (HOCH2CHO) and OH from CISOPAO, or glyoxal (GLYOX), hydroxyacetone (ACETOL) and OH from CISOPCO. The mechanism is based on that reported by Peeters and Nguyen (2012). C526O2 and C527O2 are also represented to react via 1,4 H atom shift isomerisation to form C₄ hydroperoxy hydroxycarbonyls (HMKBOOH and MACROOH), CO and OH (see Figs. S1 and S2). These reactions are uncompetitive at the high [NO] limit, and do not therefore influence the optimisation procedure described below.

¹ The protocol rules on which the MCM is based are in the process of being systematically revised, including defining updated SARs for many reaction classes relevant to tropospheric organic chemistry. This will be reported fully elsewhere.

² [http://iupac.pole-ether.fr/htdocs/datasheets/pdf/HOx_VOC8_HO_CH2C\(CH3\)CHCH2\(isoprene\).pdf](http://iupac.pole-ether.fr/htdocs/datasheets/pdf/HOx_VOC8_HO_CH2C(CH3)CHCH2(isoprene).pdf)

(iii) **Formation of 3-methylfuran:** Dehydration/cyclisation and subsequent reaction with O_2 , leading to the formation of 3-methylfuran (M3F) and HO_2 by the mechanism postulated by Francisco-Márquez et al. (2003).

The relative importance of these routes was therefore optimised on the basis of yields reported for the C_5 hydroxycarbonyls, glyoxal, glycolaldehyde, hydroxyacetone and 3-methylfuran at the high [NO] limit, as summarised in Table S2. The ratio assigned to 3-methylfuran formation was assumed to be the same for both CISOPAO and CISOPCO, with an optimised value of 0.22 resulting in a 4.1 % yield of 3-methylfuran, in good agreement with the results of Atkinson et al. (1989), Paulson et al. (1992) and Ruppert and Becker (2000). The relative importance of the other two routes in each case was varied so that the yields of glyoxal/hydroxyacetone and methylglyoxal/glycolaldehyde were each 2.6 %, consistent with the results of Volkamer et al. (2006), Galloway et al. (2011) and Paulot et al. (2009). This also resulted in a combined yield of the C_5 hydroxycarbonyls (HC4ACHO and HC4CCHO) of 11.1%, which is within the relatively wide range of reported values (Zhao et al. 2004; Baker et al., 2005; Paulot et al., 2009).

S1.3 Formation of hydroxymethacrolein (HMACR)

The δ -hydroxy oxy radical ISOPAO reacts exclusively via a 1,5 H shift isomerisation reaction involving the methyl group. At the high [NO] limit, this leads to the ultimate formation of hydroxymethacrolein (HMACR), HCHO and HO_2 via a multi-step mechanism involving a further C_5 peroxy radical (C524O2), as postulated by Dibble (2002) and Zhao et al. (2003). This mechanism is illustrated in Fig. S3. Although the importance of this route was not specifically optimised, the final mechanism predicts a yield of HMACR of 2.9 % at the high [NO] limit, which is consistent with the C_4 hydroxycarbonyl yield reported by Zhao et al. (2004) (see Table S2). C524O2 is also represented to react via 1,5 H atom shift isomerisation to form HMACR, CO and OH (see Fig. S3), although this reaction is uncompetitive at the high [NO] limit.

S1.4 1,6 H shift isomerisation reactions of CISOPAO2 and CISOPCO2

The Z- isomers of the δ -hydroxy peroxy radicals, CISOPAO2 and CISOPCO2, each undergoes a 1,6 H atom shift isomerisation reaction to produce a resonant C_5 hydroxy hydroperoxyalkenyl radical. These react with O_2 both α - and γ - to the hydroxy group with assumed equal probability, based on the appraisal of Peeters et al. (2014). The former reaction produces HO_2 and the unsaturated hydroperoxyaldehydes, C5HPALD1 (from CISOPAO2) and C5HPALD2 (from CISOPCO2).

The temperature-dependent rate expression applied to the 1,6 H atom shift isomerisation reactions (K16ISOM1) is based on the average of those reported by Peeters et al. (2014) for CISOPAO2 and CISOPCO2, but was scaled to recreate the phenomenological bulk isomerisation rate to form C5HPALD1 and C5HPALD2 ($k_{bulk} \approx 0.002 \text{ s}^{-1}$ at 295 K), reported by Crounse et al. (2011). As discussed by Peeters et al. (2014), k_{bulk} depends on the prevailing rate of peroxy radical removal through the “traditional” bimolecular reactions (i.e. with NO, NO_3 , HO_2 and the peroxy radical pool) such that the value reported by Crounse et al. (2011) corresponds to a “traditional” loss rate ($k_{tr} \approx 0.021 \text{ s}^{-1}$). Fig. S4 illustrates the variation of k_{bulk} with k_{tr} , calculated with the optimised MCM v3.3 scheme, where k_{bulk} as presented here represents only the assigned 50 % of the isomerisation reactions that form C5HPALD1 and C5HPALD2. The inset shows that the variation over the likely atmospheric range is approximately linear, in qualitative agreement with the original results of Peeters et al. (2014).

S2 Updated generic rate coefficients applied in MCM v3.3

Small revisions were made to a number of generic rate coefficients for peroxy radical reactions in MCM v3.2, and these are retained in MCM v3.3. These include those for the reactions of acyl peroxy radicals (of generic formula $RC(O)O_2$) with NO and HO_2 (denoted KAPNO and KAPHO2) and the reference rate coefficient for the reactions of peroxy radicals (RO_2) with NO and NO_3 (denoted

KRO₂NO and KRO₂NO₃). These are listed in Table S3, along with the newly assigned generic rate coefficients for peroxy radical H atom shift isomerisation reactions (denoted K14ISOM1, K15ISOM1 and K16ISOM1), and for the formation of peroxy acyl nitrates (PANs: RC(O)OONO₂) and their back decomposition (denoted KFPAN and KBPAN).

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Tables

Table S1. Listing of first-generation OH-initiated chemistry, as used to optimise the chemistry and to generate the results in Fig. 4 of the main paper. Reactions of intermediate peroxy radicals with NO₃, HO₂ and the peroxy radical pool are omitted from this listing, but are represented in MCM v3.3 (see Sect. 2.1.4).

Reaction	Rate coefficient	Comment
1) Initiation reactions		
OH + C5H8 → CISOPA	$2.70 \times 10^{-11} \exp(390/T) * 0.280$	(a),(b),(c)
OH + C5H8 → TISOPA	$2.70 \times 10^{-11} \exp(390/T) * 0.280$	(a),(b),(c)
OH + C5H8 → CISOPC	$2.70 \times 10^{-11} \exp(390/T) * 0.178$	(a),(b),(c)
OH + C5H8 → TISOPC	$2.70 \times 10^{-11} \exp(390/T) * 0.178$	(a),(b),(c)
OH + C5H8 (+O ₂) → PE4E2CO + HO2	$2.70 \times 10^{-11} \exp(390/T) * 0.042$	(a),(b),(d)
OH + C5H8 (+O ₂) → ISOP34O2	$2.70 \times 10^{-11} \exp(390/T) * 0.022$	(a),(b),(d)
OH + C5H8 (+O ₂) → ME3BU3ECHO + HO2	$2.70 \times 10^{-11} \exp(390/T) * 0.020$	(a),(b),(d)
2) Reversible hydroxyalkenyl radical + O₂ reactions		
CISOPA (+O ₂) → CISOPAO2	$5.50 \times 10^{-13} * [O_2]$	(e),(f)
CISOPAO2 → CISOPA (+O ₂)	$8.00 \times 10^{14} \exp(-10050/T)$	(e),(g)
CISOPA (+O ₂) → ISOPBO2	$6.50 \times 10^{-13} * [O_2]$	(e),(h)
ISOPBO2 → CISOPA (+O ₂)	$1.70 \times 10^{15} \exp(-11030/T)$	(e),(i)
TISOPA (+O ₂) → ISOPAO2	$1.00 \times 10^{-13} * [O_2]$	(e),(j)
ISOPAO2 → TISOPA (+O ₂)	$5.00 \times 10^{13} \exp(-9510/T)$	(e),(k)
TISOPA (+O ₂) → ISOPBO2	$6.50 \times 10^{-13} * [O_2]$	(e),(h)
ISOPBO2 → TISOPA (+O ₂)	$1.70 \times 10^{15} \exp(-11030/T)$	(e),(i)
CISOPC (+O ₂) → CISOPCO2	$5.50 \times 10^{-13} * [O_2]$	(e),(f)
CISOPCO2 → CISOPC (+O ₂)	$8.00 \times 10^{14} \exp(-10050/T)$	(e),(g)
CISOPC (+O ₂) → ISOPDO2	$6.50 \times 10^{-13} * [O_2]$	(e),(l)
ISOPDO2 → CISOPC (+O ₂)	$2.10 \times 10^{15} \exp(-11640/T)$	(e),(m)
TISOPC (+O ₂) → ISOPCO2	$1.00 \times 10^{-13} * [O_2]$	(e),(j)
ISOPCO2 → TISOPC (+O ₂)	$5.00 \times 10^{13} \exp(-9510/T)$	(e),(k)
TISOPC (+O ₂) → ISOPDO2	$6.50 \times 10^{-13} * [O_2]$	(e),(l)
ISOPDO2 → TISOPC (+O ₂)	$2.10 \times 10^{15} \exp(-11640/T)$	(e),(m)
3) Peroxy radical + NO reactions		
CISOPAO2 + NO = CISOPAO + NO2	KRO2NO*0.894	(n),(o)
CISOPAO2 + NO = ISOPANO3	KRO2NO*0.106	(n),(o)
ISOPAO2 + NO = ISOPAO + NO2	KRO2NO*0.894	(n),(o)

ISOPAO2 + NO = ISOPANO3	KRO2NO*0.106	(n),(o)
ISOPBO2 + NO = ISOPBO + NO2	KRO2NO*0.930	(n),(o)
ISOPBO2 + NO = ISOPBNO3	KRO2NO*0.070	(n),(o)
CISOPCO2 + NO = CISOPCO + NO2	KRO2NO*0.894	(n),(o)
CISOPCO2 + NO = ISOPCNO3	KRO2NO*0.106	(n),(o)
ISOPCO2 + NO = ISOPCO + NO2	KRO2NO*0.894	(n),(o)
ISOPCO2 + NO = ISOPCNO3	KRO2NO*0.106	(n),(o)
ISOPDO2 + NO = ISOPDO + NO2	KRO2NO*0.860	(n),(o)
ISOPDO2 + NO = ISOPDNO3	KRO2NO*0.140	(n),(o)
ISOP34O2 + NO = ISOP34O + NO2	KRO2NO*0.930	(n),(p)
ISOP34O2 + NO = ISOP34NO3	KRO2NO*0.070	(n),(p)
C524O2 + NO = C524O + NO2	KRO2NO*0.860	(n),(p)
C524O2 + NO = C524NO3	KRO2NO*0.140	(n),(p)
C526O2 + NO = C526O + NO2	KRO2NO*0.981	(n),(p)
C526O2 + NO = C526NO3	KRO2NO*0.019	(n),(p)
C527O2 + NO = C527O + NO2	KRO2NO*0.935	(n),(p)
C527O2 + NO = C527NO3	KRO2NO*0.065	(n),(p)
C536O2 + NO = C536O + NO2	KRO2NO	(n)
C537O2 + NO = C537O + NO2	KRO2NO	(n)
4) Peroxy radical isomerisation reactions		
CISOPAO2 (+O ₂) = C5HPALD1 + HO2	K16ISOM1*0.5	(e),(q)
CISOPAO2 = C536O2	K16ISOM1*0.5	(e),(q)
CISOPCO2 (+O ₂) = C5HPALD2 + HO2	K16ISOM1*0.5	(e),(q)
CISOPCO2 = C537O2	K16ISOM1*0.5	(e),(q)
ISOPBO2 = MVK + HCHO + OH	K15ISOM1	(e),(r)
ISOPDO2 = MACR + HCHO + OH	K15ISOM1	(e),(r)
C524O2 = HMACR + HCHO + OH	K15ISOM1	(s)
C526O2 = HMKVBOOH + CO + OH	K14ISOM1	(t)
C527O2 = MACROOH + CO + OH	K14ISOM1	(t)
C536O2 = DHPMVK + CO + OH	K14ISOM1	(t)
C537O2 = DHPMACR + CO + OH	K14ISOM1	(t)
4) Oxy radical reactions		
CISOPAO (+O ₂ , -H ₂ O) = M3F + HO2	KDEC*0.22	(u),(v)
CISOPAO (+O ₂) = C526O2	KDEC*0.23	(u),(w)
CISOPAO (+O ₂) = HC4CCHO + HO2	KDEC*0.55	(u),(x)
ISOPAO (+O ₂) = C524O2	KDEC	(u)
ISOPBO (+O ₂) = MVK + HCHO + HO2	KDEC	(u)

CISOPCO (+O ₂ , -H ₂ O) = M3F + HO2	KDEC*0.22	(u),(v)
CISOPCO (+O ₂) = C527O2	KDEC*0.38	(u),(w)
CISOPCO (+O ₂) = HC4ACHO + HO2	KDEC*0.40	(u),(x)
ISOPCO (+O ₂) = HC4CCHO + HO2	KROPRIM*[O ₂]	(y)
ISOPDO (+O ₂) = MACR + HCHO + HO2	KDEC	(u)
ISOP34O (+O ₂) = MACR + HCHO + HO2	KDEC	(u)
C524O (+O ₂) = HMACR + HCHO + HO2	KDEC	(u)
C526O = MGLYOX + HOCH2CHO + OH	KDEC	(u)
C527O = GLYOX + ACETOL + OH	KDEC	(u)
C536O = MGLYOX + HCOCH2OOH + OH	KDEC	(u)
C537O = GLYOX + HYPERACET + OH	KDEC	(u)

Comments:

(a) Rate coefficient based on preferred value of IUPAC Task Group (<http://iupac.pole-ether.fr/>); (b) Branching ratio based on a combination of SARs and optimisation to reported first-generation product yields (see text); (c) Informed by Peeters et al. (2009; 2014); (d) Informed by Park et al. (2003); (e) Based on an average of rate coefficients calculated for (or assigned to) relevant structures formed from addition of OH to isoprene, as reported by Peeters et al. (2014); (f) Based on rate coefficients for CISOPA (cis-1-OH) + O₂ → CISOPAO2 (Z-1-OH-4-OO) and CISOPC (cis-4-OH) + O₂ → CISOPCO2 (Z-4-OH-1-OO) (Peeters et al., 2014); (g) Based on rate coefficients for CISOPAO2 (Z-1-OH-4-OO) → CISOPA (cis-1-OH) + O₂ and CISOPCO2 (Z-4-OH-1-OO) → CISOPC (cis-4-OH) + O₂ (Peeters et al., 2014); (h) Based on rate coefficients for CISOPA (cis-1-OH) + O₂ → ISOPBO2 (1-OH-2-OO) and TISOPA (trans-1-OH) + O₂ → ISOPBO2 (1-OH-2-OO) (Peeters et al., 2014); (i) Based on rate coefficients for ISOPBO2 (1-OH-2-OO) → CISOPA (cis-1-OH) + O₂ and ISOPBO2 (1-OH-2-OO) → TISOPA (trans-1-OH) + O₂ (Peeters et al., 2014); (j) Based on rate coefficients for TISOPA (trans-1-OH) + O₂ → ISOPAO2 (E-1-OH-4-OO) and TISOPC (trans-4-OH) + O₂ → ISOPCO2 (E-4-OH-1-OO) (Peeters et al., 2014); (k) Based on rate coefficients for ISOPAO2 (E-1-OH-4-OO) → TISOPA (trans-1-OH) + O₂ and ISOPCO2 (E-4-OH-1-OO) → TISOPC (trans-4-OH) + O₂ (Peeters et al., 2014); (l) Based on rate coefficients for CISOPC (cis-4-OH) + O₂ → ISOPDO2 (4-OH-3-OO) and TISOPC (trans-4-OH) + O₂ → ISOPDO2 (4-OH-3-OO) (Peeters et al., 2014); (m) Based on rate coefficients for ISOPDO2 (4-OH-3-OO) → CISOPC (cis-4-OH) + O₂ and ISOPDO2 (4-OH-3-OO) → TISOPC (trans-4-OH) + O₂ (Peeters et al., 2014); (n) Generic rate coefficient KRO2NO (= 2.70 × 10⁻¹² exp(360/T) cm³ molecule⁻¹ s⁻¹) based on an average of reported data for ≥ C₂ alkyl, hydroxyalkyl, hydroxyalkenyl, oxoalkyl and hydroxyoxyalkyl RO₂ radicals, which display no significant structural dependence; (o) Branching ratio based on those used in previous versions of the MCM, but scaled slightly to provide an optimised first-generation nitrate yield of 10.0 %; (p) Based on Saunders et al. (2003); (q) Generic rate coefficient K16ISOM1 (= 4.60 × 10⁻⁹ exp(-8380/T). exp(1.00 × 10⁸/T³) s⁻¹) based on average of expressions reported for CISOPAO2 (Z-1-OH-4-OO) and CISOPCO2 (Z-4-OH-1-OO) by Peeters et al. (2014), and scaled to recreate the total yield of C5HPALD1 and C5HPALD2 reported by Crounse et al. (2011), assuming a branching ratio of 0.5 in each case (Peeters et al., 2014); (r) Generic rate coefficient K15ISOM1 (= 1.50 × 10⁻¹¹ exp(-9750/T) s⁻¹) based on average of expressions reported for ISOPBO2 (1-OH-2-OO) and ISOPDO2 (4-OH-3-OO) by Peeters et al. (2014); (s) Assigned by analogy with comment (r) to structurally-similar β-hydroxyalkenyl peroxy radicals; (t) Generic rate coefficient K14ISOM1 (= 3.00 × 10⁻⁷ exp(-5300/T) s⁻¹) based on expression reported for MACRO2 by Crounse et al. (2012), and assigned by analogy to structurally-similar α-formyl peroxy radicals; (u) Generic rate coefficient KDEC (usually assigned a value of 1.00 × 10⁻⁶ s⁻¹) is applied to prompt reactions for which there are either no competing reactions or (in conjunction with appropriate branching ratios), to a set of prompt reactions with fixed relative rates; (v) Branching ratio optimised on the basis of reported yields for 3-methylfuran (M3F) (see Table S2); (w) Branching ratio optimised to provide yields of glyoxal/hydroxyacetone or methylglyoxal/glycolaldehyde of 2.6 % at the high [NO] limit, in broad agreement with reported yields (see Table S2); (x) Branching ratio optimised on the basis of reported yields for C₅ hydroxycarbonyls (see Table S2); (y) Generic rate coefficient KROPRIM (= 2.50 × 10⁻¹⁴ exp(-300/T) cm³ molecule⁻¹ s⁻¹) for reactions of primary oxy radicals with O₂, based on the recommendation of Atkinson (2007).

Table S2. Summary of reported molar yields (%) of first-generation products from the OH-initiated oxidation of isoprene in the presence of NO_x. The MCM v3.3 yields correspond to the high [NO] limit. The displayed mean of the reported yields excludes figures in italic font, which were derived from studies with [NO] < 100 ppb and/or at pressures well below atmospheric.

Study	HCHO	MVK	MACR	M3F	C ₅ OH-carb	C ₄ OH-carb	C ₅ carb	GLYOX	ACETOL	HOCH ₂ CHO	nitrate
Atkinson et al. (1989)				4.4 ± 0.6							
Tuazon and Atkinson (1990)	63 ± 10	32 ± 7	22 ± 5								8–14
Paulson et al. (1992)		36 ± 4	25 ± 3	4.0 ± 0.2							
Miyoshi et al. (1994)	57 ± 6	32 ± 5	22 ± 2								
Chen et al. (1998)											4.4 ± 0.8
Ruppert and Becker (2000)	57 ± 6	31 ± 3	20 ± 2	4.0 ± 1.4							
Sprengnether et al. (2002)	66 ± 12 <i>59 ± 12</i>	44 ± 6 <i>44 ± 6</i>	28 ± 4 <i>27 ± 4</i>								12 ± 6 <i>8 ± 6</i>
Zhao et al. (2004)					19.3 ± 6.1	3.3 ± 1.6	8.4 ± 2.4				
Baker et al. (2005)					15						
Karl et al. (2006)		<i>41 ± 3</i>	<i>27 ± 3</i>								
Patchen et al. (2007)											<i>7.0 ± 3.1</i>
Volkamer et al. (2006)								3			
Paulot et al. (2009)		40	26		10				3.8	4.2	11.7 ± 3.0
Lockwood et al. (2010)											7.0 ^{+2.5} _{-1.5}
Galloway et al. (2011)		30.4 ± 1.3	22.0 ± 0.6					2.1 ± 1.2	2.9 ± 0.05	2.7 ± 0.8	
Liu et al. (2013)		<i>41.4 ± 5.5</i>	<i>29.6 ± 4.2</i>								
Brégonzio-Rozier et al. (2014)	<i>75 ± 11</i>	<i>27 ± 8</i>	<i>30 ± 9</i>	<i>3.3 ± 1.4</i>							
Mean	60.8 ± 4.5	35.1 ± 5.2	23.6 ± 2.8	4.1 ± 0.2	14.8 ± 4.7	-	-	2.6 ± 0.6	3.4 ± 0.6	3.4 ± 1.1	9.2 ± 3.4
MCM v3.3	63.2	36.7	23.6	4.1	11.1	2.9	6.2	2.6	2.6	2.6	10.0

Table S3. Generic rate coefficients updated or newly defined in MCM v3.2 and MCM v3.3.

Parameter	Rate coefficient	Comment
KRO2NO	$2.70 \times 10^{-12} \exp(360/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	(a)
KAPNO	$7.50 \times 10^{-12} \exp(290/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	(b)
KRO2NO3	$2.30 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	(c)
KAPHO2	$5.20 \times 10^{-13} \exp(980/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	(d)
KFPAN	$k_0 = 3.28 \times 10^{-28} [\text{M}].(\text{T}/300)^{-6.87} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ $k_\infty = 1.125 \times 10^{-11} .(\text{T}/300)^{-1.105} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ $F_c = 0.3$	(e)
KBPAN	$k_0 = 1.10 \times 10^{-5} \exp(-10100/T) .[\text{M}] \text{ s}^{-1}$ $k_\infty = 1.90 \times 10^{17} \exp(-14100/T) \text{ s}^{-1}$ $F_c = 0.3$	(e)
K16ISOM1	$4.60 \times 10^9 \exp(-8380/T) . \exp(1.00 \times 10^8/T^3) \text{ s}^{-1}$	(f)
K15ISOM1	$1.50 \times 10^{11} \exp(-9750/T) \text{ s}^{-1}$	(g)
K14ISOM1	$3.00 \times 10^7 \exp(-5300/T) \text{ s}^{-1}$	(h)
Comments: (a) Applied to the reactions of NO with non-acyl peroxy radicals (RO ₂), with a multiplier applied in some cases (see Saunders et al., 2003). Based on the average of 298 K rate coefficients reported for 14 ≥C ₂ alkyl, hydroxyalkyl, hydroxyalkenyl, oxoalkyl and hydroxy-oxyalkyl RO ₂ , which show no significant trends related to the identity and structure of R. The T dependence is based on the rounded average of the reported values within this group, which are limited to C ₂ H ₅ O ₂ , <i>n</i> -C ₃ H ₇ O ₂ and <i>i</i> -C ₃ H ₇ O ₂ . This will be reported in more detail elsewhere ³ ; (b) Applied to the reactions of NO with acyl peroxy radicals (RC(O)O ₂). Based on the current recommendation of the IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation for the reaction of NO with CH ₃ C(O)O ₂ (http://iupac.pole-ether.fr/); (c) Applied to the reactions of NO ₃ with peroxy radicals, with a multiplier applied in some cases (see Saunders et al., 2003). Based on the current recommendation of the IUPAC Task Group for the reaction of NO ₃ with C ₂ H ₅ O ₂ (http://iupac.pole-ether.fr/); (d) Applied to the reactions of HO ₂ with acyl peroxy radicals (RC(O)O ₂). Based on the current recommendation of the IUPAC Task Group for the reaction of HO ₂ with CH ₃ C(O)O ₂ (http://iupac.pole-ether.fr/). Product branching ratios also based on those recommended for the same reaction; (e) Applied to the formation and back decomposition of peroxy acyl nitrates (RC(O)OONO ₂). Based on the current recommendations of the IUPAC Task Group for the formation and back decomposition of PAN (CH ₃ C(O)OONO ₂) (http://iupac.pole-ether.fr/); (f) 1,6 H atom shift isomerisation rate coefficient applied to structures of generic formula (Z) CH ₂ (OH)-C=C-CH ₂ O ₂ . Based on average of expressions reported for CISOPAO2 (Z-1-OH-4-OO) and CISOPCO2 (Z-4-OH-1-OO) by Peeters et al. (2014), and scaled to recreate the total yield of C5HPALD1 and C5HPALD2 reported by Crounse et al. (2011), assuming a branching ratio of 0.5 in each case (Peeters et al., 2014). Currently only applied to relevant species formed during isoprene degradation in MCM v3.3; (g) 1,5 H atom shift isomerisation rate coefficient applied to structures of generic formula -C=C-C(O ₂)-C(OH)-. Based on average of expressions reported for ISOPBO2 (1-OH-2-OO) and ISOPDO2 (4-OH-3-OO) by Peeters et al. (2014). Currently only applied to relevant species formed during isoprene degradation in MCM v3.3; (h) 1,4 H atom shift isomerisation rate coefficient based on expression reported for MACRO2 by Crounse et al. (2012), and assigned to structurally-similar α-formyl peroxy radicals formed during isoprene degradation in MCM v3.3.		

³ The protocol rules on which the MCM is based are in the process of being systematically revised, including defining updated SARs for many reaction classes relevant to tropospheric organic chemistry. This will be reported fully elsewhere.

Figures

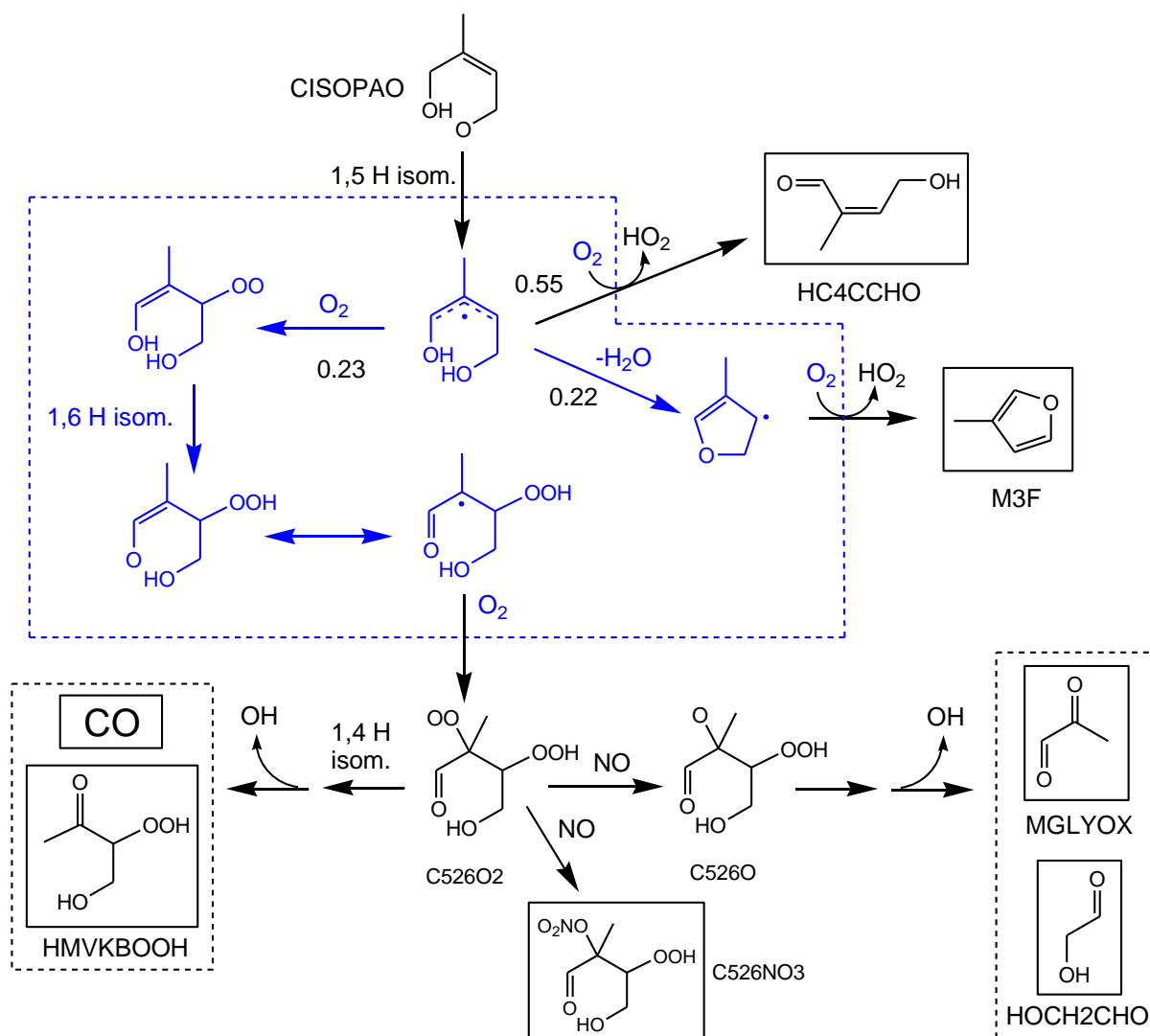


Fig. S1. Chemistry of CISOPAO initiated by 1,5 H atom shift isomerisation, leading to the products represented in MCM v3.3 (see Sect. S1.2). The chemistry in the blue box is not explicitly included in the mechanism, but is shown to illustrate the routes to the corresponding products. For clarity, the reactions of C526O2 with NO₃, HO₂ and the peroxy radical pool are not shown, but are represented in MCM v3.3.

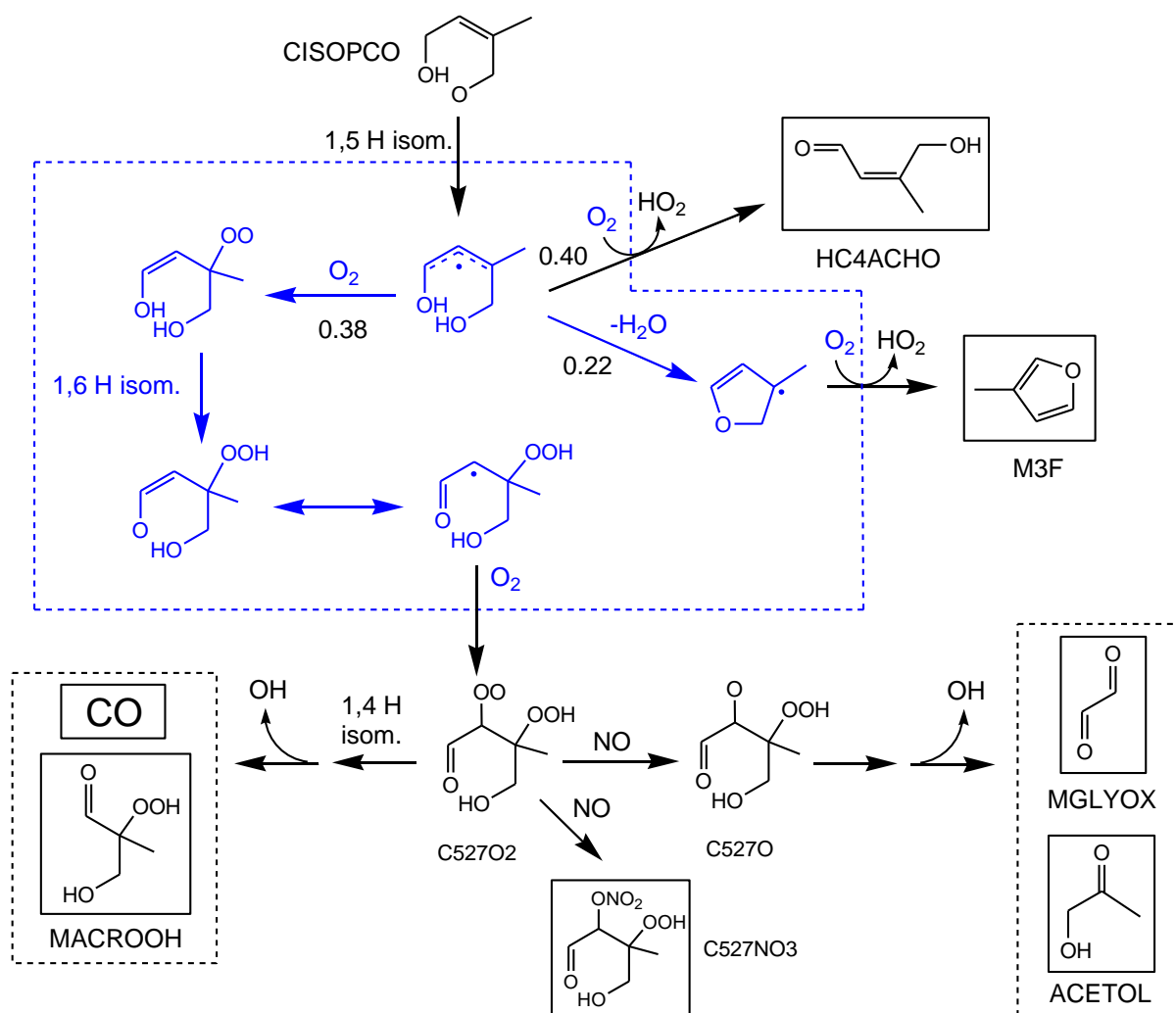


Fig. S2. Chemistry of CISOPCO initiated by 1,5 H atom shift isomerisation, leading to the products represented in MCM v3.3 (see Sect. S1.2). The chemistry in the blue box is not explicitly included in the mechanism, but is shown to illustrate the routes to the corresponding products. For clarity, the reactions of C527O2 with NO_3 , HO_2 and the peroxy radical pool are not shown, but are represented in MCM v3.3.

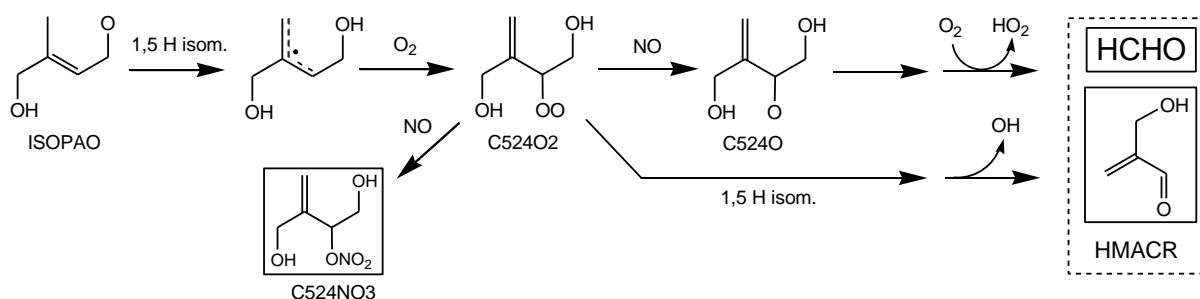


Fig. S3. Chemistry of ISOPAO initiated by 1,5 H atom shift isomerisation, leading to the formation of HMACR in MCM v3.3 (see Sect. S1.3). For clarity, the reactions of C524O2 with NO_3 , HO_2 and the peroxy radical pool are not shown, but are represented in MCM v3.3.

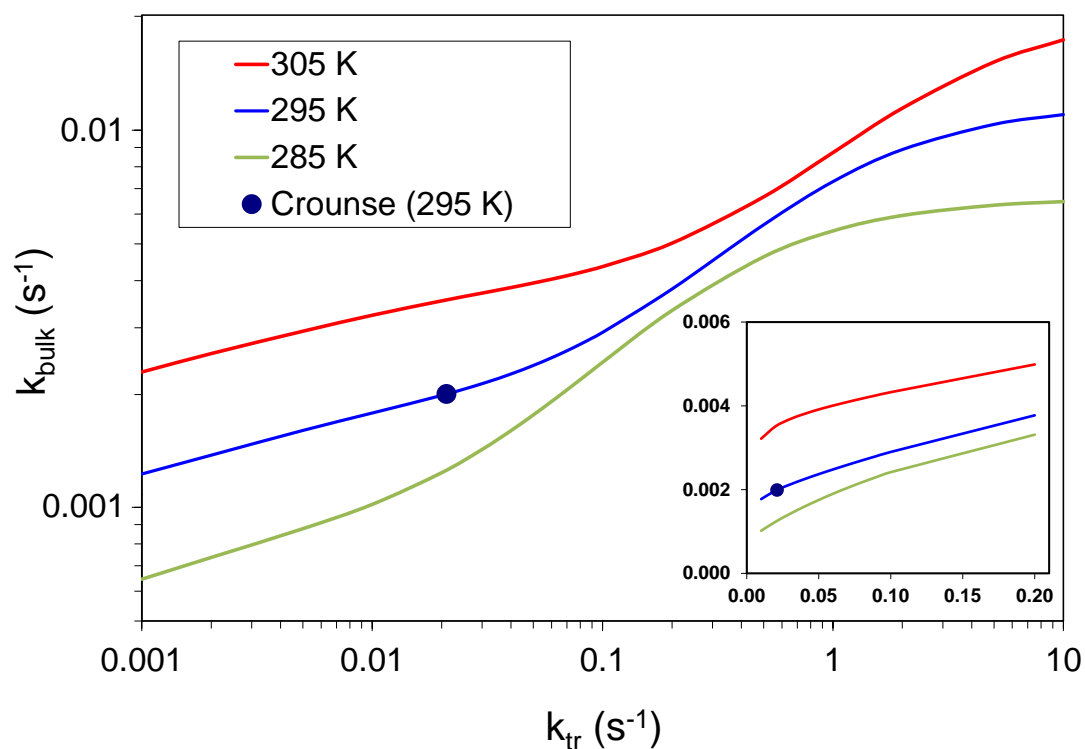


Fig. S4. Variation of the phenomenological bulk isomerisation rate to form C5HPALD1 and C5HPALD2 (k_{bulk}) with the peroxy radical loss rate through “traditional” bimolecular reactions (k_{tr}), as calculated with the optimised MCM v3.3 scheme at 285 K, 295 K and 305 K. The 295 K measurement reported by Crounse et al. (2011), as used to optimise the chemistry, is also shown (see Sect. S1.4). The inset shows the variation over the likely atmospheric range on a linear scale. (N.B. The presented values of k_{bulk} specifically represent only the assigned 50 % of the isomerisation reactions that form C5HPALD1 and C5HPALD2, such that the total effective isomerisation rates are the presented values multiplied by two).