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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 v3.3.1. 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 v3.3.1. The relative attack at positions 1 and 4 was adjusted to optimise 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 optimised addition branching ratios of 57.6 % and 34.0 % 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 0.18 resulting in a 4.2 % 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 2.5 %, 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 13.6 %, which is consistent with the yields reported by Zhao et al. (2004), Baker et al. (2005) and Paulot et al. (2009) (see Table S2).

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 3.3 % at the high [NO] limit, in excellent agreement 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.

It is noted that this fate for ISOPAO is not supported by the very recent study of Nguyen and Peeters (2015), who theoretically characterised its rapid conversion into the corresponding Z- isomer, CISOPAO. However, the above reaction of ISOPAO is currently retained, so that a route to the formation of HMACR as a minor product remains in MCM v3.3.1.

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 expressions applied to the 1,6 H atom shift isomerisation reactions (given in Table S1) are based on those reported recently for LIM1 by Peeters et al. (2014) for CISOPAO2 and CISOPCO2, but 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 v3.3.1 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 agreement with the original results of Peeters et al. (2014). Although the applied rate coefficients for the 1,6 H atom shift isomerisation reactions provide an optimised description based on currently-available information, it should be noted that

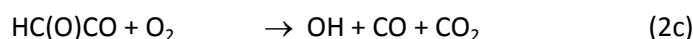
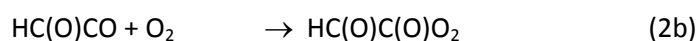
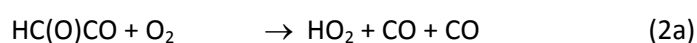
their derived values are inevitably strongly dependent on several adopted but not currently well known kinetic parameters. These include the kinetic parameters applied to the addition reactions of O₂ to the OH-isoprene adducts and reverse reactions (see Sect. 2.1.1 of the main paper; and Peeters, 2015), and also uncertainties in the reported value of k_{bulk} itself (Crounse et al., 2011).

S2 Higher generation chemistry

The following subsections give an overview of selected mechanistic information not presented in detail in the main paper.

S2.1 Chemistry of HCOCO

The chemistry of the HCOCO radical takes account of information reported in Orlando and Tyndall (2001), da Silva (2010) and Lockhart et al. (2013a). The reaction framework presented by Orlando and Tyndall (2001), reactions (1), (2a) and (2b), was used as the starting point:



Reaction (2c) was added to represent the OH forming route proposed by da Silva (2010), with OH yields subsequently characterised experimentally by Lockhart et al. (2013a).

The values of k_1 ($= 7.0 \times 10^{11} \exp(-3160/T) \text{ s}^{-1}$) and k_{2a} ($= 5.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) were taken from Orlando and Tyndall (2001), with that for k_1 being reduced by a factor of two on the basis of a reported personal communication from J. Orlando to G. da Silva (da Silva, 2010). The value assigned to k_{2b} by Orlando and Tyndall (2001) (i.e. to the route that ultimately produced CO and CO₂ in their system) was divided between reaction (2b) and the newly implemented reaction (2c), such that $k_{2b} = \alpha \times 5.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k_{2c} = (1-\alpha) \times 5.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

An optimised value of $\alpha = 3.2 \exp(-550/T)$ recreates the OH yields reported by Lockhart et al. (2013a) at atmospheric pressure, 0.38 at 212 K, 0.31 at 250 K and 0.19 at 295 K, and leads to the following relative contributions of the different channels at 295 K in air at atmospheric pressure: 0.23 (1): 0.39 (2a): 0.19 (2b): 0.19 (2c). Because it is based on the reaction framework and parameters reported by Orlando and Tyndall (2001) (corrected where necessary) it recreates the [CO]/[CO₂] product ratios reported in that study, and their dependence on temperature and [O₂]; and also those reported much earlier by Niki et al. (1985).

The importance of reaction (2b), forming the stabilised peroxy radical, HC(O)C(O)O₂, is substantially reduced compared with earlier MCM versions. Retention of this minor channel is required to account fully for the reported formation of CO₂. Orlando and Tyndall (2001) also inferred that its reaction with NO₂ was necessary as a source of NO₃ in their system. This reaction is therefore represented to form NO₃, HCO and CO₂ directly, rather than a PAN analogue, as postulated by Orlando and Tyndall (2001).

S2.2 Degradation of hydroxymethyl-methyl- α -lactone (HMML)

An overview of the degradation chemistry for HMML is shown in Fig. S5. SAR methods predict an OH rate coefficient of $4.33 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, with > 90 % attack at the -CH₂OH group. This was therefore assumed to be exclusive. The boxed chemistry is analogous to that proposed for the epoxydiol, IEPOXB, by Bates et al. (2014), but avoids the minor channel that would form a further new species (formylmethyl lactone), to limit the proliferation of minor chemistry. The subsequent chemistry is largely based on rules described in the original MCM protocol (Jenkin et al., 1997), for which there are reported precedents. The acyloxy radical is assumed to decompose through loss of

CO₂, leading to formation of a hydroxyvinyl radical (which is also one of the isomers that can be formed from OH + propyne).

The subsequent reaction of the hydroxyvinyl radical with O₂ is assumed to proceed via two channels. The first produces HCOOH and CH₃CO₃, following the generic mechanism applied to vinyl-type radicals (Jenkin et al., 1997). On the basis of reported studies of the reaction of OH with propyne (Hatakeyama et al., 1986; Yeung et al., 2005; Lockhart et al., 2013b), the second channel forms methylglyoxal and OH. The relative importance of the two channels (30:70) is based on the yields reported for HCOOH and methylglyoxal in the propyne system by Lockhart et al. (2013b).

S3 Updated generic rate coefficients applied in MCM v3.3.1

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 v3.3.1. These include those for the reactions of acyl peroxy radicals (of generic formula RC(O)O₂) with NO and HO₂ (denoted KAPNO and KAPHO2) and the reference rate coefficient for the reactions of peroxy radicals (RO₂) with NO and NO₃ (denoted KRO2NO and KRO2NO3). These are listed in Table S3, along with the newly assigned generic rate coefficient for the 1,4-H atom shift reactions for α -formyl peroxy radicals (denoted K14ISOM1), and for the formation of peroxy acyl nitrates (PANs: RC(O)OONO₂) and their back decomposition (denoted KFPAN and KBPAN).

References

- Atkinson, R., Aschmann, S. M., Tuazon, E. C., Arey, J. and Zielinska, B.: Formation of 3-methylfuran from the gas-phase reaction of OH radicals with isoprene and the rate constant for its reaction with the OH radical, *Int. J. Chem. Kinet.*, 21, 593-604, 1989.
- Baker, J., Arey, J. and Atkinson, R.: Formation and reaction of hydroxycarbonyls from the reaction of OH radicals with 1,3-butadiene and isoprene, *Environ. Sci. Technol.*, 39, 4091-4099, 2005.
- Bates, K. H., Crounse, J. D., St. Clair, J. M., Bennett, M. B., Nguyen, T. B., Seinfeld, J. H., Stoltz, B. M. and Wennberg, P. O.: Gas phase production and loss of isoprene epoxydiols, *J. Phys. Chem. A*, 118, 1237-1246, 2014.
- Brégonzio-Rozier, L., Siekmann, F., Giorio, C., Pangui, E., Morales, S. B., Temime-Roussel, B., Gratien, A., Michoud, V., Ravier, S., Cazaunau, M., Tapparo, A., Monod, A., and Doussin, J.-F.: Gaseous products and secondary organic aerosol formation during long term oxidation of isoprene and methacrolein, *Atmos. Chem. Phys.*, 15, 2953-2968, doi:10.5194/acp-15-2953-2015, 2015.
- Chen, X. H., Hulbert, D., and Shepson, P. B.: Measurement of the organic nitrate yield from OH reaction with isoprene, *J. Geophys. Res.*, 103, 25563–25568, 1998.
- Crounse, J. D., Paulot, F., Kjaergaard, H. G. and Wennberg, P. O.: Peroxy radical isomerization in the oxidation of isoprene, *Phys. Chem. Chem. Phys.*, 13, 13607-13613, 2011.
- Crounse, J. D., Knap, H. C., Ørnsø, K. B., Jørgensen, S., Paulot, F., Kjaergaard, H. G. and Wennberg, P. O.: Atmospheric fate of methacrolein. 1. Peroxy radical isomerization following addition of OH and O₂, *J. Phys. Chem. A*, 116, 5756-5762, 2012.
- Crounse, J. D., Teng, A., and Wennberg, P. O.: Experimental constraints on the distribution and fate of peroxy radicals formed in reactions of isoprene + OH + O₂, Presented at “Atmospheric Chemical Mechanisms: Simple Models – Real World Complexities”, University of California, Davis, USA, December 10-12, 2014.
- Da Silva, G.: Hydroxyl radical regeneration in the photochemical oxidation of glyoxal: kinetics and mechanism of the HC(O)CO + O₂ reaction, *Phys. Chem. Chem. Phys.*, 12, 6698-6705, 2010.
- Dibble, T. S.: Isomerization of OH-isoprene adducts and hydroxyalkoxy isoprene radicals, *J. Phys. Chem. A*, 106 (28), 6643-6650, 2002.
- Dibble, T. S.: Prompt chemistry of alkenoxy radical products of the double H-atom transfer of alkoxy radicals from isoprene, *J. Phys. Chem. A*, 108, 2208-2215, 2004.

Francisco-Márquez, M., Alvarez-Idaboy, J. R., Galano, A. and Vivier-Bunge, A.: Theoretical study of the initial reaction between OH and isoprene in tropospheric conditions, *Phys. Chem. Chem. Phys.*, 5, 1392-1399, 2003.

Galloway, M. M., Huisman, A. J., Yee, L. D., Chan, A. W. H., Loza, C. L., Seinfeld, J. H., and Keutsch, F. N.: Yields of oxidized volatile organic compounds during the OH radical initiated oxidation of isoprene, methyl vinyl ketone, and methacrolein under high-NO_x conditions, *Atmos. Chem. Phys.*, 11, 10779-10790, doi:10.5194/acp-11-10779-2011, 2011.

Greenwald, E., North, S., Georgievskii, Y., and Klippenstein, S.: A two transition state model for radical-molecule reactions: applications to isomeric branching in the OH-isoprene reaction, *J. Phys. Chem. A*, 111, 5582-5592, 2007.

Hatakeyama, S., Washida, N., and Akimoto, H.: Rate constants and mechanism for the reaction of OH (OD) radicals with acetylene, propyne and 2-butyne in air at 297 K, *J. Phys. Chem.* 1986, 90, 173-178.

Karl, M., Dorn, H.-P., Holland, F., Koppmann, R., Poppe, D., Rupp, L., Schaub, A. and Wahner, A.: Product study of the reaction of OH radicals with isoprene in the atmosphere simulation chamber SAPHIR, *J. Atmos. Chem.*, 55, 167-187, 2006.

Kwok, E. S. and Atkinson, R.: Estimation of hydroxyl radical reaction rate constants for gas-phase organic compounds using a structure-reactivity relationship: an update, *Atmos. Environ.*, 29, 1685-1695, 1995.

Lei, W., Zhang, R., McGivern, W. S., Derecskei-Kovacs, A. and North, S. W.: Theoretical study of isomeric branching in the isoprene-OH reaction: implications to final product yields in isoprene oxidation, *Chem. Phys. Lett.*, 326, 109-114, 2000.

Liu, Y. J., Herdinger-Blatt, I., McKinney, K. A., and Martin, S. T.: Production of methyl vinyl ketone and methacrolein via the hydroperoxyl pathway of isoprene oxidation, *Atmos. Chem. Phys.*, 13, 5715-5730, doi:10.5194/acp-13-5715-2013, 2013.

Lockhart, J., Blitz, M., Heard, D., Seakins, P. and Shannon, R.: Kinetic study of the OH + glyoxal reaction: experimental evidence and quantification of direct OH recycling, *J. Phys. Chem. A*, 117, 11027-11037, 2013a.

Lockhart, J., Blitz, M., Heard, D., Seakins, P. and Shannon, R.: Mechanism of the reaction of OH with alkynes in the presence of oxygen, *J. Phys. Chem. A*, 117, 5407-5418, 2013b.

Lockwood, A. L., Shepson, P. B., Fiddler, M. N. and Alaghmand, M.: Isoprene nitrates: preparation, separation, identification, yields, and atmospheric chemistry. *Atmos. Chem. Phys.*, 10, 6169-6178, 2010.

McGivern, W. S., Suh, I., Clinkenbeard, A. D., Zhang, R. and North, S. W.: Experimental and computational study of the OH-isoprene reaction: isomeric branching and low-pressure behavior, *J. Phys. Chem. A*, 104, 6609-6616, 2000.

Miyoshi, A., Hatakeyama, S., and Washida, N.: OH radical initiated photooxidation of isoprene: An estimate of global CO production, *J. Geophys. Res.-Atmos.*, 99, 18779-18787, doi:10.1029/94JD01334, 1994.

Niki, H.; Maker, P. D.; Savage, C. M.; Breitenbach, L. P. An FTIR study of the Cl-atom-initiated reaction of glyoxal, *Int. J. Chem. Kinet.* 1985, 17, 547-558.

Nguyen, V. S., and Peeters, J.: Fast (E)-(Z) isomerization mechanisms of substituted allyloxy radicals in isoprene oxidation, *J. Phys. Chem. A*, 119 (28), 7270-7276, doi: 10.1021/jp512057t, 2015.

Orlando, J. and Tyndall, G. S: The atmospheric chemistry of the HC(O)CO radical, *Int. J. Chem. Kinet.*, 33, 149-156, 2001.

Patchen, A. K., Pennino, M. J., Kiep, A. C., et al.: Direct kinetics study of the product-forming channels of the reaction of isoprene-derived hydroxyperoxy radicals with NO, *Int. J. Chem. Kinet.*, 39, 353-361, 2007.

Paulot, F., Crounse, J. D., Kjaergaard, Kroll, J. H., Seinfeld, J. H. and Wennberg, P. O.: Isoprene photooxidation: new insights into the production of acids and organic nitrates. *Atmos. Chem. Phys.*, 9(4):1479-1501, 2009.

Paulson, S. E., Flagan, R. C. and Seinfeld, J. H.: Atmospheric photo-oxidation of isoprene: part I. The hydroxyl radical and ground state atomic oxygen reactions. *Int. J. Chem. Kinet.*, 24, 79-101, 1992.

Peeters, J.: Interactive comment on "The MCM v3.3 degradation scheme for isoprene" by M. E. Jenkin et al., *Atmos. Chem. Phys. Discuss.*, 15, C2486-C2486, 2015.

Peeters, J. and Nguyen, T. L.: Unusually fast 1,6-H shifts of enolic hydrogens in peroxy radicals: formation of the first-generation C₂ and C₃ carbonyls in the oxidation of isoprene, *J. Phys. Chem. A*, 116, 6134-6141, 2012.

Peeters, J., Boullart, W., Pultau, V., Vandenberg, S., and Vereecken, L.: Structure-Activity Relationship for the addition of OH to (poly)alkenes: Site-specific and total rate constants, *J. Phys. Chem. A*, 111, 1618-1631, 2007.

Peeters, J., Nguyen, T. L. and Vereecken, L.: HO_x radical regeneration in the oxidation of isoprene, *Phys. Chem. Chem. Phys.*, 28, 5935-5939, 2009.

Peeters, J., Müller, J.-F., Stavrou, T. and Nguyen, V. S.: Hydroxyl radical recycling in isoprene oxidation driven by hydrogen bonding and hydrogen tunneling: the upgraded LIM1 mechanism, *J. Phys. Chem. A*, 118 (38), 8625-8643, 2014.

Ruppert, L. and Becker, K.-H.: A product study of the OH radical-initiated oxidation of isoprene: formation of C₅-unsaturated diols. *Atmos. Environ.*, 34, 1529-1542, 2000.

Saunders, S. M., Jenkin, M. E., Derwent, R. G., and Pilling, M. J.: Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part A): tropospheric degradation of non-aromatic volatile organic compounds. *Atmos. Chem. Phys.*, 3, 161-180, 2003.

Sprengnether, M., Demerjian, K. L., Donahue, N. M., et al.: Product analysis of the OH oxidation of isoprene and 1,3-butadiene in the presence of NO, *J. Geophys. Res.*, 107, 4269, doi:10.1029/2001JD000716, 2002.

Tuazon, E. C. and Atkinson, R.: A product study of the gas-phase reaction of isoprene with the OH radical in the presence of NO_x, *Int. J. Chem. Kinet.*, 22, 1221-1236, 1990.

Volkamer, R., Barnes, I., Platt, U., Molina, L. T., and Molina, M. J.: Remote sensing of glyoxal by differential optical absorption spectroscopy (DOAS): Advancements in simulation chamber and field experiments, in: *Environmental Simulation Chambers: Application to Atmospheric Chemical Processes*, edited by: Barnes, I. and Rudinski, J., 62, Springer, Dordrecht, Netherlands, 2006.

Yeung, L. Y., Pennino, M. J., Miller, A. M., and Elrod, M. J.: Kinetics and mechanistic studies of the atmospheric oxidation of alkynes, *J. Phys. Chem. A*, 109, 1879-1889, 2005.

Zhao, J., Zhang, R. Y. and North, S. W.: Oxidation mechanism of delta-hydroxyisoprene alkoxy radicals: hydrogen abstraction versus 1,5 H-shift. *Chem. Phys. Lett.*, 369(1-2), 204-213, 2003.

Zhao, J., Zhang, R. Y., Fortner, E. C. and North, S. W.: Quantification of hydroxycarbonyls from OH-isoprene reactions, *J. Am. Chem. Soc.*, 126, 2686-2687, 2004.

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 v3.3.1 (see Sect. 2.1.4).

Reaction	Rate coefficient	Comment
1) Initiation reactions		
OH + C5H8 → CISOPA	$2.70 \times 10^{-11} \exp(390/T) * 0.288$	(a),(b),(c)
OH + C5H8 → TISOPA	$2.70 \times 10^{-11} \exp(390/T) * 0.288$	(a),(b),(c)
OH + C5H8 → CISOPC	$2.70 \times 10^{-11} \exp(390/T) * 0.238$	(a),(b),(c)
OH + C5H8 → TISOPC	$2.70 \times 10^{-11} \exp(390/T) * 0.102$	(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	$3.50 \times 10^{-12} * [O_2]$	(e)
CISOPAO2 → CISOPA (+O ₂)	$5.22 \times 10^{15} \exp(-9838/T)$	(e)
CISOPA (+O ₂) → ISOPBO2	$3.00 \times 10^{-12} * [O_2]$	(e)
ISOPBO2 → CISOPA (+O ₂)	$8.62 \times 10^{15} \exp(-11322/T)$	(e)
TISOPA (+O ₂) → ISOPAO2	$2.50 \times 10^{-12} \exp(-480/T) * [O_2]$	(e)
ISOPAO2 → TISOPA (+O ₂)	$2.86 \times 10^{14} \exp(-9028/T)$	(e)
TISOPA (+O ₂) → ISOPBO2	$3.00 \times 10^{-12} * [O_2]$	(e)
ISOPBO2 → TISOPA (+O ₂)	$8.55 \times 10^{15} \exp(-10743/T)$	(e)
CISOPC (+O ₂) → CISOPCO2	$2.00 \times 10^{-12} * [O_2]$	(e)
CISOPCO2 → CISOPC (+O ₂)	$3.06 \times 10^{15} \exp(-10254/T)$	(e)
CISOPC (+O ₂) → ISOPDO2	$3.50 \times 10^{-12} * [O_2]$	(e)
ISOPDO2 → CISOPC (+O ₂)	$1.05 \times 10^{16} \exp(-11705/T)$	(e)
TISOPC (+O ₂) → ISOPCO2	$2.50 \times 10^{-12} \exp(-480/T) * [O_2]$	(e)
ISOPCO2 → TISOPC (+O ₂)	$2.13 \times 10^{14} \exp(-9984/T)$	(e)
TISOPC (+O ₂) → ISOPDO2	$3.50 \times 10^{-12} * [O_2]$	(e)
ISOPDO2 → TISOPC (+O ₂)	$1.05 \times 10^{16} \exp(-11569/T)$	(e)
3) Peroxy radical + NO reactions		
CISOPAO2 + NO = CISOPAO + NO2	KRO2NO*0.913	(f),(g)
CISOPAO2 + NO = ISOPANO3	KRO2NO*0.087	(f),(g)
ISOPAO2 + NO = ISOPAO + NO2	KRO2NO*0.913	(f),(g)

ISOPAO2 + NO = ISOPANO3	KRO2NO*0.087	(f),(g)
ISOPBO2 + NO = ISOPBO + NO2	KRO2NO*0.896	(f),(g)
ISOPBO2 + NO = ISOPBNO3	KRO2NO*0.104	(f),(g)
CISOPCO2 + NO = CISOPCO + NO2	KRO2NO*0.913	(f),(g)
CISOPCO2 + NO = ISOPCNO3	KRO2NO*0.087	(f),(g)
ISOPCO2 + NO = CISOPCO + NO2	KRO2NO*0.913	(f),(g)
ISOPCO2 + NO = ISOPCNO3	KRO2NO*0.087	(f),(g)
ISOPDO2 + NO = ISOPDO + NO2	KRO2NO*0.896	(f),(g)
ISOPDO2 + NO = ISOPDNO3	KRO2NO*0.104	(f),(g)
ISOP34O2 + NO = ISOP34O + NO2	KRO2NO*0.913	(f),(g)
ISOP34O2 + NO = ISOP34NO3	KRO2NO*0.087	(f),(g)
C524O2 + NO = C524O + NO2	KRO2NO*0.896	(f),(h)
C524O2 + NO = C524NO3	KRO2NO*0.104	(f),(h)
C526O2 + NO = C526O + NO2	KRO2NO*0.935	(f),(i)
C526O2 + NO = C526NO3	KRO2NO*0.065	(f),(i)
C527O2 + NO = C527O + NO2	KRO2NO*0.935	(f),(j)
C527O2 + NO = C527NO3	KRO2NO*0.065	(f),(j)
C536O2 + NO = C536O + NO2	KRO2NO	(f)
C537O2 + NO = C537O + NO2	KRO2NO	(f)
4) Peroxy radical isomerisation reactions		
CISOPAO2 (+O ₂) = C5HPALD1 + HO2	$8.14 \times 10^9 \exp(-8591/T) \cdot \exp(10^8/T^3) \cdot 0.5$	(k)
CISOPAO2 = C536O2	$8.14 \times 10^9 \exp(-8591/T) \cdot \exp(10^8/T^3) \cdot 0.5$	(k)
CISOPCO2 (+O ₂) = C5HPALD2 + HO2	$2.20 \times 10^{10} \exp(-8174/T) \cdot \exp(10^8/T^3) \cdot 0.5$	(k)
CISOPCO2 = C537O2	$2.20 \times 10^{10} \exp(-8174/T) \cdot \exp(10^8/T^3) \cdot 0.5$	(k)
ISOPBO2 = MVK + HCHO + OH	$1.04 \times 10^{11} \exp(-9746/T)$	(l)
ISOPDO2 = MACR + HCHO + OH	$1.88 \times 10^{11} \exp(-9752/T)$	(l)
C524O2 = HMAKR + HCHO + OH	$1.88 \times 10^{11} \exp(-9752/T)$	(h),(l)
C526O2 = HMKVBOOH + CO + OH	K14ISOM1	(m)
C527O2 = MACROOH + CO + OH	K14ISOM1	(m)
C536O2 = DHPMEK + CO + OH	K14ISOM1	(m)
C537O2 = DHPMPAL + CO + OH	K14ISOM1	(m)
5) Oxy radical reactions		
CISOPAO (+O ₂ , -H ₂ O) = M3F + HO2	KDEC*0.18	(n),(o)
CISOPAO (+O ₂) = C526O2	KDEC*0.19	(n),(p)
CISOPAO (+O ₂) = HC4CCHO + HO2	KDEC*0.63	(n),(q)
ISOPAO (+O ₂) = C524O2	KDEC	(n)
ISOPBO (+O ₂) = MVK + HCHO + HO2	KDEC	(n)

CISOPCO (+O ₂ , -H ₂ O) = M3F + HO2	KDEC*0.18	(n),(o)
CISOPCO (+O ₂) = C527O2	KDEC*0.30	(n),(p)
CISOPCO (+O ₂) = HC4ACHO + HO2	KDEC*0.52	(n),(q)
ISOPDO (+O ₂) = MACR + HCHO + HO2	KDEC	(n)
ISOP34O (+O ₂) = MACR + HCHO + HO2	KDEC	(n)
C524O (+O ₂) = HMACR + HCHO + HO2	KDEC	(n)
C526O = MGLYOX + HOCH2CHO + OH	KDEC	(n)
C527O = GLYOX + ACETOL + OH	KDEC	(n)
C536O = MGLYOX + HCOCH2OOH + OH	KDEC	(n)
C537O = GLYOX + HYPERACET + OH	KDEC	(n)

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) As recommended in the review comment of Peeters (2015), kinetic parameters applied to the O₂ addition and peroxy radical back decomposition reactions are based on those calculated by Peeters et al. (2014), but with each increased by a factor of five on the basis of the experimental characterisation of the equilibration of peroxy radicals in each subset, as reported in preliminary form by Crounse et al. (2014); (f) Generic rate coefficient KRO2NO ($= 2.70 \times 10^{-12} \exp(360/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) based on an average of reported data for $\geq \text{C}_2$ alkyl, hydroxyalkyl, hydroxyalkenyl, oxoalkyl and hydroxyoxyalkyl RO₂ radicals, which display no significant structural dependence; (g) Branching ratio to nitrate formation assumed equivalent for secondary and tertiary hydroxyperoxy radicals, with that for primary hydroxyperoxy radicals 20 % lower. Absolute values scaled to provide an optimised first-generation nitrate yield of 10 % (see Sects. 2.1.2 and 2.1.4 of main paper); (h) Assumed equivalent to ISOPDO2 parameter; (i) Assumed equivalent to C527O2 parameter; (j) Based on Saunders et al. (2003); (k) Based on expressions reported by Peeters et al. (2014), 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); (l) Based on expressions reported by Peeters et al. (2014); (m) Generic rate coefficient K14ISOM1 ($= 3.00 \times 10^7 \exp(-5300/T) \text{ s}^{-1}$) based on expression reported for MACRO2 by Crounse et al. (2012), and assigned by analogy to structurally-similar α -formyl peroxy radicals; (n) Generic rate coefficient KDEC (usually assigned a value of $1 \times 10^6 \text{ s}^{-1}$) 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; (o) Branching ratio optimised on the basis of reported yields for 3-methylfuran (M3F) (see Table S2); (p) Branching ratio optimised to provide yields of glyoxal/hydroxyacetone or methylglyoxal/glycolaldehyde of 2.5 % at the high [NO] limit, in broad agreement with reported yields (see Table S2); (q) Branching ratio optimised on the basis of reported yields for C₅ hydroxycarbonyls (see Table S2).

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 v3.3.1 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] < 300 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. (2015)	<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 v3.3.1	61.0	34.1	23.6	4.2	13.6	3.3	6.2	2.5	2.5	2.5	10.0

Table S3. Generic rate coefficients updated or newly defined in MCM v3.2 and MCM v3.3.1.

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)
K14ISOM1	$3.00 \times 10^7 \exp(-5300/T) \text{ s}^{-1}$	(f)
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 $\geq \text{C}_2$ 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 E/R values within this group, which are limited to $\text{C}_2\text{H}_5\text{O}_2$, $n\text{-C}_3\text{H}_7\text{O}_2$ and $i\text{-C}_3\text{H}_7\text{O}_2$. 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 $\text{CH}_3\text{C(O)O}_2$ (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 $\text{C}_2\text{H}_5\text{O}_2$ (http://iupac.pole-ether.fr/); (b) 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 $\text{CH}_3\text{C(O)O}_2$ (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 ($\text{CH}_3\text{C(O)OONO}_2$) (http://iupac.pole-ether.fr/); (f) 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 v3.3.1.		

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

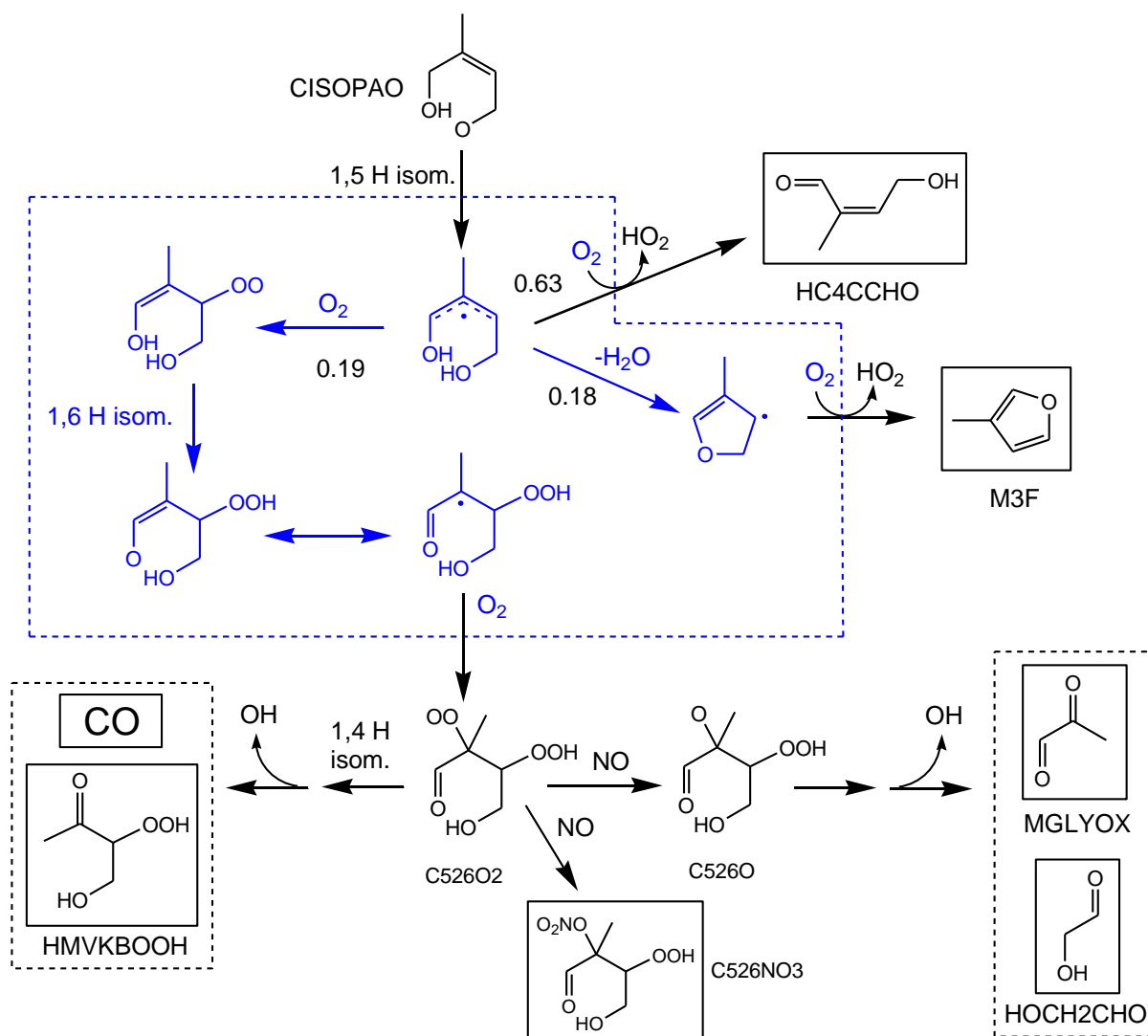


Fig. S1. Chemistry of CISOPAO initiated by 1,5 H atom shift isomerisation, leading to the products represented in MCM v3.3.1 (see Sect. S1.2). The chemistry in the blue box is not explicitly included in the mechanism, but is shown to illustrate the routes to the corresponding products. For clarity, the reactions of C526O2 with NO₃, HO₂ and the peroxy radical pool are not shown, but are represented in MCM v3.3.1.

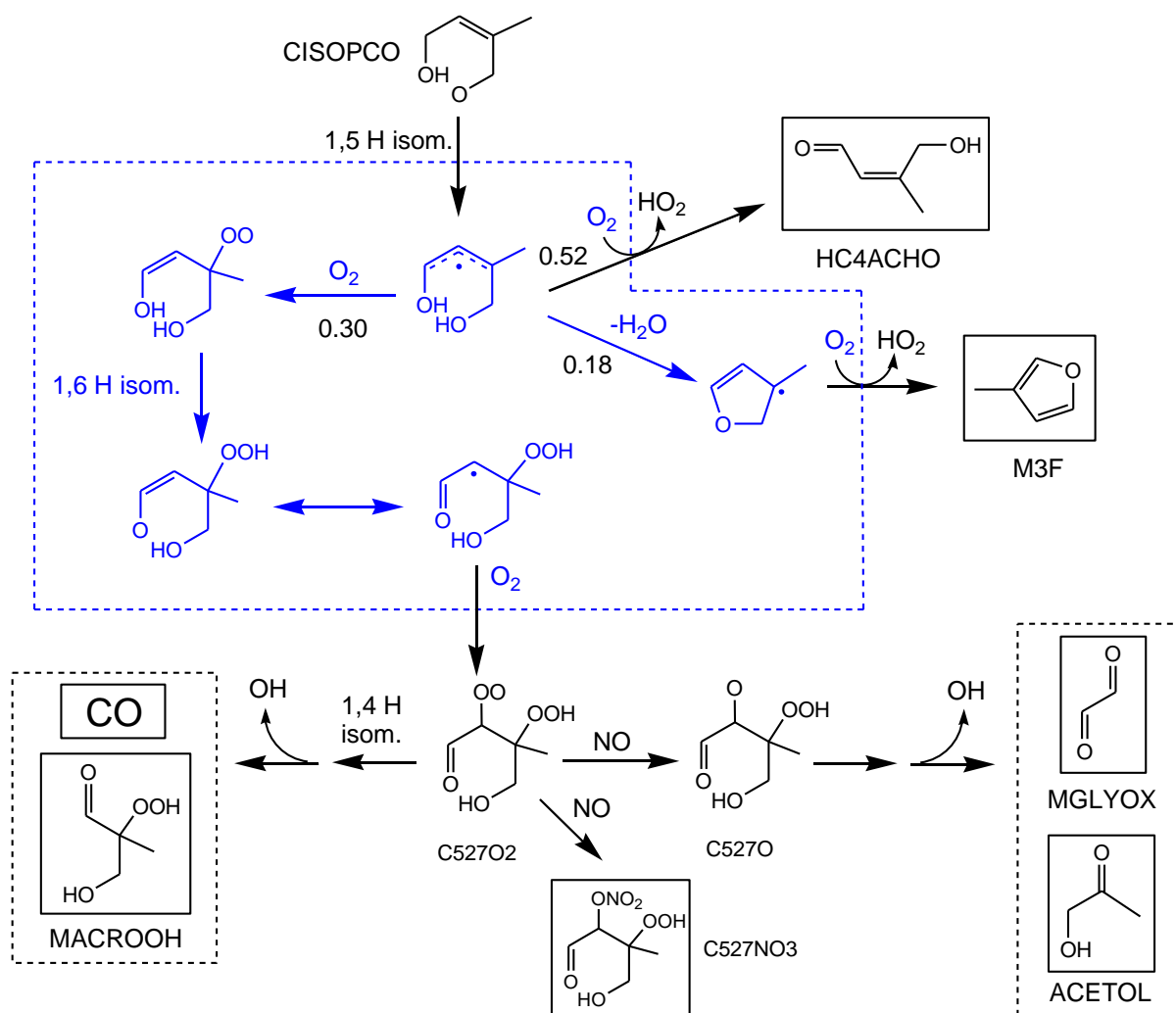


Fig. S2. Chemistry of CISOPCO initiated by 1,5 H atom shift isomerisation, leading to the products represented in MCM v3.3.1 (see Sect. S1.2). The chemistry in the blue box is not explicitly included in the mechanism, but is shown to illustrate the routes to the corresponding products. For clarity, the reactions of C527O2 with NO₃, HO₂ and the peroxy radical pool are not shown, but are represented in MCM v3.3.1.

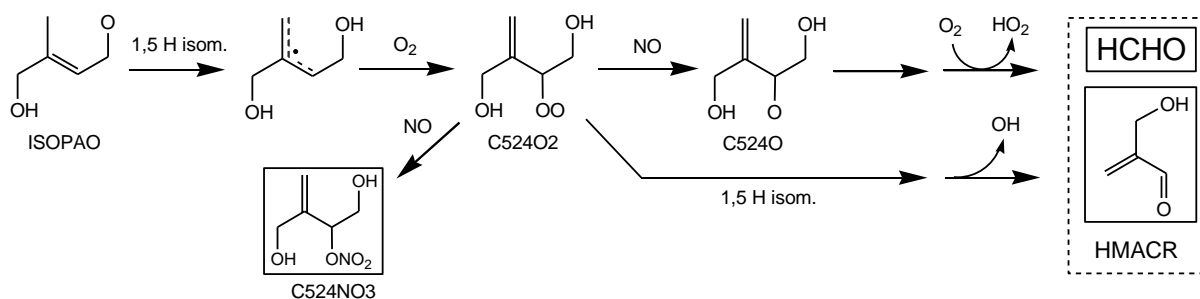


Fig. S3. Chemistry of ISOPAO initiated by 1,5 H atom shift isomerisation, leading to the formation of HMACR in MCM v3.3.1 (see Sect. S1.3). For clarity, the reactions of C524O2 with NO₃, HO₂ and the peroxy radical pool are not shown, but are represented in MCM v3.3.1.

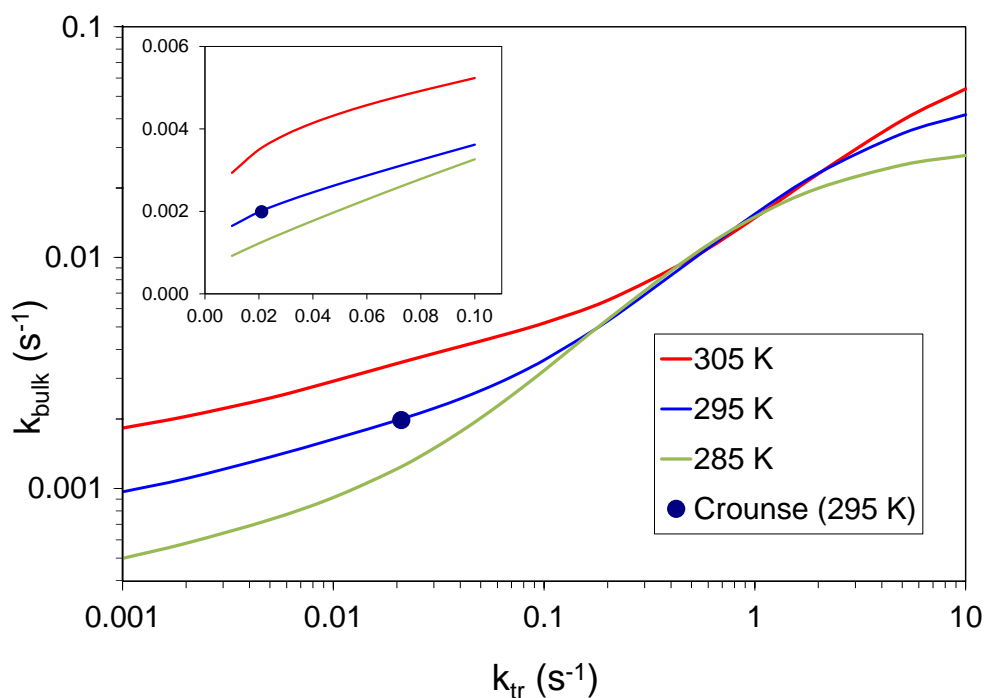


Fig. S4. Variation of the phenomenological bulk isomerisation rate to form C5HPALD1 and C5HPALD2 (k_{bulk}) with the peroxy radical loss rate through “traditional” bimolecular reactions (k_{tr}), as calculated with the optimised MCM v3.3.1 scheme at 285 K, 295 K and 305 K. The 295 K measurement reported 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).

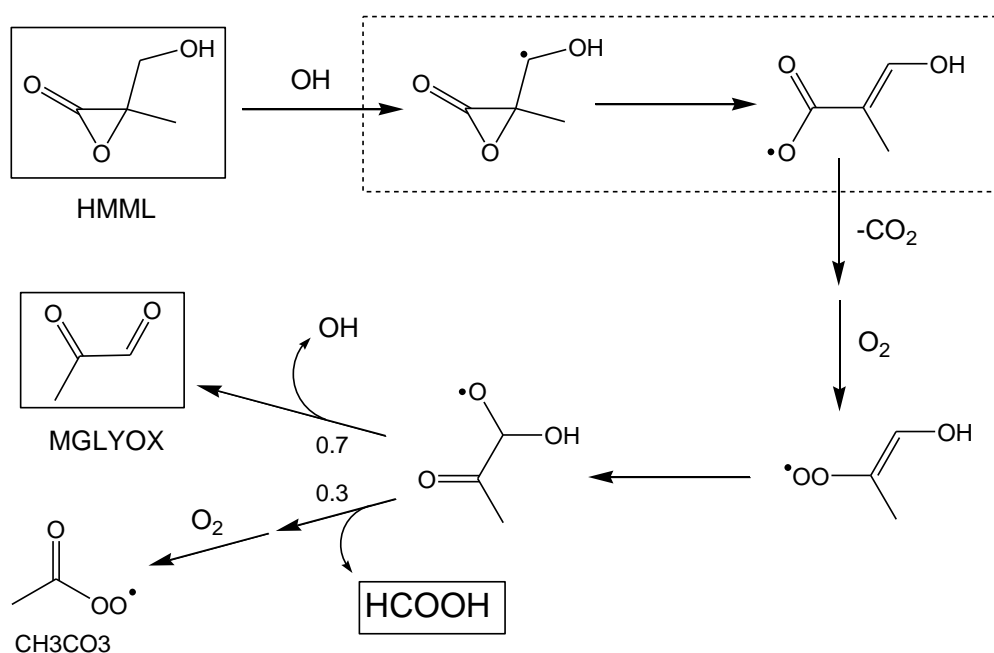


Fig. S5. Overview of the gas phase OH-initiated degradation chemistry of hydroxymethyl-methyl- α -lactone (HMML), as represented in MCM v3.3.1 .