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Impacts of mechanistic changes on HO_x formation and recycling in the oxidation of isoprene

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Abstract

Recently reported model-measurement discrepancies for the concentrations of the HO_x radical species (OH and HO₂) in locations characterized by high emission rates of isoprene have indicated possible deficiencies in the representation of OH recycling and formation in isoprene mechanisms currently employed in numerical models; particularly at low levels of NO_x. Using version 3.1 of the Master Chemical Mechanism (MCM v3.1) as a base mechanism, the sensitivity of the system to a number of detailed mechanistic changes is examined for a wide range of NO_x levels, using a simple box model. These studies place emphasis on processes for which experimental or theoretical ev-

- ¹⁰ idence has been reported in the peer-reviewed literature, in addition to examining the impact of an intrinsic simplification in the MCM v3.1 chemistry. Although all the considered mechanistic changes lead to simulated increases in the concentrations of OH at low NO_x levels, the greatest impact is achieved by implementation of a recently postulated mechanism involving isomerisation of the δ -hydroxyalkenyl peroxy radical
- ¹⁵ isomers, formed from the sequential addition of OH and O₂ to isoprene. In conjunction with necessary rapid photolysis of the resultant hydroperoxyaldehyde products, this mechanism yields approximately a factor of three increase in the simulated OH concentration at low NO_x, and is the only considered mechanism which achieves enhancements which approach those necessary to explain the reported model-measurement
- discrepancies. Combination of all the considered mechanistic changes has an effect which is approximately additive, yielding an overall enhancement of about a factor of 3.2 in the simulated OH concentration at the lowest NO_x input rate considered, with the simulated mean NO_x mixing ratios at this input rate being 42 ppt and 29 ppt with the base case and modified mechanisms respectively.
- ²⁵ A parameterized representation of the mechanistic changes is optimized and implemented into a reduced variant of the Common Representative Intermediates mechanism (CRI v2-R5), for use in the STOCHEM global chemistry-transport model. The impacts of the modified chemistry in the global model are shown to be consistent

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with those observed in the box model sensitivity studies, and the results are illustrated and discussed with a particular focus on the tropical forested regions of the Amazon and Borneo where unexpectedly elevated concentrations of OH have recently been reported.

5 1 Introduction

The role of the hydroxyl radical (OH) as initiator in the degradation of volatile organic compounds (VOCs) in the troposphere has been well established for several decades and has led to the species being termed the atmospheric "cleanser" (Heard and Pilling, 2003). In the presence of nitrogen oxides ($NO_x = NO + NO_2$) it has long been recognized that the reactions of OH with VOCs can initiate rapid sequences of reactions, in which organic peroxy radicals (RO_2), oxy radicals (RO) and the hydroperoxy radical (HO_2) can act as chain propagating species, leading to the regeneration of OH (e.g., Lightfoot et al., 1992; Jenkin and Clemitshaw, 2000). The reactions of RO_2 and HO_2 with NO play a key role in these catalytic cycles, since the associated oxidation of NO 15 to NO_2 leads to the formation of ozone following the subsequent photolysis of NO_2 :

$$RO_2 + NO \rightarrow RO + NO_2$$
 (R1)

 $HO_2 + NO \rightarrow OH + NO_2$

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In the absence of high levels of NO_x , the reactions of RO_2 with HO_2 have generally been accepted to play an important role in traditional understanding of the chemistry of VOC oxidation, leading to chain termination and a general suppression of the concentrations of the free radical species:

 $RO_2 + HO_2 \rightarrow ROOH + O_2$

However, recent direct measurements of OH and HO_2 (collectively referred to as $HO_x)$ over the Amazonian rainforest (Lelieveld et al., 2008) and the tropical forests

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(R2)

(R3)

of Borneo (Pugh et al., 2010) have suggested that, in the absence of high levels of NO_x there must be an unknown recycling mechanism for OH, as the current chemistry employed in numerical model studies cannot reproduce the measurements. Moreover, these findings are not just limited to the tropics. One can see that a clear pattern arises of model understimation for OH that is linked primarily with the as leasting of incorrect.

⁵ of model underestimation for OH that is linked primarily with the co-location of isoprene emissions (Martinez et al., 2003; Ren et al., 2008; Tan et al., 2001).

This issue has recently been addressed in the global modelling study of Butler et al. (2008) and constrained box modelling study of Kubistin et al. (2008), which have shown that model-measurement discrepancies related to the GABRIEL campaign over

- ¹⁰ the Amazonian rainforest can be reconciled by artificially increasing the extent of OH recycling at low NO_x, through a parametric adjustment to Reaction (R3) for isoprenederived RO₂ radicals, in which *n* molecules of OH are added to the reaction products. Optimised values of n = 2 and n = 3.2 were reported by Butler et al. (2008) and Kubistin et al. (2008), respectively. Although the representation is artificial, some support derives from the results of a number of recent laboratory studies, which have demon-
- strated that selected oxygenated RO_2 radicals possess radical-propagating channels for their reactions with HO_2 . (Hasson et al., 2004; Jenkin et al., 2007, 2008a, 2010; Dillon and Crowley, 2008).

Kubistin et al. (2008) also examined whether this conclusion could be explained by a variety of novel (but related) chemical pathways, including enhanced photolysis of the organic hydroperoxide (ROOH) products and competitive photolysis of the RO₂ radicals themselves, but no single chemically feasible pathway was found. However, a very recent theoretical study of Peeters et al. (2009) has highlighted that some of the isomeric isoprene-derived RO₂ radicals can potentially undergo unimolecular isomerisation re-

²⁵ actions that are estimated to be competitive with the bimolecular reactions, such as Reaction (R3), which are usually considered to dominate under low NO_x conditions. In conjunction with the resultant production of particularly photolabile unsaturated hydroperoxyaldehyde products, Peeters et al. (2009) postulated that this chemistry could be a major factor in reconciling the reported model-measurement discrepancies.

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The aim of this paper is to address the impacts of chemical mechanistic changes on the formation and recycling of HO_x during the oxidation of isoprene. The paper is split into two parts, with the first part being dedicated to investigating the fine details of this chemical system over a wide range of NO_v levels, using sensitivity tests involving the Master Chemical Mechanism version 3.1 (MCM v3.1) and a simple box model. 5 MCM v3.1 provides an explicit reaction framework of elementary reactions (described in Sect. 2), which is ideally suited as a benchmark for testing detailed mechanistic changes. It was also applied in the studies of Lelieveld et al. (2008), Butler et al. (2008) and Kubistin et al. (2008) either directly, or by virtue of being the reference mechanism from which version 2 of the Mainz Isoprene Mechanism (MIM2) was developed and 10 optimized (Tarborrelli et al., 2009). The close agreement of the performance of MIM2 and MCM v3.1 has also been confirmed for a wide range of NO, levels in the recent isoprene mechanism intercomparison of Archibald et al. (2009), using the same box model as applied in the present study. Consequently the results of the sensitivity tests reported here can be compared directly with the magnitude of the model-measurement 15 discrepancies reported for HO_x previously (Lelieveld et al., 2008; Butler et al. 2008; Kubistin et al., 2008). The sensitivity tests place emphasis on processes for which

experimental or theoretical evidence has been reported in the peer-reviewed literature, in addition to examining the impact of an intrinsic strategic simplification in the MCM v3.1 chemistry.

In the second part of the paper, a parameterized representation of the mechanistic changes is optimized and implemented into a reduced variant of the Common Representative Intermediates mechanism (CRI v2-R5), for use in the STOCHEM global chemistry-transport model, and the potential global impacts are illustrated and discussed.

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2 Chemistry of isoprene degradation in MCM v3.1

The complete degradation chemistry of isoprene, as represented in MCM v3.1, consists of 605 reactions of 201 species. The chemistry can be viewed and downloaded using the subset mechanism assembling facility, available as part of the MCM website

- ⁵ (http://mcm.leeds.ac.uk/MCM). The methodology of mechanism construction has been described in detail by Jenkin et al. (1997) and Saunders et al. (2003). Although the chemistry initiated by reaction with OH, O₃ and NO₃ is represented, the OH-initiated degradation tends to dominate under atmospheric conditions, and this chemistry is therefore the focus of the ensuing description.
- ¹⁰ The main features of the OH-initiated degradation chemistry to first generation products when NO_x is present are summarized in Fig. 1. This demonstrates that oxidation of isoprene in MCM v3.1 proceeds by sequential addition of OH and O₂ leading to the initial formation of four isomeric hydroxyl-substituted peroxy radicals (RO₂). These are formed from the initial addition of OH to the terminal carbon atoms (i.e., positions 1
- and 4), which is estimated to account for 90% of the reaction, based on the structurereactivity method described by Peeters et al. (1994), as applied with the MCM. The other 10% is estimated to proceed via addition to the internal carbon atoms. These minor channels are not represented in MCM v3.1, the branching ratios for addition of OH at positions 1 and 4 being scaled pro rata.

The relative importance of initial OH addition at positions 1 and 4 is also based on the structure-reactivity method of Peeters et al. (1994). In each case this leads to formation of an organic radical possessing an allyl resonance, such that the subsequent addition of O₂ can occur at two positions. As described by Saunders et al. (2003), addition of O₂ at the more substituted site is assumed to be favoured in each case, and is assigned a probability of 75%, leading to the initial distribution of the RO₂ radicals shown in Fig. 1.

The subsequent chemistry in the presence of NO_x leads predominantly to the formation of carbonyl products, as a result of chemistry propagated by reactions of peroxy (RO₂) and oxy (RO) radical intermediates. For example, the initial oxidation sequence

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involving ISOPDO2 proceeds via the following catalytic cycle (see Fig. 1 for species identities):

 $OH + isoprene(+O_2) \rightarrow ISOPDO2$ (R4)

$$ISOPDO2 + NO \rightarrow ISOPDO + NO_2$$
 (R5a)

$$5 \text{ ISOPDO} \rightarrow \text{MACR}(\text{methacrolein}) + \text{CH}_2\text{OH}$$
(R6)

$$CH_2OH + O_2 \rightarrow HCHO + HO_2$$

The peroxy radicals (RO_2 and HO_2) thus provide the coupling with the chemistry of NO_x , which leads to NO-to- NO_2 conversion, and formation of O_3 upon photolysis of NO_2 :

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$$NO_2 + hv \rightarrow NO + O(^{3}P)$$

 $O(^{3}P) + O_{2}(+M) \rightarrow O_{3}(+M)$

The subsequently-formed oxy radicals determine the identities of the carbonyl products generated from the degradation. In MCM v3.1, the β -hydroxyalkenyloxy radicals ISOPBO and ISOPDO are assumed to undergo exclusive C-C bond scission, leading to the formation of HCHO and the well-established C₄ carbonyl products, methacrolein (MACR), methylvinyl ketone (MVK), resulting in respective molar yields of about 68%, 22% and 34% from the NO_x-propagated chemistry, in good agreement with those reported in the literature (e.g., Calvert et al., 2000; and references therein). On the basis of the results of Ruppert et al. (2000) and Yu et al. (1995), a minor decomposition channel is also included for ISOPBO, leading to the formation of hydroxymethylvinyl ketone (MVKOH) with a molar yield of about 11%, as shown in Fig. 1, although it is noted that this process is not supported by the results of Benkelberg et al. (2000).

The δ -hydroxyalkenyloxy radicals, ISOPAO and ISOPCO, are assumed to generate the closely-related C₅ hydroxycarbonyl products 4-hydroxy-2-methyl-but-2-enal

(R7)

(R8)

(R9)



(HC4CCHO) and 4-hydroxy-3-methyl-but-2-enal (HC4ACHO), which have also been reported in the literature (Calvert et al., 2000; Baker et al., 2005). In MCM v3.1, this is assumed to occur in each case via a 1,5-H atom shift isomerisation, followed by reaction of the resulting α -hydroxy organic radical with O₂, in agreement with the appraisals

- ⁵ of Zhao et al. (2003) and Park et al. (2004). It should be noted that the same products would be formed (albeit from the alternative oxy radical) if ISOPAO and ISOPCO reacted directly with O_2 . As shown in Fig. 1, the resultant total molar yield of C_5 hydroxycarbonyl products from the NO_x -propagated chemistry is about 22%, in reasonable agreement with that reported (Calvert et al., 2000; Baker et al., 2005).
- ¹⁰ The chemistry discussed above, and represented in Reactions (R2) and (R4)–(R7), consists entirely of propagation reactions which conserve the radical population. Although that chemistry dominates when NO_x is present, some radical removal occurs as a result of the alternative terminating channels for the reactions of the peroxy radicals with NO, which form the corresponding organic nitrate product, e.g.:
- 15 ISOPDO2 + NO \rightarrow ISOPDNO₃

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As indicated by the total nitrate product yields shown in Fig. 1, the weighted average branching ratio, $k_{5b}/(k_{5a}+k_{5b})$ for first generation nitrate product formation in MCM v3.1 is assigned a value of 10%, based on a consensus of reported yields (e.g., see Pinho et al., 2005), such that the suite of oxy radicals (ISOPAO, ISOPBO, ISOPCO and ISOPDO) is formed from the propagating chemistry with a yield of 90%.

The OH-initiated degradation chemistry to first generation products when NO_x is absent, as represented in MCM v3.1, is summarized in Fig. 2. Under these conditions, removal of the peroxy radicals occurs either via parameterized "permutation reactions" with the "pool" of available organic peroxy radicals (denoted "RO₂"), or via reaction with HO₂ e.g.:

 $ISOPDO2(+RO_2) \rightarrow ISOPDO(+RO+O_2)$

 \rightarrow ISOPDOH(+R_{-H}O+O₂)

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(R5b)

(R10a)

(R10b)

 \rightarrow HCOC5(+ROH+O₂)

$ISOPDO2 + HO_2 \rightarrow ISOPDOOH + O_2$

Of these reactions only Reaction (R10a) is propagating, such that the formation of the suite of oxy radicals (ISOPAO, ISOPBO, ISOPCO and ISOPDO) is substantially reduced to a total yield of less than 50% (see Fig. 2); with the balance mainly due to 5 the formation of the hydroperoxide products, in particular ISOPBOOH. It should also be noted that the conditions considered here are representative of laboratory studies which have traditionally been applied to study isoprene degradation, in which HO_2 is formed only as a secondary radical in the system following further reactions of oxy radicals, e.g., from ISOPDO (formed in Reaction R10a) via Reactions (R6) and (R7). 10 The product yields displayed for the carbonyl, hydroperoxide and alcohol products in Fig. 2 thus represent such conditions, and generally agree well with those reported (e.g., Ruppert et al., 2000; Benkelberg et al., 2000; Lee et al., 2005). Under atmospheric conditions, the reactions of the peroxy radicals with HO₂ tend to be even more significant, such that the first generation MCM v3.1 chemistry predicts substantial rad-15 ical termination through formation of hydroperoxide products. It is noted, however, that the lifetimes of the peroxy radicals with respect to reaction with HO₂ (and RO₂) can be substantial (e.g., minutes) at the low concentrations which prevail in the atmosphere,

such that unimolecular reactions can potentially become more competitive. This is 20 considered further in the sensitivity tests described below (Sect. 3.4).

As outlined by Saunders et al. (2003) and Pinho et al. (2005), the further degradation of the major C₄ and C₅ carbonyl and hydroxycarbonyl products in MCM v3.1 is treated rigorously, and leads ultimately to the generation of CO and CO₂ via a number of well-established intermediate carbonyl products, such as hydroxyacetone ²⁵ (CH₃C(O)CH₂OH), methyl glyoxal (CH₃C(O)CHO), glycolaldehyde (HOCH₂CHO), glyoxal (CH(O)CHO) and additional HCHO. In the presence of sufficient NO_x, the chemistry is propagated by catalytic cycles similar to that presented above for the first generation chemistry, with chain terminating reactions of RO₂ with HO₂ similarly becoming

(R10c)

(R11)

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competitive as levels of NO_x decrease. In MCM v3.1, these reactions are fully terminating, and currently do not reflect the results of a number of recent laboratory studies, which have demonstrated that selected oxygenated RO_2 radicals possess significant radical-propagating channels for their reactions with HO₂: (Hasson et al., 2004; Jenkin $_5$ et al., 2007; 2008a; 2010; Dillon and Crowley, 2008). This has been found to be partic-

ularly important for the acetyl peroxy radical ($CH_3C(O)O_2$), with the product channel:

 $CH_3C(O)O_2 + HO_2 \rightarrow CH_3C(O)O + OH + O_2$ (R12)

accounting for about 40–50% of the overall reaction (Hasson et al., 2004; Jenkin et al., 2007; Dillon and Crowley, 2008). In addition to CH₃C(O)O₂, the MCM v3.1
chemistry generates a number of other acyl peroxy radicals (i.e., of generic formula RC(O)O₂), the reactions of which with HO₂ are also likely to possess significant propagating channels, by analogy. These include the methacrolyl peroxy radical (formed from methacrolein), and RC(O)O₂ radicals formed from the oxidation of HC4ACHO, HC4CCHO and HOCH₂CHO. This issue is considered further in the sensitivity tests
described below (Sect. 3.2).

As part of a systematic strategy to limit the size of the MCM, a simplified treatment is applied to the degradation of products which are formed exclusively from the reactions of RO₂ with HO₂ and with the peroxy radical pool (Jenkin et al., 1997; Saunders et al., 2003). As indicated above, hydroperoxides formed from the reactions of RO₂ with HO₂ are predicted to play a significant role in isoprene oxidation at low NO_x levels, and it is timely to examine the impact of the applied simplifications. For primary and secondary hydroperoxides, two representative channels are considered by analogy with the reaction of OH with CH₃OOH:

 $OH + ROOH \rightarrow RO_2 + H_2O$ (R13a)

 $_{25} \rightarrow R_{-H}O + OH + H_2O$ (R13b)

Reaction (R13a) is explicit representation of abstraction of the hydroperoxyl H atom, whereas Reaction (R13b), forming the corresponding carbonyl product and OH (via re-





moval of a hydrogen atom from the carbon α to the -OOH) is used to represent attack of OH at the organic group. The latter channel is invoked because the carbonyl product (R_{-H} O) is invariably already represented in the mechanism, such that no further expansion in mechanism size is required. If the total rate of attack at the organic group (by all possible pathways) is estimated to exceed the rate of channel (R13a) by more than an order of magnitude (which is the case for all the isoprene-derived hydroperoxides), Reaction (R13b) is used to represent the entire reaction, with the rate set on the basis of the total estimated reactivity. Consequently, the reactions of OH with the primary and secondary hydroperoxides ISOPAOOH, ISOPCOOH and ISOPDOOH are represented as follows:

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 $OH+ISOPAOOH \rightarrow HC4ACHO+OH+H_2O$ $OH+ISOPCOOH \rightarrow HC4CCHO+OH+H_2O$ $OH+ISOPDOOH \rightarrow HCOC5+OH+H_2O$ (R14) (R15) (R16)

These reactions thus lead to prompt quantitative regeneration of OH. In practice, a ¹⁵more rigorous application of the existing MCM protocol (i.e., not implementing the simplifications applied to hydroperoxide species) would partially generate products which retain the hydroperoxy groups. However, it is likely that further (rapid) reactions of these species would lead to delayed OH regeneration such that the currently applied representation is a reasonable compromise. It is also noted that the very recent study

of Paulot et al. (2009) has reported strong experimental evidence for prompt, quantitative OH regeneration as part of an OH-catalysed conversion of the hydroperoxides to isomeric dihydroxyepoxides. That mechanism therefore has the same direct (neutral) impact on OH, as the mechanism currently applied to the degradation of ISOPAOOH, ISOPCOOH and ISOPDOOH in MCM v3.1.

For tertiary hydroperoxides, however, it is not possible to represent the reaction by Reaction (R13b), owing to the absence of a hydrogen atom on the carbon atom α to the -OOH group. As a result, the entire reaction for all tertiary hydroperoxides in MCM v3.1



is represented by the minor channel type (Reaction R13a), with rate set on the basis of the total estimated reactivity. This is therefore the case for the major hydroperoxide, ISOPBOOH, formed in MCM v3.1, for which the reaction is thus represented as follows:

5 $OH+ISOBOOH \rightarrow ISOBO2+H_2O$

This representation is clearly a much greater simplification than those applied to the other isoprene-derived hydroperoxides, which artificially increases the lifetime of the ISOPBO2/ISOPBOOH pair, which are interconverted in conjunction with HO_x destruction. The impact of including a more rigorous representation of the reaction is therefore considered further in the sensitivity tests described below (Sect. 3.3).

3 Box model sensitivity tests using MCM v3.1

3.1 Model set-up and base case simulations

For the mechanistic sensitivity experiments, a 0-D box model using the FACSIMILE kinetics software was applied, as described fully in the recent isoprene mechanism intercomparison of Archibald et al. (2009). The model was designed to simulate a 15 well mixed 1000 m boundary layer, with input parameters representative of tropical regions (Longitude 0.0°, Latitude 3.3°S). Initial mixing ratios of long lived gases were set to concentrations relevant to the tropics: 1.7 ppm CH_4 , 100 ppb CO, 30 ppb O₃ and 2 ppb HCHO. The box received emissions of NO and isoprene, which were maintained throughout the model runs. The isoprene emissions were prescribed to vary with tem-20 perature and light intensity (Guenther et al., 1995), with an average emission rate of 1.6×10^{12} molecule cm⁻² s⁻¹. The NO emission rate was held constant throughout the model runs, using a series of rates over the range from 5.0×10^9 molecule cm⁻² s⁻¹ to 1.0×10^{12} molecule cm⁻² s⁻¹. Photolysis coefficients were calculated assuming clear sky conditions, using a parameterization previously applied with the MCM (Jenkin et 25

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(R17)

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al., 1997; Saunders et al., 2003), and dry and wet deposition were switched off for all runs. By not including deposition the results are slightly less comparable to observations but the results can be more easily interpreted in relation to the mechanistic changes.

- One of the important findings of the mechanism intercomparison of Archibald et al. (2009) was that, at the lowest levels of NO_x and highest levels of isoprene, all the considered mechanisms simulated OH mixing ratios that were considerably smaller than measurements suggest (e.g., Lelieveld et al., 2008). In order to maintain the levels of OH consistent with those that have been observed, Archibald et al. (2009)
 included an additional dummy source of OH that was related to the light-dependent
- correction factor for isoprene emissions. In the present study, runs have specifically been carried out without this additional source, to examine whether the mechanistic adjustments are able to elevate OH concentrations towards those observed.

Figure 3 shows the results of a series of base case simulations (denoted "Mechanism ¹⁵ 0") performed with the MCM v3.1 chemistry for a selection of key species or species groupings. Similarly to Archibald et al. (2009), we present the arithmetic mean mixing ratios for the species on the second day of the box model run as a function of average NO_x mixing ratio, which covers the range from 42.3 ppt to 10.2 ppb. The simulated NO_x trends show a qualitative similarity to those presented for the same species with

²⁰ MCM v3.1 in Fig. 1 of Archibald et al. (2009) (and discussed in detail in that paper), but with the impact of not including the additional dummy source of OH in the present simulations becoming increasingly apparent towards the low end of the NO_x range. In particular, the mixing ratio for OH simulated here for the lowest input rate of NO_x $([OH] = 6.0 \times 10^{-3}$ ppt, or about 1.5×10^{5} molecule cm⁻³) is approaching an order of magnitude lower than that presented by Archibald et al. (2009), with this leading to a resultant longer lifetime and correspondingly greater mixing ratios for isoprene, which is controlled mainly by reaction with OH.

In the sections that follow, the impacts of a number of mechanistic sensitivity tests (summarized in Table 1 and Fig. 3) are presented. As indicated above, these tests

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aim to consider processes for which experimental or theoretical evidence has been reported in the peer-reviewed literature, in addition to examining the impact of an intrinsic simplification in the existing MCM v3.1 chemistry.

3.2 Implementation of radical propagating channels for RO₂ + HO₂ reactions

- ⁵ As indicated above in Sect. 2, a number of recent laboratory studies have reported that the reactions of selected oxygenated RO₂ radicals with HO₂ proceed significantly by radical-propagating channels. The MCM v3.1 isoprene chemistry was therefore updated to include such channels for the relevant classes of RO₂ radical for which experimental evidence exists.
- ¹⁰ On the basis of the results reported for the reaction of HO₂ with the acetyl peroxy radical, $CH_3C(O)O_2$ (Hasson et al., 2004; Jenkin et al., 2007; Dillon and Crowley, 2008), the reactions of HO₂ with all acyl peroxy radicals of generic formula $RC(O)O_2$ were updated to include channel (R18c),

$$RC(O)O_2 + HO_2 \rightarrow RC(O)OOH + O_2$$
(R18a)

¹⁵
$$\text{RC}(O)O_2 + \text{HO}_2 \rightarrow \text{RC}(O)OH + O_3$$
 (R18b)

 $RC(O)O_2 + HO_2 \rightarrow RC(O)O + OH + O_2$

with the branching ratios, based on the recent recommendation of the IUPAC panel for $CH_3C(O)O_2$: $k_{18a}/k_{18} = 0.41$; $k_{18b}/k_{18} = 0.15$; $k_{18c}/k_{18} = 0.44$ (http://www.iupac-kinetic. ch.cam.ac.uk/). The studies of Jenkin et al. (2008a) and Dillon and Crowley (2008) have shown that the reaction of HO₂ with the simplest β -oxo peroxy radical, $CH_3C(O)CH_2O_2$, also has a minor radical propagating channel. The reactions of HO₂ with all β -oxo peroxy radicals of generic formula RC(O)C(R'R'')O₂ were therefore also updated to include channel (R19b),

 $RC(O)C(R'R'')O_2 + HO_2 \rightarrow RC(O)C(R'R'')OOH + O_2$

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(R18c)

(R19a)



$RC(O)C(R'R'')O_2 + HO_2 \rightarrow RC(O)C(R'R'')O + OH + O_2$ (R19b)

with the branching ratios, based on the recent recommendation of the IUPAC panel for $CH_3C(O)CH_2O_2$: $k_{19a}/k_{19} = 0.85$; $k_{19b}/k_{19} = 0.15$ (http://www.iupac-kinetic.ch.cam.ac. uk/). These combined changes resulted in no new species being formed relative to the base case mechanism and only an increase of 15 in the number of reactions. The resultant mechanism is denoted Mechanism 1 (see Table 1).

The impact of using Mechanism 1, compared with the base MCM v3.1 (Mechanism 0), is shown in Fig. 3. The changes logically result in generally increased mixing ratios of OH, HO₂ and RO₂, but the effect is small. At the lowest input rate of NO_x (where the increase is greatest) the respective increases are 6.9%, 1.5% and 7.4%.

3.3 Implementation of updated chemistry for ISOPBOOH

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As described above in Sect. 2, the OH-initiated degradation of all the hydroperoxide products formed from isoprene in the first generation of degradation is simplified in accordance with protocol rules which were designed to maintain a manageable ¹⁵ representation of the intermediates in the degradation of the parent VOCs in MCM v3.1. Whereas the simplifications applied to the primary and secondary hydroperoxides quantitatively propagate OH, and are probably a reasonable compromise for those formed in the isoprene system (ISOPAOOH, ISOPCOOH and ISOPDOOH), the simplification for tertiary hydroperoxides is much more severe and may have implications

- for the representation of the degradation of the major isoprene-derived hydroperoxide, ISOPBOOH. In our update we therefore focus on this species, for which the updated chemistry is shown schematically in Fig. 4. This chemistry essentially results from a more rigorous application of existing MCM protocol rules, but without imposing the major simplifications usually applied to species possessing hydroperoxide groups.
- ²⁵ Whereas the original representation (Reaction R17) allows ISOPBOOH and the associated RO_2 radical (ISOPBO2) to be interconverted as part of an HO_x destruction cycle, the more rigorous updated chemistry leads to regeneration of OH, either directly when

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the RO₂ radicals react by propagating channels to form RO, or from the subsequent degradation of terminating products which retain the hydroperoxide group (see Fig. 4). The updated chemistry resulted in an increase of 6 species and 17 reactions relative to the base case mechanism. The resultant mechanism is denoted Mechanism 2 (see

Table 1). Although the mechanism implemented here does not precisely represent the very recent experimental results of Paulot et al. (2009), the increased OH regeneration from ISOPBOOH degradation, in conjunction with the prompt OH regeneration already represented for the other isoprene-derived hydroperoxides (see Sect. 2), is expected to have a comparable first order impact on OH concentrations to the mechanism proposed by Paulot et al. (2009).

The impact of using Mechanism 2, compared with the base MCM v3.1 (Mechanism 0), is shown in Fig. 3. Once again, only small changes in the mixing ratios of the radical species are simulated, with an increase of 4.6% for OH, and near-zero changes of -0.4% and +0.7% for HO₂ and RO₂, at the lowest NO_x input rate.

15 3.4 Implementation of isomerisation reactions for RO₂

As levels of NO_x decrease, the removal of the isoprene-derived RO₂ radicals in MCM v3.1 becomes increasingly controlled by their reactions with HO₂ (e.g., reaction (R11)), or by parameterized permutation reactions with the pool of available organic peroxy radicals (e.g., Reaction R10). The rate coefficients applied to these reactions have either been measured directly in kinetics studies, or inferred from those measured for reactions of RO₂ radicals possessing structural similarities (e.g., Jenkin et al., 1998), and the resultant assembly of reactions has been found to give a generally good description of product yields measured in the laboratory for the OH-initiated oxidation of isoprene in the absence of NO_x (e.g., Ruppert et al., 2000). It is recognised, however, that the conditions traditionally applied in laboratory studies are necessarily characterised by concentrations of peroxy radicals which are many orders of magnitude higher than

by concentrations of peroxy radicals which are many orders of magnitude higher than those in the atmosphere, to facilitate reliable quantification of products yields. As a result, the rates of bimolecular second order reactions, such as Reactions (R10) and

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(R11), are elevated relative to those of any first order processes which might be occurring, such that the product distribution can potentially be unrepresentative of the atmosphere if such first order processes exist. In this respect, Perrin et al. (1998) and Jorand et al. (2003) have reported experimental evidence for the occurrence of 1,6 H to atom shift isomerisations of δ -hydroxy peroxy radicals formed during the oxidation of pentane and hexane, leading to the formation of hydroperoxycarbonyl products, e.g. in the pentane system:

 $HOCH_{2}[CH_{2}]_{2}CH(OO)CH_{3} \rightarrow HOCH[CH_{2}]_{2}CH(OOH)CH_{3}$ (R20)

 $HOCH[CH_2]_2CH(OOH)CH_3 + O_2 \rightarrow HC(O)[CH_2]_2CH(OOH)CH_3 + HO_2$ (R21)

¹⁰ On the basis of extrapolation of higher temperature data, they reported isomerisation rates of about 0.03 s⁻¹ and 0.6 s⁻¹ for the respective shifts of H atoms from a -CH₂OH group and a -CH(OH)- group at 298 K. Should similar rates also be applicable to the isoprene-derived δ -hydroperoxyalkenyl radicals, ISOPAO2 and ISOPCO2, the reactions would potentially be competitive with those likely for their reactions with HO₂ or the peroxy radical pool. For example, in the presence of 50 ppt of HO₂, the loss coefficient for each of the isoprene-derived peroxy radicals via reaction with HO₂ in MCM v3.1 is about 0.02 s⁻¹.

The possible isomerisation of isoprene-derived peroxy radicals possessing both δ -hydroxy and β -hydroxy substituents has recently been addressed as part of the the-²⁰ oretical study of Peeters et al. (2009), who used a combination of DFT and ab initio methods to elucidate potential pathways in the isoprene OH initiated degradation that may be important for the issue of recycling HO_x. Several of the potentially significant outcomes of their study have therefore been incorporated into the MCM v3.1 (Mechanisms 3a and b). The schematic in Fig. 5 summarises the major changes which have ²⁵ been made to the base mechanism, to allow a full appraisal of the impact of the RO₂ isomerisation chemistry, based on the parameters reported by Peeters et al. (2009). These include a number of important features, which are now summarised:

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(i) a rigorous representation of the conformational isomers, to reflect that only the cis-conformers of the δ -hydroxyalkenyl peroxy radicals can potentially undergo isomerisations analogous to Reaction (R20);

- (ii) a rigorous representation of the reversibility of O_2 addition to the "allyl-type" OHisoprene adducts, which was calculated to be significant. This allows redistribution of subsets of the peroxy radical population between the various isomers under atmospheric conditions, i.e., when their lifetimes with respect to onward reaction (with NO, HO₂ and RO₂) are comparable with, or longer than, those with respect to back decomposition;
- ¹⁰ (iii) inclusion of 1,6 H atom shift isomerisation reactions for the (newly-defined) cisconformers of the δ -hydroxyalkenyl peroxy radicals, CISOPAO2 and CISOPCO2, at respective rates of 1 s⁻¹ and 8 s⁻¹ (based on the reported lower limits); followed by reaction with O₂ to yield HO₂ and a hydroperoxyaldehyde product. Peeters et al. (2009) thus calculate that these reactions are likely to be the dominant onward fates of these radicals, even at ppb levels of NO;

(iv) inclusion of 1,5 H atom shift isomerisation reactions for the β -hydroxyalkenyl peroxy radicals, ISOPBO2 and ISOPDO2 at respective rates of $4 \times 10^{-3} \, \text{s}^{-1}$ and $1.1 \times 10^{-2} \, \text{s}^{-1}$ (based on the reported lower limits); followed by a concerted decomposition to yield OH, HCHO and either MVK or MACR. Peeters et al. (2009) thus calculate that these reactions provide a partial competition to Reactions (R10) and (R11) for these radicals at low NO_x.

20

With the exception of the hydroperoxyaldehyde product (HPC4CHO), no new first generation products are generated from the above mechanistic changes. The further degradation of this compound was defined using the MCM protocol, but without imposing the major simplifications usually applied to species possessing hydroperoxide groups. It should be noted, however, that the compound as shown in Fig. 5 (4-hydroperoxy-2-methyl-cis-but-2-enal) is strictly only formed from CISOPAO2, the closely related isomer (4-hydroperoxy-3-methyl-cis-but-2-enal) being formed from CISOPCO2. Because of the probable close similarity of the degradation chemistry of

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these species, the use of a single representative was considered acceptable for the main aims of the present sensitivity study, which focus on HO_x recycling and formation. It is noted, however, that this simplification potentially does have an impact on the relative production of glyoxal and methylglyoxal, and of glycolaldehyde and hydrox-yacetone, from the subsequent degradation. The updated chemistry resulted in an

overall increase of 17 species and 75 reactions relative to the base case mechanism. The further degradation of HPC4CHO in the initial update (Mechanism 3a) is dominated by removal initiated by reaction with OH. Although removal by photolysis is also represented, this makes only a minor contribution, based on the generic pa-¹⁰ rameters applied to the photolysis of the hydroperoxide and α , β -unsaturated aldehyde (methacrolein-like) groups, which assume the chromophores are independent. However, Peeters et al. (2009) also pointed out that the combination of the relatively strongly-absorbing unsaturated aldehyde chromophore, and the weak O-O bond in the

hydroperoxide group, provides the possibility of photolysis with a unity quantum yield
 (i.e., some two orders of magnitude greater than reported for methacrolein (e.g., Raber and Moortgat, 1996; Gierczac et al., 1997), as follows:

 $HPC4CHO + h\upsilon \rightarrow HC(O)C(CH_3) = CHCH_2O + OH$

5

The impact of representing this reaction with an appropriately elevated photolysis rate was therefore also considered (Mechanism 3b).

The impact of using Mechanisms 3a and 3b, relative to the base MCM v3.1 (Mechanism 0) is shown in Fig. 3. Implementation of the isomerisation reactions without an elevated photolysis rate for HPC4CHO (Mechanism 3a) has a notable impact on the levels of OH, HO₂ and RO₂, with the effect becoming progressively larger as the NO_x input decreases. At the lowest NO_x input rate, respective changes of 27%, 52% and -33% were simulated for OH, HO₂ and RO₂. The changes for HO₂ and RO₂ mainly reflect the enhanced conversion of the latter to the former via the 1,6 H-shift isomerisation chemistry for the cis-δ-hydroxyalkenyl peroxy radicals. About half of the simulated mixing

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(R22)

ratios of NO_x for the given NO_x input rates towards the low end of the range. The NO_x increase is mainly due to a further reduced ability of the newly implemented chemistry to form oxidised organic nitrogen species (in particular, isoprene nitrates) at low NO_x. The remainder of the simulated increase in OH is mainly a result of the direct OH for-⁵ mation from the implementation of the 1,5 H atom shift isomerisation reactions for the β -hydroxyalkenyl peroxy radicals.

As shown in Fig. 3, implementation of the enhanced photolysis of HPC4CHO via Reaction (R22), in conjunction with its formation via the 1,6 H-shift isomerisation reactions of the cis- δ -hydroxyalkenyl peroxy radicals (Mechanism 3b), leads to a much increased impact on radical levels, in particular on those of OH. At the levest NO, input rate, re-

- ¹⁰ impact on radical levels, in particular on those of OH. At the lowest NO_x input rate, respective increases of 210%, 57% and 29% were simulated for OH, HO₂ and RO₂. This result further emphasises that mechanistic changes which are required to yield the enhancements in OH levels which approach those inferred from field observations require not only recycling of HO_x, but also significant net formation of OH via processes which
- are effectively chain branching; in this case through the combination of the propagating isomerisation reactions with the radical-forming photolysis Reaction (R22). This essentially allows values of n>1 in the parameterisations of Butler et al. (2008) and Kubisitin et al. (2008) to be achieved via a plausible mechanism. The increases in OH concentration of up to about 200% are also in good quantitative agreement with
- those inferred by Lelieveld et al. (2008) as required to close the model-measurement discrepancy gap, using the traceable MIM2 mechanism.

As indicated above, some experimental support for the 1,6 H-shift isomerisation reactions of the cis- δ -hydroxyalkenyl peroxy radicals comes from the reported observation of the analogous process for δ -hydroxy peroxy radicals formed during alkane oxidation (Perrin et al., 1998; Jorand et al., 2003). In addition to this, evidence for the formation of hydroperoxy-methyl-butenal isomers (represented here by HPC4CHO) in low yield (<10%) has recently been reported by Paulot et al. (2009), during photolysis of H₂O₂/isoprene/air mixtures in the Caltech environmental chamber. The conditions of their studies yielded relatively low concentrations of radicals (compared with

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many previous product studies), apparently allowing the unimolecular peroxy radical isomerisation reactions to make a contribution. A scoping simulation was therefore carried out using Mechanism 3b for the experimental conditions described by Paulot et al. (2009). The results confirm that the peroxy radical isomerisation reactions potentially make a contribution, but predict a yield of HPC4CHO of about 25-30%, which 5 is somewhat higher than reported. The simulated importance of the isomerisation reactions is potentially sensitive to variation of many of the parameters calculated by Peeters et al. (2009), including the extent to which the reversibility of the various O_2 addition reactions allows the peroxy radical population to be redistributed, and the rates of the isomerisation reactions themselves. In this respect, it is noted that da 10 Silva et al. (2010) have very recently reported 1,5 H atom shift isomerisation rates for the isoprene-derived β -hydroxyalkenyl peroxy radicals, calculated using DFT methods, which are about an order of magnitude lower than those reported by Peeters et al. (2009): although the isometrisation reactions of the δ -hydroxyalkenyl peroxy isometris

- ¹⁵ were not considered. Although a detailed appraisal of the sensitivity of the system to the uncertainties in all the relevant parameters is considered outside the scope of the present study, a further illustrative set of simulations was carried out in which the rates of the isomerisation reactions for the cis- δ -hydroxyalkenyl and β -hydroxyalkenyl peroxy radicals were all decreased by an order of magnitude (Mechanism 3c). As shown
- ²⁰ in Fig. 3, this change logically reduces the enhancement in simulated radical levels, although the effect of the added chemistry is still notable. At the lowest NO_x input rate, the respective enhancements for OH, HO_2 and RO_2 are 94%, 27% and 21%, compared with MCM v3.1 (Mechanism 0).

These mechanistic changes also have an impact on the simulated levels and distribution of the well-established first generation carbonyl products, MACR, MVK and HCHO, as shown in Fig. 6. In partial agreement with the recent appraisal of Karl et al. (2009a, b), implementation of the peroxy radical isomerisation chemistry postulated by Peeters et al. (2009) (Mechanisms 3a and 3b) tends to increase the simulated MVK/MACR ratios, and decrease the simulated (MVK+MACR)/isoprene ratios over

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the range of NO_x inputs considered. However, the level of increase in MVK/MACR, and its dependence on NO_x, apparently differs markedly from that reported by Karl et al. (2009a, b). Whereas elevated MVK/MACR ratios, up to about 6, are simulated at the high end of our considered NO_x range (10 ppb NO_x, of which about 1 ppb is NO), the ratio decreases as the NO_x input is lowered. At NO_x levels more typical of where 5 measurements have been made (1 ppb or less), ratios in the range 1-2 are simulated in good agreement with reported observations. This should be compared with the value of MVK/MACR ≈ 8 reported by Karl et al. (2009b). Although the present study is not aiming to simulate specific field campaign conditions, and this may contribute to the discrepancy, it is noted that the representation of the competition of the isomerisation 10 chemistry with other peroxy radical reactions apparently differs between the two studies. In the relevant NO_x regime, the onward reaction of the MVK and MACR precursor β -hydroxyalkenyl peroxy radicals, ISOPBO2 and ISOPDO2 respectively, has contributions from their reactions with NO, HO₂ and the peroxy radical pool (RO₂), and from the 1,5 H shift isomerisation reactions. Of these, only the reactions with HO₂ do not 15

- generate MVK or MACR. The value of the rate coefficient applied to the HO₂ reactions in the present mechanisms, 1.6×10^{-11} cm³ molecule⁻¹ s⁻¹ (at 298 K), is based on that inferred from the database for RO₂ radicals with similar substituents (Saunders et al., 2003) and agrees well with the value of $(1.74\pm0.25)\times10^{-11}$ cm³ molecule⁻¹ s⁻¹
- ²⁰ reported subsequently by Boyd et al. (2003) for isoprene-derived peroxy radicals. In contrast, Karl et al. (2009b) used a value a factor of two lower, such that the HO₂ reaction is less able to inhibit MVK formation from the slower 1,5 H shift isomerisation of ISOPBO2. In addition to this, they do not apparently represent formation of MVK and MACR from the respective reactions of ISOPBO2 and ISOPDO2 with the RO₂ radical pool, or the structural dependence of the corresponding rate coefficients
- (Jenkin et al., 1998). In the present mechanisms, the parameterised rate coefficient assigned to the reaction of the RO_2 pool with the secondary radical (ISOPDO2) is greater than that for the tertiary radical (ISOPBO2) by a factor of four, such that the former is able to supplement MACR formation to a greater extent than the latter can

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supplement MVK formation. As shown in Fig. 7, the present simulations also produce correlations of (MVK+MACR)/isoprene vs. MVK/MACR which can apparently be reconciled with the observations reported by Karl et al. (2009b). For example, the Mechanism 3a simulation with a NO_x input rate of 5.0×10^{10} molecule cm⁻² s⁻¹ yields a mean NO_x mixing ratio of about 500 ppt, and respective values of 0.46 and 1.32 for (MVK+MACR)/isoprene and MVK/MACR, which compare well with the reported values

of 0.44±0.05 and 1.34±0.10 (Karl et al., 2009b).

Karl et al. (2009b) also report that the implementation of the peroxy radical isomerisation chemistry postulated by Peeters et al. (2009) leads to a substantial inhibition in hydroxyacetone formation. It is possible, however, that the postulated rapid photolysis

hydroxyacetone formation. It is possible, however, that the postulated rapid photolysis of one of the main hydroperoxy-methyl-butenal products (4-hydroperoxy-3-methyl-cisbut-2-enal),

 $HC(O)CH = C(CH_3)CH_2OOH + hv \rightarrow HC(O)CH = C(CH_3)CH_2O + OH$

can initiate a sequence of reactions forming hydroxyacetone significantly on a comparatively short timescale (about 30 min), this comparatively prompt secondary source apparently not being represented in their simulations. A likely dominant 1,5 H shift isomerisation of the product radical, followed by addition of O₂, generates HOCH₂C(CH₃) = CHC(O)O₂ which is the cis-conformer of the MCM species HC4ACO3, a precursor to hydroxyacetone formation in MCM v3.1.

- ²⁰ In view of the results presented here, it is suggested that the chemical mechanism postulated by Peeters et al. (2009) should not be ruled out solely on the basis of the apparent distortion of carbonyl product ratios it causes, owing to the potential sensitivity of these calculated ratios to mechanistic assumptions which are independent of the isomerisation reactions and associated chemistry outlined by Peeters et al. (2009).
- ²⁵ However, that postulated chemistry clearly requires experimental verification by appropriately designed laboratory studies (i.e., under conditions of low NO_x and low RO_2 concentrations which have generally not been fully accessed in previous studies).

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(R23)

3.5 Combined impact of major changes

A further set of runs was carried out with a mechanism in which the major mechanistic changes described above in Mechanisms 1, 2 and 3b were combined (Mechanism 4). The aim here was to assess the maximum possible enhancement in HO_x levels which

⁵ can be supported by the proposed mechanistic changes. This procedure included the incorporation of radical propagating channels for the reactions of HO_2 with all newly-defined acyl peroxy and β -oxo peroxy radicals generated in Mechanism 2 and in the Mechanism 3 variants. The combined updated chemistry in Mechanism 4 resulted in an overall increase of 23 species and 96 reactions relative to the base case mecha-10 nism.

The impact of using Mechanism 4, relative to the base MCM v3.1 (Mechanism 0) is shown in Figs. 3, 6 and 7. Although the simulated effect on species mixing ratios is clearly dominated by the implementation of the RO_2 isomerisation chemistry and associated rapid photolysis of HPC4CHO, the combined influence of the changes on the radical levels is slightly more than additive. As shown in Fig. 3, respective increases of 224%, 105% and 63% were simulated for OH, HO_2 and RO_2 , relative to Mechanism 0 at the lowest NO_x input rate. The simulated daytime average NO_x mixing ratio at this input rate is 29.3 ppt.

4 Generation of a reduced representation of the mechanistic variations

To facilitate investigation of the impact of the mechanistic changes represented in the combined Mechanism 4 in chemistry-transport models, a substantially reduced representation was developed for use with version 2 of the Common Representative Intermediates mechanism (CRI v2) and its reduced variants. As described by Jenkin et al. (2008b), CRI v2 is a lumped chemistry mechanism of intermediate complexity, the performance of which is traceable to MCM v3.1. The isoprene mechanism represents a substantial reduction over that in MCMv3.1, represented by 28 species and 95 re-

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actions. It has recently been evaluated in the isoprene mechanism intercomparison of Archibald et al. (2009) and its performance was found to be in good agreement with that of MCM v3.1 over a wide range of conditions. The CRI v2 isoprene mechanism is also an unchanged component of a set of reduced, emissions-lumped CRI v2 variants (Water et al. 2008), the meet reduced of which (CRI v2 R5) has been very recently.

⁵ (Watson et al., 2008), the most reduced of which (CRI v2-R5) has been very recently implemented into a global model (Utembe et al., 2010).

The changes outlined above for Mechanism 1 were readily incorporated into the CRI v2 chemistry, the intermediate RO_2 radicals possessing acyl or β -oxo character being easily identifiable. No change was made in relation to Mechanism 2, because the set of isoprene-derived hydroperoxides is represented by a single lumped species (RU14OOH), the OH-initiated degradation of which already quantitatively regenerates OH by a process analogous to that shown above in Reactions (R14)–(R16). The most challenging adaptation relates to incorporation of the RO₂ radical isomerisations (Mechanisms 3a and b), because the complete set of isoprene-derived peroxy radicals is represented by the single lumped species, RU14O2 (as is the case for most reduced

isoprene mechanisms). Two additional reactions were added, to represent isomerisation of the β -hydroxyalkenyl RO₂ isomers (Reaction R24) and the cis- δ -hydroxyalkenyl RO₂ isomers (Reaction R25),

 $RU14O2 \rightarrow HCHO + UCARB10 + OH$

²⁰ RU14O2 \rightarrow HPUCARB12+HO₂

(here, UCARB10 is a lumped C_4 carbonyl product which represents both MVK and MACR in CRI v2, and HPUCARB12 is a newly-defined hydroperoxyaldehyde product which corresponds to HPC4CHO in the detailed mechanism). The competition of these reactions with the alternative reactions for RU14O2 (i.e., the existing reactions with NO,

²⁵ HO₂, and the peroxy radical pool) was determined by running a set of reference box model simulations using the detailed mechanism illustrated in Fig. 5 and represented in Mechanisms 3a and b. In these simulations, the NO concentration was fixed at a set of values over the range $2.46 \times 10^7 - 2.46 \times 10^{12}$ molecule cm⁻³ (1 ppt–100 ppb at 298 K

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(R24)

(R25)

and 760 Torr), and the combined formation rate of the products from each type of isomerisation reaction was quantified relative to the formation rate of products derived from the combined (pseudo-first order) reaction of all the RO₂ isomers with NO. The global first order loss rates for the RO₂ + NO reactions could then be used to define effective rate coefficents (k_{24} and k_{25}) for each type of RO₂ isomerisation reaction for the complete range of conditions. The derived values of k_{24} and k_{25} were found to vary with NO concentration because, as indicated above in Sect. 3.4, the relative population of the RO₂ isomers changes with NO_x level by virtue of the reversibility of O₂ addition. However, the variation was found to be modest at levels of NO less than about 10¹⁰ molecule cm⁻³ (i.e. when the isomerisation reactions are able to compete more significantly), such that low NO_x limiting values of $k_{24} = 4 \times 10^{-3} \text{ s}^{-1}$ and $k_{25} = 8 \times 10^{-2} \text{ s}^{-1}$ could reasonably be assigned. It is noted that the generic rate coefficient assigned to the competing reactions of the RO₂ radicals with NO in both the detailed and reduced mechanisms, $8.5 \times 10^{-12} \text{ cm}^3$ molecule⁻¹ s⁻¹ (at 298 K), agrees well with the consen-

sus of recently reported values for isoprene-derived peroxy radicals (e.g., Miller et al., 2004; Park et al., 2004).

The hydroperoxyaldehyde product, HPUCARB12, was degraded via both reaction with OH and photolysis to generate appropriate intermediates already represented in CRI v2, with the photolysis reaction generating OH as follows:

20 HPUCARB12 + $hv \rightarrow$ RU12O2 + OH

25

The co-product, RU12O2, is a lumped radical used to represent an appropriate set of species in MCM v3.1, which includes the species HC4ACO3 referred to above in Sect. 3.4. In the reduced mechanism (denoted Mechanism 4R), the photolysis rate was set to correspond to the high value applied in Mechanism 3b and in the full detailed mechanism, Mechanism 4.

As shown in Fig. 8, Mechanism 4R was found to compare well with Mechanism 4 for a set of key species, over the complete range of NO_x input rates considered in the box modelling studies. The main difference in performance is a divergence in

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(R26)

the simulated levels of NO_x with decreasing NO_x input, which derives from a slightly reduced propensity of the newly-implemented chemistry in the reduced mechanism to form oxidised organic nitrogen reservoirs. The simulated daytime average NO_x mixing ratio at the lowest NO_x input rate is about 50 ppt.

5 Global model studies

The global impacts of inclusion of HO_x formation and recycling from isoprene oxidation were investigated using an updated version of the UK Meteorological Office tropospheric chemistry transport model (STOCHEM) originally described by Collins et al. (1997). STOCHEM is a global 3-dimensional CTM which uses a Lagrangian approach to advect 50 000 air parcels using a 4th-order Runge-Kutta scheme with advection time steps of 3 hours. The transport and radiation models are driven by archived meteorological data, generated by using the U.K. Meteorological Office numerical weather prediction models as analysis fields, with a resolution of 1.25° longitude and 0.83° latitude and on 12 vertical levels extending to 100 hPa. Full details of the model version employed are given in Derwent et al. (2008), with recent updates (including implementation of the CRI v2-R5 chemistry) reported in detail by Utembe et al. (2010).

Two experiments were performed to investigate the impacts of the mechanistic revisions described above, and a base case reference run against which the results could be compared using the unmodified CRI v2-R5 chemistry (Utembe et al., 2010). In

- ²⁰ be compared using the unmodified CRI v2-R5 chemistry (Utembe et al., 2010). In each run, the model was allowed to spin up for a period of 12 months, and analysis was performed on the subsequent 12 months of data. The first sensitivity experiment (denoted Mechanism 4R) involved use of the optimised reduced mechanism described in the preceding section, which is representative of a consolidation of all the mecha-
- nistic changes and is expected to yield particularly notable impacts on simulated OH radical levels in remote areas characterised by high emission rates of isoprene. The second experiment investigated the impact of reducing the efficiency of the dominant

peroxy radical isomerisation chemistry based on the study of Peeters et al. (2009). This was achieved through reducing the peroxy radical isomerisation rates, k_{24} and k_{25} , by an order of magnitude (denoted Mechanism 4Ra), to allow comparison with the impact of the similar sensitivity test performed with the detailed mechanism (Mechanism 3c Mechanism 2b) as described in Sect. 2.4. The results of these experiments are

vs. Mechanism 3b) as described in Sect. 3.4. The results of these experiments are summarised in Fig. 9, and in Tables 2 and 3.

The effect on the simulated monthly-mean OH concentrations in the surface model layer relative to the base case is shown in Fig. 9, for the example months of February and August. Increases in OH levels are generally simulated for all land areas with Mechanism 4R (panels a and b), whilst changes over the oceans tend to be close to

zero. Logically, the greatest increases (up to about 40%) are simulated for regions where isoprene emissions are highest and NO_x emissions are lowest (the tropics in February and the tropics as well as forested boreal regions in August).

10

Tables 2 and 3 summarise the results for selected species for the $5^{\circ} \times 5^{\circ} \times -1$ km surface grid boxes representative of the tropical forests of the Amazon (centred on 2.5° S, 67.5° W) and Borneo (centred on 2.5° N, 117.5° E), which are broadly relevant to the locations of the recently reported HO_x measurements (Lelieveld et al., 2008; Pugh et al., 2010). The simulated enhancements in OH over the Amazon with Mechanism 4R (Table 2) are about 40% in both February and August, with a concurrent reduction

- of approximately 25% in isoprene mixing ratios. Although these changes are somewhat smaller than those simulated at the low end of the NO_x range in the box model studies, it should be noted that the global model resolution is fairly coarse, such that regions of particularly low NO_x cannot be adequately resolved. As a result, the simulated NO_x mixing ratios (about 500 ppt) are much greater than those reported for the
- specific pristine forest locations, which are typically 20 to 50 ppt (Lelieveld et al., 2008; Butler et al. 2008). However, the changes in OH and isoprene mixing ratios are fully consistent with those calculated for comparable conditions in the box modelling studies (e.g., the box model simulation with Mechanism 4 predicts respective changes in daytime-averaged OH and isoprene levels of 54% and -27% relative to the Mecha-

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nism 0 base case run which yielded a daytime-averaged NO_x level of 489 ppt and an isoprene level of 6.1 ppb). This suggests that a calculation at finer resolution could yield the greater than 200% enhancements in OH levels predicted in the box model studies at the low end of the considered NO_x range (about 30–40 ppt). The changes

- ⁵ in OH levels (23–25%) simulated for the Borneo grid box with Mechanism 4R (Table 3) are slightly smaller than those for the Amazon, even though the simulated NO_x mixing ratios are lower (about 200–300 ppt). This reflects a compensating influence of the generally lower modelled abundance of isoprene in this region, which leads to a partial dilution in the impact of the chemistry. As shown in Tables 2 and 3 the mechanistic changes implemented in Mechanism 4R lead to increases of about 30% in HO₂ radical
- ¹⁰ changes implemented in Mechanism 4R lead to increases of about 30% in HO₂ radical levels, and near zero effects on ozone, which is also consistent with the results of the box model studies.

An order of magnitude reduction in the rates of the peroxy radical isomerisation reactions, k_{24} and k_{25} (Mechanism 4Ra), still yields a notable impact. The geographical ¹⁵ changes in OH levels (Fig. 9, panels c and d) show the same general pattern as those simulated with Mechanism 4R, with maximum increases of about 15% relative to the base case. The effects on all the species for the example Amazon and Borneo locations (Tables 2 and 3) are consistently just over a factor of two lower than those simulated with Mechanism 4R, a sensitivity which is fully consistent with that observed ²⁰ in the detailed box modelling studies. This suggests that a calculation at fine resolution

In the detailed box modelling studies. This suggests that a calculation at fine resolution with Mechanism 4Ra could result in enhancements in OH levels approaching 100%, as predicted in the box model studies at the low end of the considered NO_x range.

It is interesting to note that, although the dominant regional impact on OH formation results from the isoprene-specific chemistry involving the peroxy radical isomerisation

²⁵ reactions, the implementation of the propagating channels for the reactions of HO₂ with relevant RO₂ radicals (particularly $CH_3C(O)O_2$) has a comparable globally-integrated impact. This is because the chemistry is relevant not only to the degradation of isoprene, but also to the degradation of the majority of emitted anthropogenic and biogenic VOCs.

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6 Summary and conclusions

The sensitivity of isoprene degradation chemistry to a number of detailed mechanistic changes has been examined using MCM v3.1 as a reference base case mechanism, with particular focus on the impacts of these changes on the recycling and formation

- ⁵ of OH radicals. The implementation of radical propagating channels for the reactions of HO₂ with relevant classes or organic peroxy radical (namely acyl and β oxo peroxy radicals), and the partial revision of the degradation chemistry for first generation hydroperoxides, each resulted in a comparatively small impact on the system, with a combined simulated increase of about 10% in the concentrations of OH at the low end of
- ¹⁰ the considered NO_x range. A much greater impact was achieved by implementation of a recently postulated mechanism which involves isomerisation of the δ -hydroxyalkenyl and β -hydroxyalkenyl peroxy radical isomers, formed from the sequential addition of OH and O₂ to isoprene (Peeters et al., 2009), which yields a factor of 3.10 increase in the simulated OH concentration at low NO_x. Within this mechanism, the isomerisation
- ¹⁵ of the δ -hydroxyalkenyl peroxy radical isomers, in conjunction with rapid photolysis of the resultant hydroperoxyaldehyde products, was found to be the most significant component. A reduction in the peroxy radical isomerisation rates by an order of magnitude from the reported (lower limit) rates reduces the enhancement in OH concentrations to a factor of 1.94.
- ²⁰ Combination of all the considered mechanistic changes has an effect which is approximately additive, yielding an overall enhancement of a factor of 3.24 in the simulated OH concentration at the lowest NO_x input rate considered. The simulated mean NO_x mixing ratios at this input rate (42 ppt and 29 ppt with the base case and modified mechanisms, respectively) are comparable to those reported for the pris-
- tine forest locations where elevated concentrations of OH have been observed (e.g., Lelieveld et al., 2008; Butler et al., 2008). The mechanistic variations considered here thus achieve enhancements which approach those necessary to explain the reported model-measurement discrepancies, with the impact dominated by the mechanism pro-

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posed in the theoretical study of Peeters et al. (2009). It is important, therefore, that the details of this mechanism are either confirmed or refuted by laboratory study, under conditions of low NO_x and low RO_2 concentrations which have generally not been fully accessed in previous studies.

- ⁵ Application of a parameterized representation of the mechanistic changes in the STOCHEM global chemistry-transport model demonstrated that the greatest impact of the modified chemistry on OH concentrations logically occurs in remote regions characterized by high emission rates of isoprene, although a widespread low-level global impact also results from the processes which are not isoprene-specific (namely, im-
- ¹⁰ plementation of the propagating channels of the reactions of HO_2 with relevant RO_2 radicals, particularly $CH_3C(O)O_2$). The magnitude of the impact in the high isoprene emission regions was found to be consistent with that observed in the box model sensitivity studies, with the results being illustrated and discussed with a particular focus on the tropical forested regions of the Amazon and Borneo, where unexpectedly elevated ¹⁵ concentrations of OH have recently been reported.

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 project, for SRU. The development of STOCHEM was supported by Defra through their SSNIP contract AQ 0902 (RGD).

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Mechanism number	Description	
0	MCM v3.1	
1	MCM v3.1 with radical propagating channels incorporated for all acyl peroxy + HO ₂ and β -oxo peroxy + HO ₂ reactions.	
2	MCM v3.1 with updated chemistry incorporated for the OH-initiated degradation of the major hydroperoxide ISOPBOOH	
За	MCM v3.1 with isomerisation reactions (and associated subsequent chemistry) included for isoprene-derived peroxy radicals, based on Pootors et al. (2009)	C
3b	Mechanism 3a with enhanced photolysis rate for hydroperoxyalde- hyde products, based on Peeters et al. (2009).	
3c	Mechanism 3b with rates of isomerisation reactions for isoprene- derived peroxy radicals reduced by a factor of 10.	
4	A consolidation of the changes outlined above in Mechanisms 1, 2 and 3b.	

Table 1. Description of main mechanistic sensitivity runs performed (see Sects. 3.2-3.4).

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Table 2. Mixing ratio and percentage changes from the base case for a selection of species in a $5^{\circ} \times 5^{\circ} \times \sim 1$ km grid box centred at 2.5° S and 67.5° W representative of the Amazon Forest. % = ((Sensitivity Run-BASE)/BASE)*100.

Period	OH (ppt)	HO ₂ (ppt)	NO _x (ppt)	O ₃ (ppb)	isoprene (ppb)
Base					
February	0.018	11.5	497.4	43.4	6.4
August	0.022	8.8	519.6	45.9	4.1
Annual Mean	0.028	9.9	590.2	52	3.9
	OH (%)	HO ₂ (%)	NO _x (%)	O ₃ (%)	isoprene (%)
Mech. 4R		_		-	
February	39.0	30.0	-1.6	0.0	-26.7
August	37.8	35.3	-5.6	-3.4	-21.5
Annual Mean	29.7	28.7	-4.8	-3.0	-23.3
Mech. 4Ra					
February	14.6	11.7	-2.6	0.3	-8.8
August	15.1	13.0	-2.7	-0.9	-6.9
Annual Mean	12.9	11.0	-3.1	-0.7	-7.9

Table 3. Mixing ratio and percentage changes from the base case for a selection of species in a
5°×5°×~1 km grid box centred at 2.5° N and 117.5° E representative of Borneo. % = ((Sensitivity
Run-BASE)/BASE)*100.

Period	OH (ppt)	HO ₂ (ppt)	NO _x (ppt)	O ₃ (ppb)	isoprene (ppb)
Base					
February	0.049	7.9	204.7	21.9	1.1
August	0.066	8.0	349.0	25.5	0.6
Annual Mean	0.059	8.5	319.5	26.7	1.0
	OH (%)	HO ₂ (%)	NO _x (%)	O ₃ (%)	isoprene (%)
Mech. 4R		_ · ·		0	
February	24.6	34.0	2.9	-4.6	-29.2
August	22.5	31.6	-5.0	-4.6	-21.1
Annual Mean	23.2	30.9	-1.4	-4.9	-25.4
Mech. 4Ra					
February	11.1	15.5	0.2	-1.8	-14.6
August	9.7	12.3	-2.7	-1.6	-9.1
Annual Mean	9.9	12.6	-1.6	-1.8	-11.5

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Fig. 1. MCM v3.1 representation of the OH initiated degradation of isoprene to first generation products, in the presence of sufficient NO_x such that NO provides the dominant reaction partner for the peroxy radicals. Species names correspond to those appearing in MCM v3.1. Closed-shell products are displayed in boxes, along with their molar yields.

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Fig. 2. MCM v3.1 representation of the OH initiated degradation of isoprene to first generation products, in the absence of NO_x (routes to formation of initial peroxy radicals are as shown in Fig. 1). Species names correspond to those appearing in MCM v3.1. Closed shell products are displayed in boxes, along with their molar yields (N.B., HCHO, HC4ACHO and HC4CCHO are generated by more than one displayed reaction, such that their respective total molar yields are 30.7%, 5.8% and 9.9%).

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Fig. 4. Schematic representation of the main features of the updated representation of the OH initiated degradation of the major isoprene-derived hydroperoxide, ISOPBOOH, as applied in the sensitivity tests (Mechanism 2). This was used to replace the existing highly simplified representation, Reaction (R17).

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Fig. 5. Schematic representation of the OH initiated degradation of isoprene to first generation products in Mechanisms 3a and 3b. With the exception of the initial OH addition ratio, the mechanism and parameters are taken from the theoretical study of Peeters et al. (2009), and facilitate a full appraisal of the impact of the RO₂ isomerisation chemistry on HO_x recycling. $k_i = 1.5 \times 10^{-12} \text{ cm}^3$ molecule⁻¹ s⁻¹; $k_{ii} = 3.0 \times 10^{-13} \text{ cm}^3$ molecule⁻¹ s⁻¹; $k_{iii} = 1.4 \times 10^{-12} \text{ cm}^3$ molecule⁻¹ s⁻¹; $k_{iv} = 1.0 \times 10^{-12} \text{ cm}^3$ molecule⁻¹ s⁻¹. The initial OH addition ratio is unchanged from MCM v3.1 (see Sect. 2 and Fig. 1), but is very close to that calculated by Peeters et al. (2009).

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Fig. 6. Simulated mixing ratios and product ratios for carbonyl products of isoprene oxidation as a function of NO_x mixing ratio, using MCM v3.1 (Mechanism 0) and selected mechanism variants described in Table 1. All values are daytime averages over the second day of the simulations, calculated from 06:00 to 18:00 local time in the model.

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Fig. 7. Simulated correlations of (MVK+MACR)/isoprene vs. MVK/MACR using MCM v3.1 (Mechanism 0) and selected mechanism variants described in Table 1, for NO_x input rates $\leq 10^{11}$ molecule cm⁻² s⁻¹. The observations box identifies the values (MVK+MACR)/isoprene = 0.44±0.05 and MVK/MACR = 1.34±0.10, reported by Karl et al. (2009b).

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Fig. 8. Simulated mixing ratios of selected species using the (MCM v3.1-based) Mechanism 4 and the corresponding reduced (CRI v2-based) mechanism, Mechanism 4R.

Fig. 9. Percentage difference plots for the global model sensitivity runs, relative to the base case for OH. $\% = ((Run-Base)/Base)^*100$: **(a)** February, Mechanism 4R; **(b)** August, Mechanism 4R; **(c)** February, Mechanism 4Ra; **(d)** August, Mechanism 4Ra.

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