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21st August 2015

acp-2015-152: The MCM v3.3.1 degradation scheme for isoprene. Jenkin et al.

Following careful consideration of the comments and suggestions raised during the review and discussion of the above paper, we are pleased to submit a revised version of the manuscript. In conjunction with this, the mechanism itself has also been refined, and will be made available online as MCM v3.3.1 at <http://mcm.leeds.ac.uk/MCM>, in the near future. As a result, we have slightly changed the title of the paper (as shown above).

The changes made to the mechanism and manuscript are fully in line with the intentions that we previously summarised in the final author response at the end of the discussion phase (Atmos. Chem. Phys. Discuss., 15, C4078, 2015). Below we also provide an itemised list of the actual changes that have been made to the manuscript.

I hope the information is clear, and the changes made to the manuscript acceptable; but please let me know if there are any problems or concerns.

Best regards

Mike Jenkin

Dr M.E. Jenkin

acp-2015-152: The MCM v3.3.1 degradation scheme for isoprene. Jenkin et al.

The following is a sequential list of main changes made to the manuscript, identified in terms of the place in the original discussion document where the change was made. Where appropriate, the item is cross-referenced to the corresponding referee comment, using the comment numbering we adopted in our final discussion response (Atmos. Chem. Phys. Discuss., 15, C4078, 2015).

Section 2.1.1, page 9713, line 27: (Jozef Peeters, comment A1): At this point initially (and at several other points in the manuscript) we have referred to the mechanistic framework reported by Peeters et al. (2014) as the “Leuven Isoprene Mechanism (LIM1)”, as requested by the referee.

Section 2.1.1, page 9714, line 9: (Jozef Peeters, comments A1-A3): We have adopted the referee’s recommendation to apply the LIM1 kinetic parameters for O₂ addition to the hydroxyalkenyl radical and peroxy radical back decomposition, but with each scaled by a factor of 5 based on the recent results of Crouse et al. (2014). The revised text reads as follows:

“As recommended in the review comment of Peeters (2015), the 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 recently reported in preliminary form by Crouse et al. (2014). The resultant kinetic parameters are given in Table S1.”

Section 2.1.2, page 9715, line 3: (Jozef Peeters, comments A1-A3): We have adopted the referee’s recommendation to apply the LIM1 kinetic parameters for the 1,5 H-shift reactions for each of ISOPBO2 and ISOPDO2, rather than the geometric mean rate coefficient applied previously to both reactions. The revised text reads as follows:

“The applied isomerisation rates are the LIM1 values calculated recently by Peeters et al. (2014), as presented in Table S1, with these also being generally consistent with those reported by da Silva et al. (2010).”

Section 2.1.2, page 9715, line 21 (and elsewhere): (Jozef Peeters, technical comment): As requested by the referee, we have changed the names of the species originally called DHPMVK and DHPMACR. These are now called DHPMEK and DHPMPAL, respectively.

Section 2.1.2, page 9715, line 22: (Jozef Peeters, comments A1-A3; and Referee 2, opening comment): We have applied the LIM1 kinetic parameters for the 1,6 H-shift reactions for each of CISOPAO2 and CISOPCO2, scaled to recreate the value of k_{bulk} (at 295 K and $k_{\text{tr}} = 0.021 \text{ s}^{-1}$) reported by Crouse et al. (2011). Structurally averaged parameters are no longer applied. The revised text reads as follows:

“The temperature-dependent rate expressions applied to the 1,6 H atom shift isomerisation reactions 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 (k_{bulk}) to form the unsaturated hydroperoxyaldehyde products (C5HPALD1 and C5HPALD2) for the conditions of the experiments reported by Crouse et al. (2011) (see Sect. S1.4 for further details).”

Section 2.1.2, page 9715, line 28: (J.-F. Müller, comment B1): We have modified the methodology applied to the branching ratios of the propagating and terminating channels of the reactions of NO with the first-generation β - and δ -hydroxy peroxy radicals. The revised text reads as follows:

“The branching ratios applied to the propagating and terminating channels of the reactions of the β - and δ -hydroxy peroxy radicals with NO have been revised in MCM v3.3.1. The branching ratios to nitrate product formation from the terminating channels are assumed to be equivalent for the secondary peroxy radical (ISOPDO2) and the tertiary peroxy radical (ISOPBO2), but the remaining (primary) peroxy radicals are assigned terminating channel ratios that are 20 % lower. This reflects the well-established lower propensities of primary peroxy radicals to form nitrates (e.g. Carter and Atkinson, 1989; Lightfoot et al., 1992), which is also supported by the recent study of Teng et al. (2015) for hydroxyperoxy radicals formed from the reactions of OH with alkenes. The absolute values applied to the branching ratios were adjusted to result in an optimised total first-generation yield of nitrate products of 10 % at the high [NO] limit (see Sect. 2.1.4).”

Section 2.1.3, page 9717, line 9: (Jozef Peeters, comment A4): We have pointed out that the retention of the previous (relatively minor) chemistry for ISOPAO and ISOPCO is not supported by the very recent results of Nguyen and Peeters (2015). The following text has been added:

“It is noted that these fates for ISOPAO and ISOPCO are not supported by the very recent study of Nguyen and Peeters (2015), who theoretically characterised their rapid conversion into the corresponding Z- isomers (CISOPAO and CISOPCO), the chemistry of which is discussed below. However, the above reactions of ISOPAO and ISOPCO are currently retained, so that a route to the formation of HMA CR as a minor product remains in MCM v3.3.1.”

Section 2.1.3, page 9718, line 5: (Jozef Peeters, comment A4): We have added some discussion of the uncertainty in the sources of 3-methylfuran in the revised manuscript, including the possible role of heterogeneous processes. The following text has been added:

“.....The agreement of the yields of 3-methylfuran in those “NO_x present” studies, in conjunction with the reported time dependence of its production (e.g. Benkelberg et al., 2000; Lee et al., 2005), appear to indicate that it is formed (at least partially) as a first-generation product in the gas phase. However, it is noted that it is also likely formed by heterogeneous reactions of the C₅ unsaturated hydroxyaldehyde products, HC4CCHO and HC4ACHO (Dibble, 2007), such that there are uncertainties in the contribution of its gas phase formation.”

Section 2.1.4: This section describes the optimisation of the first generation chemistry. A number of small changes have been made throughout the section, e.g. in relation to quoting product yields calculated with the refined mechanism, which differ (usually only slightly) from those originally reported for MCM v3.3.

Section 2.1.4, page 9719, line 12: (Jozef Peeters, comments A1-A3): The description of the [NO]-dependence of the first generation product yields of MVK and MACR has been revised to point out that the increased MVK/MACR ratio at ppb levels of NO (calculated with the refined mechanism) is not supported by some published results – but that the notable increase at lower [NO] is supported by the recent results of Crouse et al. (2014). The revised/added text reads as follows:

“The yields calculated for the major products HCHO (61.0 %), MVK (34.1 %) and MACR (23.6 %) at the high [NO] limit are therefore consistent with the respective reported yields of (60.8 ± 4.5) %, (35.1 ± 5.2) % and (23.6 ± 2.8) % in “high NO_x” studies (see Table S2). As shown in Fig. 4, the mechanism predicts an increase in the yields of these products at lower [NO], with respective maximum values of about 77 %, 49 % and 27 % at about 1-2 ppb NO. The relative yield of MVK and MACR generally increases with decreasing [NO], with the rapid increase at the low end of the scale being consistent with the preliminary results of Crouse et al. (2014), as discussed by Peeters (2015). However, it is noted that both the absolute yields of MVK (approaching 50 %) and MVK/MACR ratios (≈1.8) are not fully consistent with those reported by Karl et al. (2006) and Liu et al. (2013), based on experiments carried out with NO mixing ratios of about 0.2 and 9 ppb, respectively. These studies both report MVK yields of about 41 % and MVK/MACR ratios in the range 1.4-1.5 (i.e. similar to those at the high [NO] limit).”

Section 2.1.4, page 9720, line 9: (Jozef Peeters, comment A5): The previously reported discussion of the probable contribution of 1,4 H-shift reactions for the α-formyl peroxy radicals, C526O2 and C527O2, by Peeters and Nguyen (2012) is now acknowledged and referenced. The revised text reads as follows:

“As discussed further below (Sects. 2.2.1 and 2.2.3), 1,4 H atom shift isomerisation reactions are included for C526O2 and C527O2, for consistency with newly implemented chemistry for the methacrolein-derived α-formyl peroxy radical, MACRO2, as also suggested by Peeters and Nguyen (2012).”

Section 2.1.4, page 9720, line 23: (J.-F. Müller, comment B1): The text describing the performance of the updated methodology applied to the branching ratios of the propagating and terminating channels of the reactions of NO with the first-generation β- and δ-hydroxy peroxy radicals has been revised, and an extra Figure panel (Fig. 5b) has been included. It now reads as follows:

“.....Compared with MCM v3.2, the main consequence of the revised branching ratios applied to the individual peroxy radical isomers in MCM v3.3.1 (described in Sect. 2.1.2) is an increased contribution

of the tertiary β -hydroxynitrate (ISOPBNO₃) and a decreased contribution of the secondary β -hydroxynitrate (ISOPDNO₃). The resultant relative contributions of these β -hydroxy isomers, and the fractional contribution of the δ -hydroxy isomers (ISOPANO₃ and ISOPCNO₃) at the high [NO] limit (shown in Fig. 5b) are consistent with the preliminary results of Crouse et al. (2014). However, the distribution does not appear to match the results of any of the previously reported studies (Giacopelli et al., 2005; Paulot et al., 2009b; Lockwood et al., 2010), which display some variability (Fig. 5a). The mechanism predicts a slight decrease in the total first-generation nitrate yield as [NO] is lowered, falling to about 8 % at the low end of the considered range (see Fig. 4). This results mainly from the impact of competing isomerisation reactions for selected peroxy radicals. The associated [NO]-dependences of the β -hydroxy isomer ratio, and the δ -hydroxy isomer contribution, are consistent with the preliminary results of Crouse et al. (2014) (see Fig. 5b).”

Section 2.1.4, page 9721, first paragraph: (Jozef Peeters, technical comment): References to Peeters et al. (2014) and Crouse et al. (2011) have been added to reinforce the origin of the mechanisms being discussed.

Section 2.1.4, page 9721, line 9: (Jozef Peeters, technical comment): The “Addition and Correction” amendment of Crouse et al. (2012), has been cited, as requested by the referee. The revised text reads as follows:

“.....As shown in Fig. 3, the chemistry initiated by the 1,6 H atom shift isomerisation reactions also provides additional first generation routes to methyl glyoxal and (particularly) glyoxal, which are most effective at intermediate [NO], when the reactions of NO with the α -formyl peroxy radicals C536O₂ and C537O₂ can compete with their 1,4 H atom shift isomerisation reactions. Evidence for operation of these routes has been reported by Crouse et al. (2012a), through detection of the hydroperoxycarbonyl co-products, HCOCH₂OOH and HYPERACET (see Fig. 3).”

Sections 2.2.2 and 2.2.3: These sections describe the degradation chemistry of nitrates and hydroperoxides. A number of small changes have been made throughout these sections, e.g. in relation to quoting product yields and lifetimes calculated with the refined mechanism, which differ (usually only slightly) from those originally reported.

Section 2.2.2, page 9725, line 22: (J.-F. Müller, comment B4): The additional recommendations of J.-F. Müller for the photolysis rates of β -nitrooxy aldehydes have been adopted in the refined mechanism, and reference to the discussion comment (Müller, 2015) has been added.

Section 2.2.5, page 9728, line 19: (Referee 2, comment C1): The chemistry of the HCOCO radical is now described in greater detail in the supplement, as referred to at this point in the revised manuscript. The material in the supplement is based on that given in the author response to this referee comment.

Section 2.2.7, page 9729, line 14: (J.-F. Müller, comment B2): HMML and MAE have been included in the list of other products in this section. An additional channel (forming methyl glyoxal and OH) has been included in MCM v3.3.1 for the gas phase reaction of OH with HMML. The mechanism of this reaction is now presented in the supplement, as referred to at this point in the revised manuscript. The material in the supplement is largely based on that given in the author response to this referee comment.

Section 2.2.7, page 9729, line 14: (J.-F. Müller, comment B6): The rates and products of the photolysis reactions of HVMK and HMAc have been revised on the basis of information given in Peeters et al. (2014). The following text has been added:

“In the specific cases of HVMK and HMAc, removal via rapid photolysis (initially forming OH and a stabilised hydroxyvinyl radical) is also represented, as recommended by Peeters et al. (2014), and in the discussion comment of Müller (2015). This leads to clear sky photolysis lifetimes of about an hour for HVMK and HMAc (for solar zenith angle = 30°)”

Section 3.2: This section describes the performance of MCM v3.3.1 (compared with MCM v3.1 and MCM v3.2) for a range of idealised atmospheric conditions. Some changes have been made throughout this section, in relation to the simulated daytime-averaged levels of key species formed during isoprene degradation and fluxes through key reactions – which differ slightly from those originally calculated using MCM v3.3 (as also illustrated in Figs. 10-15).

Section 3.2.2, page 9733, line 21: (Referee 2, minor comment): The presentation and description of the OH recycling fluxes has been clarified in the text and in Fig. 11. In particular, the expression implying that OH is formed directly from the 1,6 H-shift reactions of CISOPAO2 and CISOCO2 has been removed. The revised text now reads:

“Particularly important contributions are simulated to result from the chemistry initiated by the 1,6 H atom shift isomerisation reactions of CISOPAO2 and CISOPCO2 (including the 1,4 H shift reactions of C536O2 and C537O2 and the photolysis of C5HPALD1 and C5HPALD2; see Sects. 2.1.2 and 2.2.4).....”

The corresponding sources in Fig. 11 are sources (1) and (4), which are described as follows in the figure caption:

“(1) First generation chemistry of C536O2 and C537O2 (Fig. 3), dominated by their 1,4 H shift reactions.”

“(4) Reaction sequence following the rapid photolysis of C5HPALD1 and C5HPALD2 (Fig. 9), including subsequent rapid photolysis of HMAc and HVMK (Sect. 2.2.7).”

Section 3.2.4, page 9737, line 29: (J.-F. Müller, comment B2): The possible contribution of the reaction of OH with HMML as a source of HCOOH is now discussed. The following text has been added:

“The reaction of OH with HMML partially forms HCOOH, as represented in MCM v3.3.1 (see Sects. 2.2.7 and S2.2). This source is simulated to make a notable contribution (about 30 %) to HCOOH formation towards the high end of the NO_x range for the conditions of these simulations, although its major source remains the reaction of water vapour with the stabilised Criegee intermediate CH₂OO, formed from isoprene ozonolysis (40-50% relative humidity). However, representation of reactive uptake of HMML on aerosol particles (e.g. Kjaergaard et al., 2012) would reduce the importance of its gas phase degradation as a source of HCOOH.”

Other comments:

A number of other corrections were made to the mechanism, as a result of the discussion comments. These had only a very minor or negligible effect on mechanism performance, and are therefore not documented in the manuscript:

J.-F. Müller, comment B6: The products of the photolysis of NC4CHO (formed from the NO₃-initiated oxidation) have been amended as suggested in MCM v3.3.1.

Referee 2, comment C2: The reactions of HO₂ with the acyl peroxy radicals C3MCOBCO3 and MC3COBCO3 (formed from further oxidation of the minor unsaturated dicarbonyl product C4MDIAL) now correctly form C5PACALD1 and C5PACALD2 in MCM v3.3.1, rather than the duplicate species (C4COBCO3H and MC3OBCO3H), which have been removed from the mechanism.

As indicated in the author response, these production routes for the C5PACALD species during isoprene degradation are sufficiently small that the impact of this correction was found to have a negligible effect on the idealised atmospheric simulations.

In conjunction with that correction, the chemistry of a further nine related PACALD species has been updated to include rapid photolysis in MCM v3.3.1. Those species are not formed from isoprene degradation but are generated from unsaturated dicarbonyls that are formed most importantly from aromatic hydrocarbon degradation (like C4MDIAL itself).