Geoscientific

Model Development

Discussions

[GMDD]

Interactive

comment

Interactive comment on "Chemistry and deposition in the Model of Atmospheric composition at Global and Regional scales using Inversion Techniques for Trace gas Emissions (MAGRITTEv1.0). Part A. Chemical mechanism" *by* Jean-François Müller et al.

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Reply to Anonymous Referee #2

We thank the referee for their comments and respond to the points raised below.

The authors integrated all the major advancements and originally contributed to large portion of them. Their critical understanding of the relevant chemical processes, far from being all achieved, adds to the value of manuscript. Impact of recent experimental and theoretical advancements of the global budgets of organic acids is very interesting. The model is fairly well described and the evaluation seems appropriate for use in global models. However, a box model comparison between MAGRITTEv1.0 and MCMv3.3.1, the mechanism presented by Wennberg et al. 2018 or even their detailed mechanism would add useful information about the model performance. I wish the authors could provide such data and information.

We thank the Reviewer for the suggestion. We added a new section "Box model comparison with other isoprene mechanisms". We intercompare the MAGRITTE mechanism version 1.1, MCMv3.3.1 and the reduced Caltech mechanism. We don't believe useful to include the "full" version of the Caltech mechanism in this comparison, as it does not treat the further degradation of numerous oxidation products. We perform 30-hour simulations using KPP, starting at 9 AM with 2 ppbv isoprene. NOx is fixed at either 1 or 0.1 ppbv. The photolysis rates are calculated for mid-July clear-sky conditions at 30°N, using the TUV model of Madronich (1993). For computational efficiency, the photorates are parameterized as a function of solar zenith angle using MCM-type expressions (Saunders et al., 2003). All rate coefficient expressions are available at the MAGRITTE repository (http://doi.org/10.18758/71021042). Since Wennberg et al. does not provide detailed recommendations for the calculation of photolysis rates, we use our own expressions in their mechanism.

Note that the new version (v1.1) of the MAGRITTE mechanism differs from the initial version (v1.0) described in the GMDD paper. The most important updates include

(1) updated product distribution of the 1,6-H-shift isomerisation of the Z-δ-OH-peroxys from ISOP+OH, including a higher HPALD yield (0.75 instead of 0.25), in agreement

with recent laboratory data (Berndt et al., 2019) and with theoretical calculations, as described in detail in the revised version of the manuscript (see also our Reply to Reviewer #1),

(2) inclusion of the bimolecular reactions of the Z-δ-OH-peroxys from ISOP+OH, following a comment of Reviewer #1,

(3) calculation of RONO2 yields in RO2+NO reactions following Wennberg et al. (2018).

The comparisons show that MAGRITTEv1.1 leads to lower HOx recycling than the Caltech mechanism. Sensitivity calculations show that the difference is primarily due to (i) differences in the Z-δ-OH-peroxy isomerisation rates and products, and (ii) differences in the product distribution of hydroperoxycarbonyl (especially HPACET and HPAC) photolysis. Important differences between the mechanisms are also found for e.g. carboxylic acids, PANS, nitrates and methanol, as discussed in the revised version of the manuscript.

1) Bulk isomerization rates
Please explain more the counter-intuitive concept by which the bulk isomerization rate of the lumped (beta- and delta-) species ISOPBO2 and ISOPDO2 should linearly increase with the traditional RO2 sink rate (kp). Why is it not or it has to be different than what Crounse et al. (2011) reported? Even if correct, neglecting the RO2 sink due to permutation reactions should yield non-negligible errors/deviations from the analytical solution. Please explain why the neglect and in case provide an estimate of the deviation caused by it.

We provide now a better justification of the bulk isomerisation rate expressions:

"Based on a detailed steady-state analysis, the bulk isomerisation rate of ISOPBO2 and ISOPDO2 was shown to increase linearly with the sink rate (k_p) of the traditional peroxy reaction (Peeters et al., 2014). The reason for this behaviour is that at low k_p, the ratio of the Z-δ-OH-peroxys over the lower-energy β-OH-peroxys is close to their equilibrium ratio, of order of only ∼0.01, whereas at the high k_p limit, where all peroxys have a similar lifetime, their ratio is governed by their initial formation branching ratio, which is an order magnitude higher (Peeters et al., 2014; Teng et al., 2017)." Note that the linear dependence of bulk isomerisation rates on k_p was verified experimentally by Teng et al. (2017).

Neglecting the RO_2 sink due to permutation reactions in those bulk isomerisation rate expressions has a negligible impact, estimated at ∼0.6% of the bulk isomerisation rate for ISOPDO2, and even less for ISOPBO2.

2) Reproducibility of results
The chemical mechanism of MAGRITTEv1.0 is not exactly what can be downloaded at the link given. A few sample differences are listed below. The reaction of CH3OH with OH is standard in the manuscript but in MAGRITTE.eqn file one finds two reactions with one including the water vapor catalysis by Jara-Toro et al. 2017.

We thank the Reviewer for pointing this out. Updated equation and species files are now available at the MAGRITTE repository. The water vapor catalysis proposed by Jara-Toro et al. is not included, as it was recently disproved by a recent laboratory study (Chao et al., 2019).

The rate constant for the reaction

CH3O2 + HO2 = 0.9 CH3OOH + 0.1 HCHO

is 4.1E-13*exp(750/TEMP) and 3.8E-13*exp(780/TEMP), respectively.

Corrected.

Concerning the 1,6-H-shift of ISOPDO2 in the .eqn file one finds
ISOPDO2 = 0.25 HO2 + 0.25 HPALD2 + 0.75 OH + 0.75 CO + 0.75 DIHPCHO :
4.253E8*exp(-7254/TEMP) ;
ISOPDO2 + NO = NO + 0.25 HO2 + 0.25 HPALD2 + 0.75 OH + 0.75 CO + 0.75 DIHP-
CHO : 6.29E-19*exp(4012/TEMP) ;
ISOPDO2 + HO2 = HO2 + 0.25 HO2 + 0.25 HPALD2 + 0.75 OH + 0.75 CO + 0.75
DIHPCHO : 4.90E-20*exp(4962/TEMP) ;

The last two reactions constants are not the ones reported in Table 2.

Corrected.

PYRA (pyruvic acid) is listed in Table 1. However, it is neither in Table 2 nor in the .eqn
file.

Corrected (PYRA is not a model species).

Overall, it might be that the authors uploaded another version of MAGRITTE. Please
upload a v1.0 that is faithful to the Tables in the manuscripts. The files should bear the
information about the exact model version.

The new version of the mechanism (v1.1) supersedes version v1.0. The files now
bears the information about the model version.

Moreover, no file with the actual functions used for many rate constants is given. This
is also the case for the cross-sections and quantum yields used for computing the
photolysis frequencies. Please also provide this information.

We thank the Reviewer for the excellent suggestion. We now provide the functions

used for calculations of rate constants (including photolysis rates as discussed above) in the MAGRITTE repository, as well as data files with the absorption cross-sections of polyfunctional carbonyls not found in current recommendations (IUPAC, JPL). The photolysis parameters of other compounds are readily available from e.g. those recommendations.

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