Atmos. Chem. Phys. Discuss., 10, C10554–C10559, 2010
www.atmos-chem-phys-discuss.net/10/C10554/2010/

Atmospheric Chemistry and Physics Discussions

Interactive comment on “Modeling secondary organic aerosol formation from isoprene oxidation under dry and humid conditions” *by* F. Couvidat and C. Seigneur

F. Couvidat and C. Seigneur

couvidaf@cerea.enpc.fr

Received and published: 1 December 2010

(1) References added.

(2) Reference added (Pandis et al., 1991).

(3) There is in fact no cut-off value. The model is based on the RACM2 mechanism for gas phase chemistry. Therefore, this gas-phase chemistry model simulates all reactions simultaneously, but some reactions will dominate depending on the NO_x level. We used the no-NO_x conditions (where the compound formed under high-NO_x conditions cannot possibly be formed) to determine yields and saturation vapour pressures of the compound formed under low-NO_x conditions. For the high-NO_x conditions, the

compounds formed under low-NO_x conditions can be formed in small amounts.

(4) The UNIFAC-activity coefficient computation is done iteratively here. For this study, 0D simulations are computationally very fast but an iterative computation can indeed be very demanding in terms of computational cost. It would be possible to reduce the frequency of such calculations for 3D calculations with some loss of accuracy. We added a comment to that effect in the article.

(5) Reference added (Goliff and Stockwell, 2008).

(6) This statement comes from the article of Kroll et al. (2006). Reference to Kroll et al. (2006) has been added where the different loss pathways are discussed.

(7) The text was incorrect and R8 has been replaced by R7. It is the reaction of ISOP with itself that can be important only if concentrations of isoprene are high. If concentrations of isoprene are lower, ISOP will likely react with another radical present in higher concentrations.

(8) Changes of temperature were taken into account by using the Clausius-Clapeyron equation and enthalpies of vaporization measured under low-NO_x and high-NO_x conditions. The precision of the extrapolation depends on the precision of the enthalpies of vaporization. Those enthalpies of vaporization are now presented in Table 1.

(9) We agree that this statement is out of place. It has been moved to the part were SOA loss is discussed and we elaborate now on the uncertainties associated with this loss mechanism (it could occur either in the gas phase or in the particle phase).

(10) The parameterization was developed in this work.

(11) The equation of Clausius-Clapeyron was used for the extrapolation to other temperatures. The RACM2 gas-phase chemistry simulates the impact of humidity on the gas-phase chemistry. For the particulate phase, the simulation of an aqueous phase is described in section 4.2.

(12) We are referring to the activity coefficients of BiMGA and BiNGA. The sentence has been rephrased for more clarity.

(13) The stoechiometric coefficients and the saturation vapor pressures of the compounds were selected to minimize the error between the model and the measurements. It is expected that in some cases, the model overestimates the results and that in some other case, it underestimates the results. A perfect fit is not possible and as the model reproduces results of the experiments within their uncertainties, those differences are not really significant. Therefore, we only discussed the case where the model did not fall within the range of experimental uncertainties.

(14) The impact of OH concentrations was not discussed because we used a kinetic constant for H_2O_2 degradation based on Kroll et al. (2006). As the evolution of isoprene concentrations as a function of time is in good agreement with the isoprene degradation observed by Kroll, we consider that the OH concentrations are correctly simulated by the gas-phase mechanism and the impact of OH concentrations was not studied. A comment was added to clarify this point in section 2.1.

(15) We agree that this paragraph should be move to the section “model development”. Table 1 has been modified to provide all information regarding SOA precursors.

(16) The decrease of SOA concentrations is due to lower NO_2 concentrations during the oxidation. The inhibition of SOA formation for low $[NO_2]/[NO]$ ratios is due to the MPAN chemistry. Simulations show that SOA begin to form nearly 1 hour after the beginning of oxidation. To observe high concentration of SOA, MPAN formation must be favored after 1 hour and so, a high $[NO_2]/[NO]$ ratio after 1 hour must be observed. For an initial $[NO_2]/[NO]$ ratio of 0.1, the ratio after 1 hour is: 53 for 100 ppb, 52 for 200 ppb, 31 for 300 ppb and 7 for 400 ppb. The decrease of SOA for a NO_x concentration superior to 200 ppb is due to the drop of NO_2 during oxidation. This discussion has been added in section 3.1.

(17) Fig. 5 shows that for the whole range of NO_x concentrations studied, the concentrations of SOA are higher in the high-NO_x case than in the low-NO_x case (concentration around $3.5\mu g.m^{-3}$). Concentrations for $[NO_2]/[NO]=1$ are always greater than $3.5\mu g.m^{-3}$. This is confirmed by Fig. 6 which shows the evolution of the yield with the initial concentration of isoprene for $[NO_2]/[NO]=1$. For the different concentrations of NO_x, the yield is higher under high-NO_x conditions than under low-NO_x conditions. It is for $[NO_2]/[NO]=0.1$ that the yield can be lower if NO_x concentrations are high.

(18) There is no simple explanation for these trends. They are due to the competition between several reactions (formation of MPAN favored when $[NO_2]$ increases, inhibition of MPAN when [NO] increases). Moreover, as the concentration of isoprene increases, the concentration of NO_x has to increase to stay in the high-NO_x regime. The trends observed here are probably due to all these factors.

(19) Changes of temperature were taken into account by using the Clausius-Clapeyron equation. Reference to this equation has now been added in section 2.1 where enthalpies of vaporization are mentioned.

(20) The increase of $2\mu g.m^{-3}$ is for a change of temperature from 20℃ to 0℃ and not 10℃ to 0℃.

(21) Reference added.

(22) The reference temperature (298 K) has been added in both the text and the table.

(23) The organic phases in cases 1 and 2 are both non-ideal. In case 1, the activity coefficient of BiMGA is 39.7 and the activity coefficient of BiNGA is 9.31. BiNGA is the main constituent of the organic phase in that case. In that case, the activity coefficients mainly depend mostly on the chemical composition of the POA rather than on the total mass of organics. For a mass of POA of 1 $\mu g.m^{-3}$ (not shown), the activity coefficients are 39.8 for BiMGA and 9.29 for BiNGA. For case 2, the phase is non ideal due to the interactions of organic compound with water. But, the activity coefficients do not really change from 10 to 100 $\mu g.m^{-3}$ (not shown). In both case 1 and case 2, the

weak dependence of the activity coefficients on the mass of the absorbing phase is not surprising. As BiNGA and BiMGA are dilute either in POA or water, the values of their activity coefficients are near their values at infinite dilution. However, under atmospheric conditions, with more SOA compounds from other precursors, the activity coefficients could be very different.

(24) Changed.

(25) It is indeed 0.027. Changed.

(26) Changed.

(27) A lower yield under high-NO_x conditions than under low-NO_x conditions is only observed by Kroll when concentrations of NO_x are very high ($[NO_x]$ greater than 400 ppb). For lower NO_x concentrations (more representative of atmospheric conditions), the yield is higher. This is already explained in part 3.1.

(28) Changed.

(29) AEC is now defined.

(30) Compounds formed under low-NO_x conditions are highly hydrophilic and tend to condense on an aqueous particle but not on an organic particle. Therefore, “as the compounds formed are highly hydrophilic and condense almost entirely on organic particles” was corrected and replaced by “as the compounds formed are highly hydrophilic and condense almost entirely on aqueous particles”.

(31) a) Yes, it should be Fig. 9. Corrected. b) Concentration of isoprene for Fig 9. was 10 ppb and not 50 ppb. c) The two graphs were inverted. Corrected and clarified.

(32) As oligomerization is not explicitly treated but only implicitly treated by using an effective partitioning constant, taking into account oligomerization does not impact the computational time here.

(33) Several references added: Gao et al. (2004), Jang et al. (2005), Liggio et al. (2005)

(34) Corrected.

(35) Sentence clarified by adding the statement as suggested.

(36) Sentence clarified by adding the statement as suggested.

(37) low-NO_x replaced by NO_x-free as suggested.

(38) Assumed atmospheric conditions (T and RH) has been added.

(39) Conditions added.

(40) Changed.

(41) Changed.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 20559, 2010.