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Comment on acp-2020-1295

Anonymous Referee #2

Referee comment on "Study of different Carbon Bond 6 (CB6) mechanisms by using a concentration sensitivity analysis" by Le Cao et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2020-1295-RC2, 2021

General Comments

Three versions of the Carbon Bond 6 chemical mechanisms (CB6r1, CB6r2 and CB6r3) are implemented in a photochemical box model (KINAL) and compared in 7 day simulations without and with emissions, i.e., 6 simulations in total. The analysis focuses on concentrations of O3, NOx (NO + NO2) and HCHO averaged over the final 24 hours of each simulation (day 7). Sensitivity analysis of concentrations [c(i)] to the individual reaction rate constants [k(j)] of each mechanism is performed by computing log-normalized sensitivity coefficients S(ij) [= d ln c(i)/d ln k(j)] for day 7 of each box model simulation. The CB6r3 mechanism is currently available in the Community Multiscale Air Quality model (CMAQ; https://www.epa.gov/cmaq) and CB6r2 is currently available in the Comprehensive Air quality Model with extensions (CAMx; www.camx.com) although CAMx also includes CB6r4. CB6r1 was used very little because CB6r1 was quickly superseded by CB6r2. Sensitivity analysis of chemical mechanisms is useful to help modelers understand how the mechanisms influence their atmospheric simulations. The sensitivity analysis will be most useful when performed for conditions that are representative of many atmosphere simulations.

Specific Comments

The 7-day scenario with no emission has little relevance to how chemical mechanisms are used in atmospheric models. It is difficult to think of atmospheric conditions where an air parcel begins with substantial concentrations of ozone and precursors (initial NOx = 70 ppb with VOC/NOx = 4.8 and initial O3 = 100 ppb, from Table 1) but then receives no input of either biogenic or anthropogenic emission over 7 days. It would be more atmospherically relevant to analyze the no emission simulations on day 2 or day 3. Figure 1 shows that the no emission simulations diverge by day 3 and, most likely, a main cause of differences after 2-3 days is the updated organic nitrate reactions of CB6r2 as summarized at line 110.

The 7-day scenario with emission produces O3 above 300 ppb which is rarely observed in the atmosphere at ground level. In the atmosphere, O3 accumulation is moderated by surface deposition and diluted by daily increase and decrease in the boundary layer depth. It is unclear whether the box model included either deposition or dilution due to cycling of boundary layer depth. If the effects of deposition and dilution cannot be included in the

box model, the model results can be analyzed on day 2 or day 3 when the O3 concentration is closer to atmospherically relevant conditions.

The HCHO concentration in simulations with emission reaches 50 ppb which is high compared to atmospheric measurements. HCHO may accumulate too much because the box model has no dilution due to cycling of the boundary layer depth. Conducting the sensitivity analysis with very high HCHO concentrations limits relevance to the atmosphere. The discussion at lines 467 to 487 compares the box model HCHO sensitivity results to results of 3D simulations and ambient measurements but it is difficult to have confidence in these comparisons because the box model HCHO concentrations are about an order of magnitude larger than in the 3D simulations.

The study conclusions are limited to the box model conditions that have been analyzed and presented. At minimum, the discussion of conclusions should clearly state that conclusions are drawn from box model conditions that are substantially different from the conditions present in most 3D model simulations of the atmosphere. A better solution would be to reanalyze the box model results focusing on day 2 or 3 and then update the conclusions, which may add new conclusions. The same comment applies to the summary of conclusions included in the abstract.

Figure 2 and similar Figures present much information in a concise format and are useful. However, identifying the contribution of an individual reaction in Figure 2 is difficult. The authors can add a Table in the supplementary material listing the values of S(ij) from Figure 2 and the similar Figures.

The manuscript is written clearly although one aspect of language should be clarified. The word "discrepancy" means a difference that is not expected. In this study, the mechanism versions are different and so they produce different concentrations which isn't a discrepancy. Change the word discrepancy to difference.

Technical Corrections

Line 8: Using the model species name CXO3 in the abstract will be difficult for many readers to understand. This statement could be re-written to say that the fate of larger PAN-type compounds (PANX) is influential in these box model scenarios.

Line 20: Harmful effects of air pollution occur at concentrations lower than air quality standards.

Line 37: The correct citation for the Carbon Bond lumping method is Gery et al., 1989

Line 74: This paragraph doesn't mention previous relevant studies (Derwent 2017, 2020) that compare CB6 to other mechanisms. It would be useful to cite these studies and note that Derwent used CB6r3 although with changes to the inorganic reactions so that all the mechanisms compared had the same inorganic reactions.

Line 86: The statement that changes brought about by mechanism updates are "unknown" is contradicted by the review of earlier findings presented in the preceding paragraph. A different statement that could be made is that the motivation of this study is to better understand the effects of mechanism changes. The same comment applies at line 3.

Table A1 includes species that are part of the CMAQ aerosol scheme (i.e., TERPRXN, BENZRO2, TOLRO2, XYLRO2, PAHRO2) but play no part in CB6 gas-phase chemistry (i.e., they have no gas-phase removal reactions). It would be clearer to delete them from Table A1. Also, CMAQ changed the name of the CB species representing xylenes (XYL) to

XYLMN (meaning xylene minus naphthalene) and added a naphthalene species (NAPH) for SOA chemistry.

Table A1. Add a Table footnote that reactions 223 to 231 were added to the mechanisms in this study to represent box model emissions but they aren't part of the CB6 mechanisms.

Table A1. For clarity, add a Table footnote to the table specifying where the authors obtained each version of CB6. This Table is cleverly constructed.

New References

Derwent, R.G., 2020. Representing Organic Compound Oxidation in Chemical Mechanisms for Policy-Relevant Air Quality Models under Background Troposphere Conditions. Atmosphere, 11(2), p.171.

Derwent, R., 2017. Intercomparison of chemical mechanisms for air quality policy formulation and assessment under North American conditions. Journal of the Air & Waste Management Association, 67(7), pp.789-796.