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Atmospheric
Chemistry
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Discussions

Interactive comment on "Comparison of tropospheric chemistry schemes for use within global models" *by* K. M. Emmerson and M. J. Evans

Anonymous Referee #2

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1. General comments

This manuscript presents a series of 5-day photochemical simulations and uses them to compare among several different representations of photochemistry. This type of intercomparison is always useful. The manuscript provides useful information and is worth publishing.

The main weakness is that the intercomparisons are limited and do not provide a good basis for evaluating the chemistry of alkenes and aromatics. The authors may have overlooked the limitations, , and some caveats are needed. The authors might consider some additional test cases, although this is not necessary.

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Paradoxically, the relatively good results for OH from the CB-IV mechanism should provide a warning about the limited nature of the tests. The CB-IV mechanism was designed for polluted urban situations and omits reactions that are known to be important in the free troposphere. These omissions do not result in obvious errors in the tests.

Despite these weaknesses, the manuscript is worth publishing. There are some details that need to be corrected and some questions that warrant additional discussion or explanation.

2. Specific comments

1. The TORCH test case has been included with the specific intent of testing the mechanisms in an urban situation with high VOC. This is a useful approach, especially since TORCH provides a test with extensive initial VOC, including species not explicitly represented in the mechanisms. The other test cases, derived from a global simulation, are limited to VOC species that are explicitly represented in most of the mechanisms.

The problem with the TORCH test case is that emissions are set to zero for the 5-day period. This means that short-lived VOC are rapidly removed and have limited impact on results. Stated differently: the measured ambient concentrations underestimate the impact of the more reactive VOC. The reactive species represent a small fraction of ambient VOC, but they represent a much larger fraction of emissions and a larger fraction of VOC reactivity.

These limitations can be seen in the results for PAN in Figure 5. The CB-IV mechanism shows good agreement with the others during daytime over the first 36 hours, but afterwards its results radically diverge from the others. This suggests that after 48 hours the chemistry is dominated by acetone (missing from CB-IV) rather than the short-lived species.

These limitations may also explain the good results from TOMCAT (p. 19971), despite its omission of all short-lived species (alkenes and aromatics). It might be reasonable

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to omit non-biogenic alkenes and aromatics in global models, these limited test cases are not intended to prove it.

This omission can be corrected by appropriate caveats and discussion in the manuscript. The authors might consider an additional test case with constant primary VOC (comparable to the tests with constant "NO_x").

2. The most obvious omission in the CB-IV mechanism is the reaction $OH+HO_2$. This reaction is unimportant in urban environments but has a significant impact on OH chemistry in the free troposphere. Despite this omission, results for CB-IV show good agreement for OH with the other mechanisms.

Zaveri and Peters (1999) noted that CB-IV implicitly assumed that the RO_2 products from reactions of organics with OH all react with NO to produce NO_2. This is clearly not true for the cases shown here (which include NO_x as low as 2 ppt), so it is also worrisome that discrepancies for remote O_3 do not appear.

While this might be viewed as a favorable reflection on CB-IV, I believe it more likely reflects limitations in the testing. This may be related to comment 3.

There are no obvious modifications to correct this, but I urge the authors to give some thought to why this occurs.

3. The authors have carefully selected scenario input values (Table 2) based on an objective procedure, using a principal component analysis of results from a global model. One problem is that the scenarios all appear to be extreme cases. They represent either the surface (>940 hPa) or the upper troposphere near the tropopause (<150 hPa). They represent extremes of either very low (<0.005 ppb) or very high (>0.1 ppb) NO_2. There is no representation of conditions between 300 and 900 hPa, or for NO_2 between 0.05 and 0.1 ppb, each of which would represent most of the troposphere.

If possible, consider adding one or more scenarios that represent average tropospheric conditions.

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4. The authors have chosen to include VOC species that are omitted from individual mechanisms in a way that preserves the total carbon content of the omitted species (p. 19965 and p. 19971). While this choice is reasonable, it is not the standard approach for lumped and surrogate-species methods. The standard approach is to represent omitted species in a way that preserves OH reactivity. In some cases the authors? approach conflicts with specific recommendations associated with the mechanisms of their antecedents.

For example:

Benzene has been represented as propene in the GEOS-CHEM mechanism (with a reaction rate 10 times higher than benzene) and as toluene in CBM-IV. (The instructions for CBM-IV represent benzene as "nonreactive".)

Ethylbenzene is represented by xylene in the GEOS-Ito and CBM-IV. The antecedents of these mechanisms (e.g. Lurmann et al., 1986) specify that ethylbenzene should be represented as toluene, which it resembles in structure and reactivity.

Acetone is assigned to OLE (olefin) in CBM-IV, despite difference in reactivity by a factor of 10 or more. Similarly, C_2H_5OH is assigned to OLE.

Me-2-pentene and Me-3-pentene is assigned to ALK7 in GEOS-Ito, rather than to an alkene species.

The CBM-IV mechanism also uses the designation "PAR" (paraffins, in carbon atoms) to represent miscellaneous VOC, so that (for example) pentene is represented as OLE+2 PAR and ethylbenzene as TOL+PAR. This is apparently not included.

The choice for acetone obviously affects results for CB-IV. The others probably have little effect, since test results are dominated by long-lived alkanes and acetone. The text should discuss the issue and add caveats.

5. Results for the inorganic tests (Table 4) show a significant difference between GEOS-CHEM and GEOS-Ito. From the description on p, 19961 these mechanisms

are identical except for the treatment of some organic species. An explanation needs to be given for the different results.

One possibility is that the authors have implemented the GEOS-CHEM mechanism as it appeared in Bey et al. (2001) and did not include subsequent updates to rate constants, which appeared in on-line publications. In any case, this should be clarified.

6. The text (p. 19968, top, and p. 19972, line 20) refers to the differences between IUPAC and JPL kinetics and recommends collaboration between IUPAC and JPL to establish standard rates. In this context, I urge the authors to refer to Gao et al. (1996). Gao et al. did a Monte Carlo calculation based on reported uncertainty ranges in reaction rate constant. They found that these lead to a 20 % uncertainty in calculated O_3, OH and other species.

The findings from Gao et al. relate to many aspects of this paper. They suggest that the difference between IUPAC and JPL may reflect the true uncertainty of photochemical calculations rather than a failure to provide standardized values. More generally, it is worth asking whether the differences in the reaction mechanisms shown here result from different reaction sequences, products and stoichiometries or whether they reflect differences in reaction rates. I urge the authors to briefly discuss this issue.

7. The conclusion attributes the difference in PAN between the mechanisms to different yields of CH_3CO_3 from acetone (p. 19972, line 26). This is not discussed in the main part of the paper, except for noting the omission of acetone in CB-IV (p. 19968, line 16). I urge the authors to add a brief explanation. Are they referring to different representation of products of the reactions of acetone with OH, or are they referring to different rate constants?

8. Table 2 has some important omissions. It does not give the initial concentration for acetone, which is identified as a major source of difference between the mechanisms in subsequent analysis. It is also not clear whether the initial conditions include other species from the global model (p. 19964) that are not included in Table 2. This should

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be clarified. If the initial conditions include lumped alkanes and higher aldehydes from the global model the text should state how these are represented in the different mechanisms.

9. The text should refer to the CBM-Z mechanism developed by Zaveri and Peters (1999) in the context of CBM-IV. The CBM-Z represents an extension of the original CBM-IV for remote conditions and is more suitable for global simulations than the original CBM-IV.

10. The discussion of N_2O_5 (p. 19963 and 19967) should refer to Dentener et al. (1993), which identified the importance of the nighttime N_2O_5 reaction in global models. The N_2O_5+H_2O reaction is closely related to the aerosol reaction of N_2O_5 discussed by Dentener et al. Because the importance of N_2O_5 is emphasized in the conclusion, this would be a useful reference. The N_2O_5+H_2O is often omitted in the expectation that the aerosol reaction dominates.

11. The text (p. 19967, line 26) refers to different rates for O_3+HO_2 and other reactions in CB-IV relative to MCM. This provides a reasonable explanation for the lower O_3 in CB-IV in the inorganic test cases, since O_3+HO_2 is usually a major sink for O_3 in the remote troposphere. It is less clear why GEOS-chem has lower O_3. The text refers only to a 14 % difference in O_3+NO, but this has no obvious impact on O_3. The text also refers to differences between IUPAC and JPL reaction rates here, but the rates from CB-IV date to 1989 and are probably not due to IUPAC versus JPL. It is useful that the authors have tried to identify specific rates here, and the section does not need to be changed. However, they should give some thought to this. (See also 5 above.)

12. The text (p. 19970, line 10) refers to differences in the treatment of NO_3+VOC and NO_3+RO_2 reactions as a source of differences in nighttime NO_3. It would be useful to give specific examples of this from the mechanisms.

3. Technical corrections

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Abstract, line 18: "Night-time chemistry is badly represented. " This is an exaggeration. It should just say that differences are found for NO_3.

Page 19963, lines 9-14 and elsewhere: The text refers to NO_x, defined as $NO+NO_2$, but then presents an expanded definition that includes NO_3 and other species. Subsequently it is unclear which NO_x they are referring to. (The paragraph beginning on p. 11969, line 23 appears to switch back and forth between the two definitions.) Because NO_x is routinely used to represent $NO+NO_2$ I urge the authors to find a different abbreviation for their expanded NO_x.

Page 19967, line 1: The text refers to "no boundary conditions" and "constant NO_x" boundary conditions, apparently referring to the cases defined on p. 19963, line 6. This is confusing because the term ?boundary condition? is not normally used this way. It might be clearer to refer to these as "zero emissions" and "constant NO_{xE}" cases.

Page 19968, line 15: "variations in the PAN concentrations calculated by CBM-IV vary by up to a factor of 5. " Confusing wording.

Page 19970, Line 9: "which compare the rate of NO_3...". The wording is confusing.

Table 2: "principle" should be "principal".

4. References

Dentener, F.J., and Crutzen P.J., Reaction of N2O5 on tropospheric aerosols,: impact on the global distributions of NOX, O3 and OH, J. Geophys. Res., 98, 7149-7163, 1993.

Gao, D., W. R. Stockwell and J. B. Milford, Global uncertainty analysis of a regional-scale gas phase chemical mechanism. J. Geophys. Res., 101 9071-9078, 1996.

Lurmann, F. W., A. C. Lloyd, and R. Atkinson, A chemical mechanism for use in long-range transport/acid deposition computer modeling, J. Geophys. Res., 91, 10905-10936, 1986.

Zaveri, R. A. and Peters, L. K., A new lumped structure photochemical mechanism for large-scale applications, J. Geophys. Res. 104, 30387-30415, 1999.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 19957, 2008.

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