REVIEW 1

We thank the reviewer for helpful comments and suggestions! Replies to all points included in the reviews are given below, and the manuscript is revised accordingly.

General comments:

The authors explore the implications of including the HNO3 forming branch of the reaction HO2+NO, using the Oslo CTM2. The results are broadly similar to those published by Cariolle et al, 2008. In addition to Cariolle et al, the authors calculate the impact of including this reaction channel on radiative forcing due to changes in O3 since preindustrial times. The study demonstrates the significance of including this branch in their 3D chemistry-transport model, and suggests that further studies should be carried out to assess the impacts. However the validity of this HNO3 forming branch will have to be confirmed by more laboratory studies before any certain conclusions can be drawn. I think this study will be suitable for publication in ACP after improvements to the manuscript and analysis, and modifications of appropriate texts. My suggestions/comments are as detailed below.

Reply:

We agree that confirming the laboratory studies is important. Multi-model comparisons would also be helpful (see replies below).

Specific comments:

(1) This paper is lacking a detailed analysis of the ozone budget (i.e., the global annual chemical production and loss, STE, the tropospheric ozone burden – as the impact seems to be mainly in the troposphere). Hopefully, by obtaining this information more light will be shed on the interplay between different processes under the scenarios with and without including the HNO3-forming branch, and on certain differences between the results presented in this study and those of Cariolle et al (2008). This may also help to explain why the Oslo CTM2 has a high-ozone bias in the upper troposphere.

Reply:

We agree that discussing the ozone budget is important, and have included calculated values of stratosphere-troposphere exchange (STE) fluxes and tropospheric and stratospheric burdens. It should be noted that these are based on the model tropopause, which we explain in the revised manuscript (section 3.5), and may not be directly comparable to literature values. This is a common problem, and for a multi-model comparison, a clear definition on how to calculate STE and burdens should be agreed upon to make model results comparable.

A detailed study of chemical production and loss is unfortunately out of scope of this work, but we hope that the budget numbers will help explain the results. The discussion on chemistry in the text is rewritten in accordance with this. We do not think the annual global production/loss numbers

will improve the results considerably, i.e. it does not justify the time setting up new time-consuming model simulations.

Our main motivation for the study was to use a CTM with tropospheric and stratospheric chemistry, since the reaction has the largest impact in the tropical upper troposphere and lower stratosphere, and to look at trends since pre-industrial times and the changes in radiative forcing.

(2) The budget calculations should apply to not only the runs for 2000 but also to those for pre-industrial times. Assessing the response of including the HNO3-forming branch in the pre-industrial condition will provide valuable information on how such a change impacts a very different atmosphere in terms of NOx loading, and to explain the impact on the ozone trend.

Reply:

We have included the budget numbers (section 3). The change in ozone burden is larger in 2000 than under pre-industrial conditions. To shed more light on the global numbers, we also compare this to the change in the tropics (15S-15N, 5.5-15km), where the reaction has the largest impact.

Tropospheric burden of O3 (year 2000) changes from 349 Tg to 310 Tg when reaction (2) is included, i.e. a 11% reduction. The reduction is mainly located in the tropics, as seen from Figure 4. For the pre-industrial case, the burden changes from 226 Tg to 204 Tg (9.9% reduction). The numbers are listed in a new table (table 4 in the revised text), also as Dobson Units. Note that the burdens differ slightly to the numbers used in RF-calculations, as stated in the text (section 5) and in the table caption (the cause is a slightly different tropopause in the CTM and in the RF calculations).

The STE flux of O3 is 408 Tg/year for REF_2000 (see section 3.5 in revised document). Reaction (2) increases this negligibly by 1% to 412 Tg/year, due to smaller O3 production in the tropical upper troposphere, reducing the tropical upward flow of O3. STE is the net flux, and will therefore increase when the upwards transport of O3 from the troposphere is reduced. In the long run, this may reduce stratospheric O3 slightly and possibly reduce transport of O3 back into the troposphere. For the pre-industrial reference run, the STE is 533 Tg/year, with a small increase (0.27%) when reaction (2) is included. A smaller change is expected since the tropospheric burden is smaller and stratospheric burden larger.

(3) In section 4.1 on “Modelled and measured O3”, the authors display comparisons between modelled monthly mean total ozone columns from R2_2000 run and TOMS (fig. 5); the agreement seems reasonable. However the authors should also display the same plots from REF_2000 run (or the difference between R2_2000 and RE_2000) to show the effect of including the HNO3-forming branch.

Reply:

In Figure 3 the reader can see the effect on the zonal mean ozone column due to the new reaction. In our results, there are small differences in the zonal direction for a given latitude, and the month-to-month variation is generally captured in Figure 3. The effect of reaction (2) should therefore be seen by looking at both figures. We have included some text on the regional differences (both section 3 and 4) and how to relate Figure 5 and 3, and hope this will answer the questions raised. Both R2_2000 and REF_2000 may be considered to match TOMS well, and we have included a comment on that.

(4) The figure caption of Fig 5 is wrong; it should be “monthly mean total column of ozone”.

Reply: Thanks. The text is corrected.

(5) At the end of Section 4.1, the authors should be specific about which region the “significant improvement in the model’s ability : : :” occur in.

Reply:

We have changed the text to be clearer on this (section 4.1). The region is the tropics, where the reaction is most important.

(6) Page 14814, line 15: please rephrase the sentence ‘: : : and concluded without much discussion : : :” I guess, in this case, the authors of Cariolle et al (2008) might not want to speculate on what they are not sure about.

Reply:

We appreciate the suggestion, and have rephrased the sentence. Our point is that Cariolle et al (2008) *does* make a quite large point out of the fact that their calculations tends to make their results worse (both in conclusion and abstract), and they do not discuss possible reasons for it, other than that there may be outstanding uncertainties in their NOx/HNO3 partitioning. The reader is to a large extent left with the impression that it is more likely that the reaction should not exist, unless one realizes that their NOx/HO3 partitioning may differ from other models. We have rewritten this paragraph (section 4.2); see the next reply for further comments.

(7, part 1) The last 3 paragraphs of Section 4.2 should be deleted or rewritten. For example, There is no basis for the assertion that small increases of surface or lightning NOx emissions would change significantly the conclusion of the Cariolle study. This is pure speculation as there is no sensitivity study even with the authors' own model. There are many processes that could potentially make model results "worse" or "better".

Reply:

We agree with the reviewer, and have rewritten the paragraphs. We have changed the focus to the Oslo CTM2, and explain possible reasons why our results differ from Cariolle et al. Several factors may contribute to differences, e.g. the strength of the NOx source. From preliminary simulations with the Oslo CTM2, a 20% reduction of lightning NOx, from 5 Tg(N) to 4 Tg(N), is found to reduce the tropical upper tropospheric O3 by about 7% annually.

(7, part 2) Model evaluations should not be based on including/excluding one parameter, especially when the models have certain biases (often they do). Here the authors should prompt a more comprehensive model-intercomparison study to understand different responses and interactions between and within the models.

Reply:

We agree that there is need of understanding model responses and we include a discussion/suggestion for this in the manuscript.

(8) In section 5 on "Radiative forcing", the authors only displayed modified changes of ozone and RF between PI and 2000, as a result of including the HNO3 forming branch. It would be useful to also show the differences in RF between REF_PI and REF_2000 or R2_PI and REF_PI.

Reply:

We have included the R2-REF difference in tropospheric RF due to changes from pre-industrial and present, as figure 8c. As noted before, the stratospheric differences are minor, so we do not show that. From the tropospheric difference, we see that the effect of R2 on RF is mainly located in the sub-tropical region. This corresponds well with the region where R2 has the largest impact on O3 (Figure 3). The text is revised with respect to this.

(9) In conclusion, the authors should point out that a multi-model study would be useful to determine the effect of including the HNO3 forming branch.

Reply:

We agree; the text is now rewritten pointing this out. It seems that several models already have tested the reaction, and a multi-model comparison should also include the H2O effect when it has been well established how to treat it in a model. When looking into the H2O effect, a possible change in H2O since pre-industrial times could also be taken into account.

Technical corrections:

p14802, line 2: change “atmospheric O3” to “tropospheric O3”:

Reply: Done

p14802, line 6: it is unclear how this can affect the climate significantly. Suggest to replace “climate” with “radiative forcing”.

Reply: We agree, and have changed the text.

In the abstract, please also state how much the modelled ozone changes due to the inclusion of the HNO3 forming branch.

Reply: Thanks for pointing this out.

p14802, line 24: replace “major source of O3” with “major source of photochemically produced ozone in the troposphere”:

Reply: Done

p14806, line 20: should be “new reaction”, typo:

Reply: Done

p14810, line 6: delete one “the”:

Reply: Done

References:

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