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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Impact of the new HNO_3-forming channel ofthe HO_2+NO reaction on tropospheric HNO_3, NO_x, HO_x and ozone" *by* D. Cariolle et al.

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Referee 2

Referee 2 has many specific comments and suggestions to improve the clarity and writing of the paper. We will take them into account in the revised paper to be submitted to ACP. In particular the following clarifications can be given:

-Concentrations of CO and O_2. The HNO_3 formation in the $OH + NO_2$ reaction contributed up to 10 % of the yield from the HO_2+NO reaction at typical concentrations of CO, O_2 and NO used in these experiments, as also calculated by numerical simulation of the kinetics in the reactor (see Butkovskaya et al., 2007 for details).

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- NASA versus IUPAC datasets. The NASA-JPL evaluation panel's recommended value and the one recommended by the IUPAC panel (Atkinson et al., 2006) are very similar, the IUPAC one being higher by only 14% at 200 K and 10 % at 300K. The use of the IUPAC value will not change the conclusions of this paper.

- Relative role of HNO_3 formation by reaction $NO + HO_2$ versus $NO_2 + OH$ at tropopause level. The ratio R between the rates of HNO_3 formation by these 2 reactions is equal to: R=([NO].[HO2]/[NO2].[OH]).(k1b/k4). The first term of the product corresponds to an "atmospheric"; component that depends on the NOx and HOx profile concentrations. Evaluated from the 2D model at the equator, this term increases from a value of 40 at ground level to a peak value of about 220 at 10 km. The second term k1b/k4 shows an increase from 0.004 at ground level to 0.01 at 15 km. So we can conclude that the differences in the altitude profiles of NOx and HOx species are as important as the temperature dependency of the k1b reaction constant for the effectiveness of reaction R1b. The two factors act in the same direction. This will be stressed in the revised version of the manuscript.

Referee 4

Referee 4 also has some specifics comments and suggestions to improve the clarity of the paper, they will be taken into account in the revised manuscript. We detail below our response to the specific comments made.

- The role of acetone as a source of HOx depends strongly on its quantum yield for photolysis, which is temperature dependent. Recent determinations of this quantum yield (e.g., Nadasdi et al., 2007) agree with previous evaluations (e.g. Blitz et al., 2004) to within 10 %. Acetone can thus still be a significant source of HOx in the UT (Arnold et al., 2004). However the model OH responses in relative terms to the introduction of reaction R1b will not depend strongly on the acetone source of HOx since it acts as an additional sink of HOx with no major feedback on the acetone HOx source by photolysis.

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- The GEOS-CHEM model is driven by assimilated winds calculated by the Goddard Earth Observing System at 4°x5° horizontal resolution and 30 levels in the vertical. Surface sources of NOx are 42 Tg N yr^{-1} (anthropogenic, biomass burning and soil) while upper troposphere sources amount to 4 Tg N yr^{-1} (lightning and aircraft). The model description is given by Bey et al.(2001). Adequate references will be given in the revised manuscript.

- OH budget. Recent evaluations by Bloss et al. (2005) give a mean northern and southern hemispheric OH concentrations of 0.91 x$10^6 cm^3$ and 1.03 x$10^6 cm^3$ respectively, consistent with the global value of 0.97 x10^6 cm^3 given by our run NEW3D. This latter reference will be given in the revised manuscript.

- The 3D model underestimate of observations of O3 in the 7-10 km range reflects issues with an overestimate in the GEOS tropopause mass flux which is in excess. To maintain a 500 Tg yr^{-1} cross tropopause O_3 flux, lower than observed O_3 concentrations are necessary within the model stratosphere. Thus, the model tends to underestimate the O_3 concentration in this tropopause region. However, the 3D model O_3 response to the introduction of reaction R1b is very close to the response by the 2D model in this altitude range, a reduction in the 10 % range. Thus, our conclusions on the impact of reaction R1b on the O_3 content is not altered by the existence of a bias in the 3D model in the UT.

Suggestions have been made by the referees to improve the clarity of some figures. These will be implemented as much as possible.

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