

Interactive comment on “The HNO₃ forming branch of the HO₂+NO reaction : pre – industrial – to – present trends in atmospheric species and radiative forcings”

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Received and published: 9 July 2011

Søvde et al. present the results of a modeling study looking at the impact of the inclusion of a HNO₃ forming branch in the HO₂ + NO reaction (the major O₃ forming reaction in the troposphere). Their simulations are performed under both present day and simulated pre-industrial conditions and the affect that the new reaction has to the models simulation of O₃ and NO_y is evaluated. By comparison to present day measurements of NO_y, based on CARIBIC aircraft data, the authors conclude it is difficult to determine whether the change to the chemistry has improved the agreement between the model and the observations. However, improved agreement between modeled and

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observed O₃ lends some support for the inclusion of the HNO₃ branch in the HO₂ + NO reaction. Radiative forcing calculations were then performed on the modified run and it was shown that the reductions in tropospheric O₃ lead to a significant reduction in the calculated RF.

General comment: The manuscript is generally well written, easy to follow and the subject matter falls well within the scope of ACP. The affects on O₃ RF are indeed significant and merit further work on this subject, but the experiments themselves are, in general, not novel (the same parameterization for this reaction already being used in the study by Cariolle et al. [2008]). My major criticism of this work is in the parameterization of the HNO₃ forming channel of the HO₂ + NO reaction, which (as stated in the on-line comment by Dr J.-F. Müller) does not take into account the H₂O dependence that the reaction has been shown to exhibit (Butkovskaya et al. 2009). The importance of the HO₂-H₂O adduct on reactions such as the HO₂ + HO₂ reaction has been included in models for many years now. In this manuscript the authors should also investigate the importance of the HO₂-H₂O adduct on the HO₂ + NO reaction. This work would also greatly benefit from detailed analysis of the global (tropospheric and stratospheric) O₃ and NO_y budgets. The affects that the O₃ reductions have on the methane lifetime also need to be more quantitatively discussed. After consideration of these comments and those below, I feel this work will be suitable for publication in ACP.

Minor comments: p 14802 line 2: Change atmosphere to tropospheric. p 14804 line 13: By reaction modeling I presume they mean quantum chemical modeling? p 14807 line 2: I presume that the pre-industrial simulation was driven using the year 2000 wind fields. Climate models predict different temperature/humidity profiles between the pre-industrial and the year 2000. Can the authors suggest what impact this might have? p 14808 line 7: Has the latest kinetics of the NO₂ + OH reaction been included in this study? Mollner et al. [2010] have shown that inclusion of updates to the kinetics of the NO₂ + OH reaction can have important consequences for tropospheric O₃. Inclusion of this update would be valuable or at least a comment on the potential impacts. p

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14808 line 20: By how much has the flux changed? A table of key fluxes for both sets of simulations would be very useful. p 14809 line 27: Again you should be able to diagnose what is going on here. Is the change in methane lifetime driven by changes in the tropical lower troposphere/upper troposphere/extra tropics? Some more diagnostics would be useful here. p 14810 line 6: remove second "the". p 14810 line 7: remove first "and".

References: Butkovskaya, N., Rayez M. T., Rayez J. C., Kukui A. and Le Bras G. : Water dependence effect on the HNO₃ yield in the HO₂ + NO reaction: Experimental and theoretical evidence, *J. Phys. Chem. A*, 113, 11327-11342, 2009. Cariolle, D., Evans, M. J., Chipperfield, M. P., Butkovskaya, N., Kukui, A., and Le Bras, G.: Impact of the new HNO₃-forming channel of the HO₂+NO reaction on tropospheric HNO₃, NO_x, HO_x and ozone, *Atmos. Chem. Phys.*, 8, 4061-4068, doi:10.5194/acp-8-4061-2008, 2008. Mollner, A.K., Valluvadasan S., Feng L., Sprague M.K., Okumura M., Milligan D.B., Bloss W.J., Sander S.P., Martien P.T., Harley R.A., McCoy A.B. and Carter W.P.L.: Rate of Gas Phase Association of Hydroxyl Radical and Nitrogen Dioxide, *Science*, 330, 646-649, 2010.

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 11, 14801, 2011.