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## ***Interactive comment on “The HNO<sub>3</sub> forming branch of the HO<sub>2</sub>***

***+NO reaction : pre – industrial – to –***

***present trends in atmospheric species and radiative forcings” by O. A. Søvde et al.***

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Søvde et al. present the results of a modeling study looking at the impact of the inclusion of a HNO<sub>3</sub> forming branch in the HO<sub>2</sub> + NO reaction (the major O<sub>3</sub> 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 O<sub>3</sub> and NO<sub>y</sub> is evaluated. By comparison to present day measurements of NO<sub>y</sub>, 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 O<sub>3</sub> lends some support for the inclusion of the HNO<sub>3</sub> branch in the HO<sub>2</sub> + NO reaction. Radiative forcing calculations were then performed on the modified run and it was shown that the reductions in tropospheric O<sub>3</sub> 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 O<sub>3</sub> 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 HNO<sub>3</sub> forming channel of the HO<sub>2</sub> + NO reaction, which (as stated in the on-line comment by Dr J.-F. Müller) does not take into account the H<sub>2</sub>O dependence that the reaction has been shown to exhibit (Butkovskaya et al. 2009). The importance of the HO<sub>2</sub>-H<sub>2</sub>O adduct on reactions such as the HO<sub>2</sub> + HO<sub>2</sub> reaction has been included in models for many years now. In this manuscript the authors should also investigate the importance of the HO<sub>2</sub>-H<sub>2</sub>O adduct on the HO<sub>2</sub> + NO reaction. This work would also greatly benefit from detailed analysis of the global (tropospheric and stratospheric) O<sub>3</sub> and NO<sub>y</sub> budgets. The affects that the O<sub>3</sub> 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 NO<sub>2</sub> + OH reaction been included in this study? Mollner et al. [2010] have shown that inclusion of updates to the kinetics of the NO<sub>2</sub> + OH reaction can have important consequences for tropospheric O<sub>3</sub>. 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 HNO<sub>3</sub> yield in the HO<sub>2</sub> + 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 HNO<sub>3</sub>-forming channel of the HO<sub>2</sub>+NO reaction on tropospheric HNO<sub>3</sub>, NO<sub>x</sub>, HO<sub>x</sub> 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.

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