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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Combining Bayesian methods and aircraft observations to constrain the HO[.] + NO₂ reaction rate" *by* B. H. Henderson et al.

B. H. Henderson et al.

barronh@gmail.com

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We thank the referee for their review and recommendations to improve the paper. The two main recommendations are separately addressed below.

Referee 2: "2) there is a temperature dependence for the minor channel at low pressures, published by Bean et al. (2003), that predicts lower yields of HOONO at lower temperatures, as predicted here."

To address the temperature dependence identified by Bean et al. (2003), we have amended the text in the conclusions as follows:

> The update to the temperature dependency may relate to emerging literature on HO_x/NO_x reactions. For instance, a second channel for the $HO\cdot$ + NO_2 reaction forms isomers of HOONO (Nizkorodov and Wennberg, 2002). These isomers can photolyze or dissociate to reform $HO\cdot$ and NO_2 thereby reducing the net forward reaction rate. The formation rate is temperature dependent (Bean et al., 2003), as is the fate. Given the uncertainty in fate, HOONO is not explicitly simulated in this study although HOONO may contribute to the findings here.
>
> (continued in second part of response)

Referee 2:"1) Does the analysis shed light on the possibility of a small (1-2%) yield of the HNO3 channel in the HO2+NO reaction, observed experimentally Butkovskaya, LeBras and co-workers? My guess is that even a small yield is inconsistent with the current results, unless offset by even larger reduction in the rate of R12."

As the referee points out, the possibility of a small yield of HNO_3 from HO_2 + NO was not accounted for in this study and has the potential to influence the results. Based on the temperature sensitivity described by Butkovskaya et al. (2007), we calculate the branching ratio to be between 0.63% and 0.65% for the "all" and "initial" conditions. To be conservative, we performed sensitivity simulations with a yield of 0.7% and 1%. At 0.7% the inferred k(NO_2+OH) is 63% of the base value, and at 1% the inferred k(NO_2+OH) is 60% of the base value (compare to the 78% value in the standard results). These results do not account for water vapor enhancements described by Butkovskaya et al. (2009). These enhancements were only characterized at 298K, and Butkovskaya et al. (2009) conclude the article with the following statement: "since the observed water effect appears to be potentially important for atmospheric modeling, the measurements of the water enhancement factor will be extended to cover as much as possible the ranges of tropospheric temperatures and pressures." Further

study is needed to account for the role of water vapor and establish a parameterization that is appropriate for the upper troposphere.

As expected, adding a HNO_3 yield to the HO_2 + NO reaction enhances the inferred reduction of the rate R12. The HNO_3 yield could also enhance the suggestive reduction to k(HO_2+NO) (0.95 of base value in Figure 4c). We believe that fully accounting for an update, such as the Butkovskaya et al. (2007) would require a multi-variate inference approach. Although we find the interaction of rates to be very interesting, we believe that introducing a multi-variate approach is outside the scope of this paper, but could be explored in subsequent work. To address this, we have added the following to the paragraph started above:

> Also the formation of HNO_3 from HO_2 + NO (e.g., Butkovskaya et al., 2005), has the potential to further reduce the inferred R12 value. The inference framework in this study uses a univariate approach that will not account for updates to multiple uncertain rates. Updates to recommended rates, which are used as the base mechanism for this paper, could alter the inference values reported here.

Referee 2: "Pg 14. Line 3 'was also be"'

This has been corrected.

REFERENCES:

Bean, B. D.; Mollner, A. K.; Nizkorodov, S. A.; Nair, G.; Okumura, M.; Sander, S. P.; Peterson, K. A.; Francisco, J. S.: Cavity Ringdown Spectroscopy of cis-cis HOONO and the HOONO/HONO2 Branching Ratio in the Reaction OH + NO2 + M, J. Phys. Chem. A, 107(36), 6974–6985, doi:10.1021/jp034407c, 2003.

Butkovskaya, N. I.; Kukui, A.; Pouvesle, N.; Bras, G. L.: Formation of Nitric Acid in the Gas-Phase HO2

+ NO Reaction: Effects of Temperature and Water Vapor, J. Phys. Chem. A, 109(29), 6509–6520, doi:10.1021/jp051534v, 2005.

Butkovskaya, N.; Kukui, A.; Le Bras, G.: HNO3 Forming Channel of the HO2 + NO Reaction as a Function of Pressure and Temperature in the Ranges of 72−600 Torr and 223−323 K, J. Phys. Chem. A, 111(37), 9047-9053, doi:10.1021/jp074117m, 2007.

Butkovskaya, N.; Rayez, M.-T.; Rayez, J.-C.; Kukui, A.; Le Bras, G.: Water Vapor Effect on the HNO3 Yield in the HO2 + NO Reaction: Experimental and Theoretical Evidence, J. Phys. Chem. A, 2009, 113 (42), pp 11327–11342

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