

The following contains the comments of the referee (black), our replies (blue) indicating changes that will be made to the revised document (red).

## **Reviewer #2: Anthony Hynes**

This review was submitted by A.J. Hynes, senior author on the D'Ottone et al. study. I have not read the other review that was submitted and apologize for any duplication of points.

The manuscript presents a new study of the three body recombination between OH and NO<sub>2</sub>. The major importance of the reaction in both tropospheric and stratospheric chemistry is established. Interestingly, however, the authors cite a recent modeling study that suggests that the uncertainty associated with this reaction is the largest uncertainty in predicting OH, O<sub>3</sub> etc in global models. As noted in the manuscript it is now clear that there are a number of major challenges associated with obtaining rate coefficients that are appropriate for use in atmospheric models. Firstly it is now clear that the channel to form HOONO makes a significant contribution to the total rate coefficient at 298K under atmospheric conditions. However this is not expected to be an efficient termination reaction for OH. Hence a knowledge of the branching ratio between the HNO<sub>3</sub> and HOONO channels is required. Because of the pressure dependence it is critical that rate coefficients are appropriate for air over the pressure and temperature ranges used for modeling the troposphere and stratosphere. Again the reaction is unusual in that O<sub>2</sub> and N<sub>2</sub> have significantly different three body efficiencies for the total reaction hence measurements in N<sub>2</sub> are not adequate for modeling. It is also unclear if this unusual difference is applicable to both channels or just to the HNO<sub>3</sub> channel. Experiments to resolve these issues are difficult to perform and the dataset under atmospheric conditions is limited. I would suggest that relatively recent work by Mollner et al, and this manuscript make claims that their datasets are somehow more accurate than prior work and I believe these claims are exaggerated. In this manuscript the authors suggest that "In-situ measurement of NO<sub>2</sub> using two optical-absorption set-ups enabled generation of highly precise, accurate rate coefficients in the fall-off pressure range, appropriate for atmospheric conditions." However the majority of the data focuses on studies in N<sub>2</sub>, and, because it is now clear that N<sub>2</sub> and O<sub>2</sub> have significantly different three body efficiencies this statement is misleading. The work is worthy of publication after revision and there is some careful work examining the pitfalls associated with various approaches to in-situ monitoring of NO<sub>2</sub>.

We thank Anthony Hynes for his careful review. Our work does not (cannot) address the branching ratio to formation of HNO<sub>3</sub> and HOONO. This does not impact on the accuracy of our determination of  $k_5$ . We have emphasized this at the end of the Introduction and also as an outlook in the Conclusions.

**Introduction:** We note that the rate coefficients we obtain represent the total loss rate coefficient ( $k_5$ ) for OH loss (i.e. the sum of  $k_{5a}$  and  $k_{5b}$ ).

**Conclusions:** We derive a parameterization of the overall rate coefficient and show that present, divergent evaluations of  $k_5$  result in significant differences, both underestimating and overestimating the rate coefficient in different parts of the atmosphere. Further study on the temperature and pressure dependence of the branching ratios to HNO<sub>3</sub> and HOONO formation as well as on the atmospheric fate of HOONO are required to fully understand and model the atmospheric impact of the title reaction.

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However I think we need to put this dataset squarely in the context of prior work. Figure 1 shows the results of the 4 studies that are in very good agreement on the pressure dependence of the reaction at ~298K. [1-4] and the current work lies a little above the other studies because it was performed at 293 K. The high pressure flow tube study of Donahue et al.[5] is not shown and it is widely accepted that the rates reported in this study are too slow. Figure 1a shows an expanded plot between together with a 20% error bar at a value of  $1.1 \pm 0.1 \times 10^{-11}$ . All these studies monitor the sum of channels producing HNO<sub>3</sub> and HOONO and, as reported by Mollner, the branching ratio for formation of HOONO is pressure dependent and significant at 760 Torr. Based on Figures 1 and 1a, I would suggest that there is no reason to suggest that any of these data sets are significantly more precise or accurate than the others and any parametrization, using either the JPL or IUPAC formalism should encompass all of these results. For most studies of chemical kinetics the agreement between these studies would be considered excellent.

Accurate values of  $k_5$  are of paramount importance in atmospheric chemistry. As explained in the manuscript, we believe that an uncertainty of 20 % (the size of the error bar mentioned) is unacceptably large and is the result of systematic uncertainty in some of the kinetic studies. Indeed, within the combined ( $2\sigma$ ) uncertainties, the results of some individual studies do not overlap and therefore they do not agree. We have taken great pains to reduce systematic uncertainty and increase the precision of our data by carefully measuring NO<sub>2</sub> in-situ at multiple wavelengths. One indicator of underestimated experimental uncertainty is scatter in plots of  $k_5$  versus pressure. As we indicate in the supplementary information, the fall-off parameterization we derive reproduces nearly all of our datapoints within 5%. This is not true of all the datasets.

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Figure 2 shows a comparison of the data in O<sub>2</sub>. The work from the current manuscript lies above the data from Dottone and Mollner which I would suggest are in excellent agreement. However again the current work was performed at 293 K so direct comparisons is not possible.

Based on our measurement of the T-dependence, one would observe a 4% increase in the rate constant going from 298 to 293 K. The slight difference in temperature does not explain the difference in  $k_5$ .

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Fig.3 shows a comparison of D'Ottone and Mollner, the only work in air and the discrepancy is rather larger than might be expected based on the similarity of the results in pure N<sub>2</sub> and O<sub>2</sub>.

We would agree with this statement.

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Finally Fig. 4 shows results at 273 K in N<sub>2</sub> and it can be seen that the results from D'Ottone et al. are the only data set that extends to atmospheric pressure. Based on these observations there are a number of questions for the authors to address.

There seems to be a problem with this Figure. The present data (referred to as Crowley) is not consistent with the values we tabulated. Indeed, we list (Table 1) only one value for  $k_5$  at 273 K. It appears that data at 273 and 293 have been mixed.

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My calculations converting Torr at specific temperatures to total number density are not consistent with those in the manuscript, can the authors please check.

We have recalculated. Our numbers are correct. This has been clarified in personal communication with the reviewer.

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Why were the ~room temperature experiments performed at 293K making a direct comparison with three prior datasets difficult.

The effect of temperature on  $k_5$  is not so large as to preclude comparison of data at 293 and 298 K. Also, the rate coefficient at 298 K can easily be calculated from our temperature dependent parameterization.

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Given that the results in O<sub>2</sub> appear to lie above prior data and the discrepancy between D'Ottone and Molner results in air, why were no experiments in air performed to confirm these results.

From our data in O<sub>2</sub> and N<sub>2</sub> we calculate that (at pressures of 15 to 900 Torr) the differences in  $k_5$  that would be observed between air and N<sub>2</sub> is 2-4%. As working at atmospheric pressure of air impairs the detection of OH and thus the precision of the experiment we saw no value to be gained from such experiments.

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Were O<sub>2</sub> experiments performed after the N<sub>2</sub> results?

No, they were performed intermittently. We are not sure if this is the background to the question, but can confirm that rate coefficients measured several months apart under the same conditions gave the same result (to better than 2-3% percent). This reproducibility is largely through use of in-situ optical monitoring of NO<sub>2</sub>.

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Why did the authors not extend their 273K experiments to 760 Torr to provide a direct comparison with the results of D'Ottone et al.

The difference (in  $k_5$ ) when going from 298 K to 273 K is not great. We preferred to extend the T dependence towards lower temperatures in order to better define the T-dependence.

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Parameterizations:

Although this work contains an extensive discussion of the data parameterization there is no discussion of the fact that this is a two channel reaction and the parameters for each channel are likely to be different and, most critically, only the HNO<sub>3</sub> channel is likely to act as an OH termination step in the atmosphere. This seems to be certainly the case in modeling urban pollution events. The main reason for using the IUPAC rather than the NASA formalism is that the IUPAC provides values of  $k_0$  and  $k_\infty$  that are physically meaningful and can be compared with theory and experiment i.e. indirect determinations of  $k_\infty$ . If one applies a single parameterization to this dataset I don't really see what difference there is between using the IUPAC or NASA formalism. The parameters lose their physical meaning. The work here provides the sum of the rate coefficients for both channels in N<sub>2</sub>. This should not be used in atmospheric models and corrections for the lower third body efficiency in air and the HNO<sub>3</sub> branching ratio need to be taken into account. This should be stated explicitly in the manuscript.

In our manuscript, we indicate that the differences between IUPAC and JPL parametrizations are more than just a formalism issue. We showed that the choice of  $F_c$  as well as the decision to parametrize  $k(M, T)$  using low pressure limit rate constant  $k_0$  and high pressure limit rate constant  $k_\infty$  obtained from measurements can lead to significant errors.

Accurate values of  $k_5$  represent an important step to understanding the impact of the title reaction in atmospheric chemistry. We agree totally that, ideally, our parameterization of  $k_5$  needs to be combined with temperature and pressure dependent branching ratios for formation of HNO<sub>3</sub> and

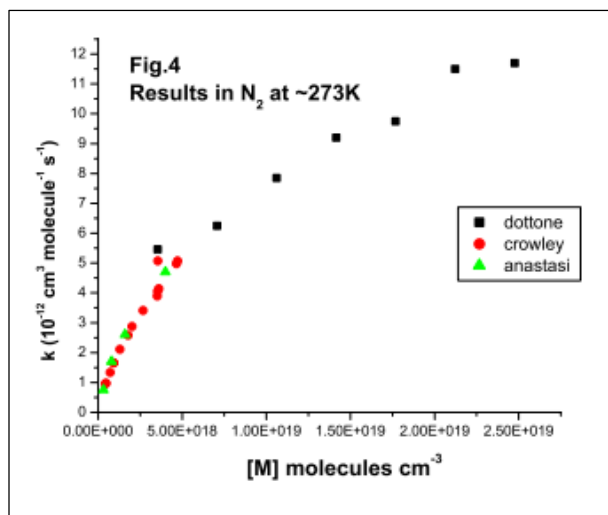
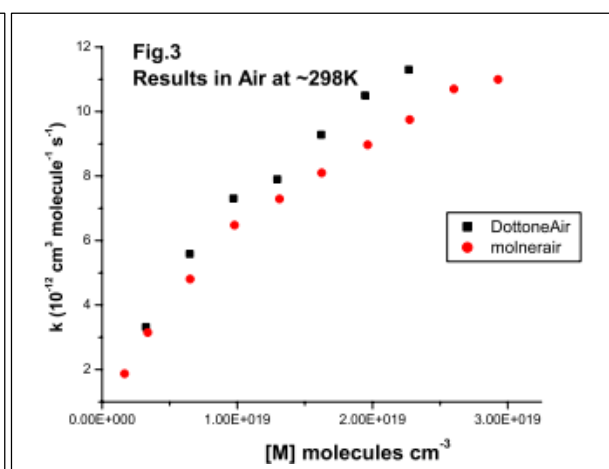
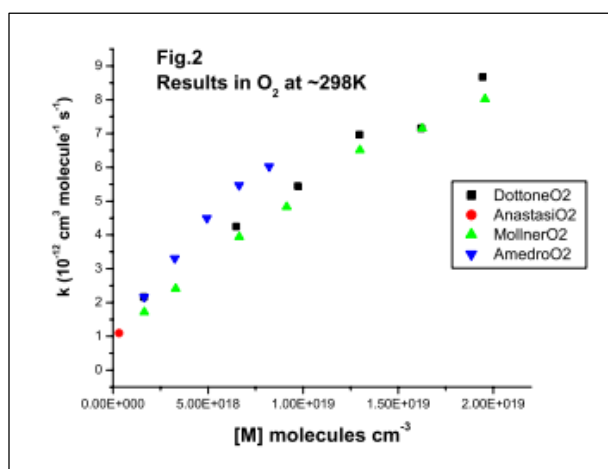
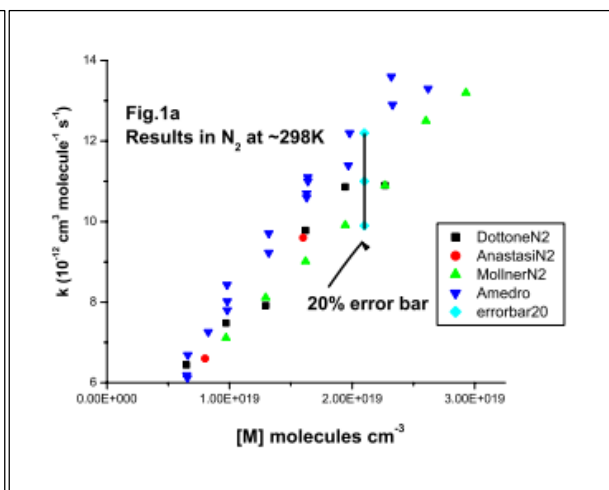
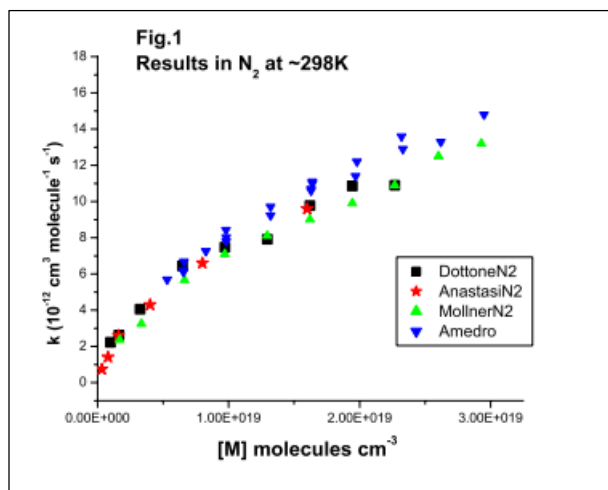
HOONO in order to rigorously assess the impact of the title reaction. We have added the following text:

**Introduction:** The fate of HOONO is thought to be dominated by thermal decomposition at temperatures typical of the mid-latitude boundary layer, with the reaction with OH and photolysis potentially contributing at higher altitudes and lower temperatures where its thermal lifetime is longer. The impact of the title reaction as a HOx and NO<sub>x</sub> sink thus depends on the relative efficiency of formation of HNO<sub>3</sub> and HOONO and the fate of HOONO.

**Introduction:** We note that the rate coefficients we obtain represent the total loss rate coefficient ( $k_5$ ) for OH loss (i.e. the sum of  $k_{5a}$  and  $k_{5b}$ ).

**Conclusions:** We derive a parameterisation of the overall rate coefficient and show that present, divergent evaluations of  $k_5$  result in significant differences, both underestimating and overestimating the rate coefficient in different parts of the atmosphere. Further study on the temperature and pressure dependence of the branching ratios to HNO<sub>3</sub> and HOONO formation as well as on the atmospheric fate of HOONO are required to fully understand and model the atmospheric impact of the title reaction.

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[2] D'Ottone, L., Campuzano-Jost, P., Bauer, D., and Hynes, A. J.: A pulsed laser photolysis-pulsed laser induced fluorescence study of the kinetics of the gas-phase reaction of OH with NO<sub>2</sub>, *J. Phys. Chem. A*, 105, 10538-10543, 2001.

[3] 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.

[4] Manuscript in review

[5] Donahue, N. M., Dubey, M. K., Mohrschladt, R., Demerjian, K. L., and Anderson, J. G.: High-pressure flow study of the reactions OH+NO<sub>x</sub>→HONO<sub>x</sub>: Errors in the falloff region, *J. Geophys. Res. -Atmos.*, 102, 6159-6168, 1997.