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Atmospheric Chemistry and Physics Discussions

Interactive comment on “Kinetics of the OH + NO_2 reaction: Rate coefficients (217–333 K, 16–1200 mbar) and fall-off parameters for N_2 and O_2 bath-gases” *by* Damien Amedro et al.

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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 NO2. 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, O3 etc in global models. As noted in the manuscript it is

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Discussion paper

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 HNO3 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 O2 and N2 have significantly different three body efficiencies for the total reaction hence measurements in N2 are not adequate for modeling. It is also unclear if this unusual difference is applicable to both channels or just to the HNO3 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 exaggereated. In this manuscript the authors suggest that “In-situ measurement of NO2 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 N2, and, because it is now clear that N2 and O2 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 NO2. 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 ± 0.1 x 10-11 . All these studies monitor the sum of channels producing

HNO3 and HOONO and, as reported by Molner, 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 paramatization, using either the JPL or IUPAC formulism should encompass all of these results. For most studies of chemical kinetics the agreement between these studies would be considered excellent. Figure 2 shows a comparison of the data in O2. 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 so direct comparisons is not possible. 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 N2 and O2. Finally Fig. 4 shows results at 273 K in N2 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. My calculations converting Torr at specific temperatures to total number density are not consistent with those in the manuscript, can the authors please check. Why were the $\sim$ room temperature experiments performed at 293K making a direct comparison with three prior datasets difficult. Given that the results in O2 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. Were O2 experiments performed after the N2 results? 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.

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 HNO3 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 formulism is that the IUPAC provides values of k0 and k∞. that are physically meaningful and can be compared with theory and experiment i.e. indirect determinations of k∞. If one applies a single parameterization to this dataset I don't really see what difference there is between using the IUPAC or NASA formulism. The parameters loose their physical meaning. The work here provides the sum of the rate coefficients for both channels in N2. This should not be used in atmospheric models and corrections for the lower third body efficiency in air and the HNO3 branching ratio need to be taken into account. This should be stated explicitly in the manuscript. References:

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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 NO2, 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] Manscript 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+NOx->HONOx: Errors in the falloff region, J. Geophys. Res. -Atmos., 102, 6159-6168, 1997.

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2019.

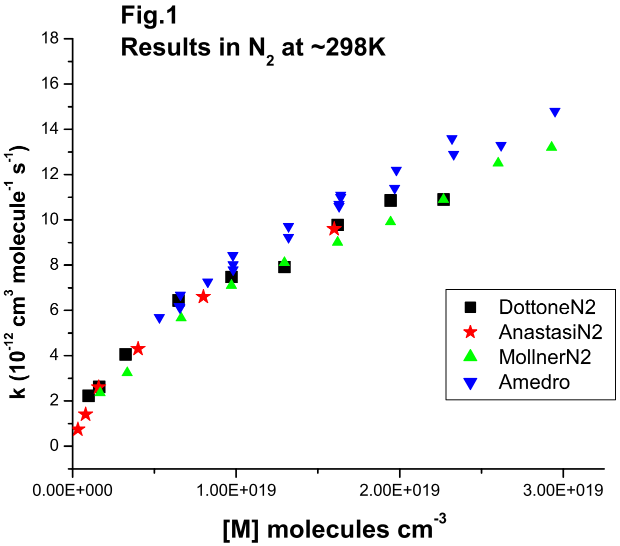
Fig.1
Results in N2 at ~298K
k (10-12 cm3 molecule-1 s-1)
0
2
4
6
8
10
12
14
16
18
0.00E+000
1.00E+019
2.00E+019
3.00E+019
[M] molecules cm-3
DottoneN2
AnastasiN2
MollnerN2
Amedro

Fig. 1.

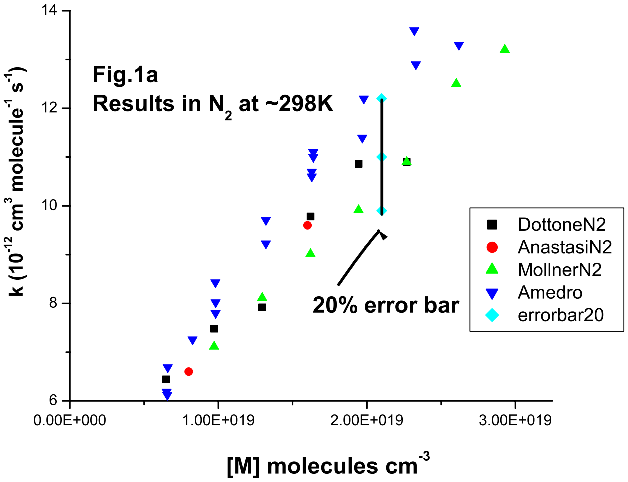

Fig. 2.

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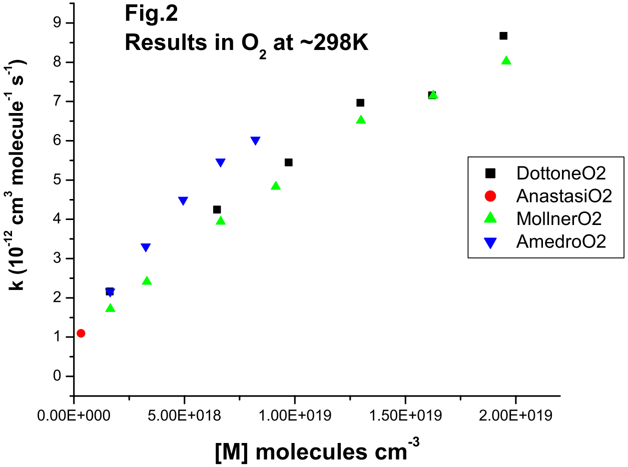
Fig.2
Results in O_2 at ~298K
k (10^{-12} cm^3 $molecule^{-1}$ s^{-1})
9
8
7
6
5
4
3
2
1
0
0.00E+000
5.00E+018
1.00E+019
1.50E+019
2.00E+019
[M] molecules cm^{-3}
■ DottoneO2
● AnastasiO2
▲ MollnerO2
▼ AmedroO2

Fig. 3.

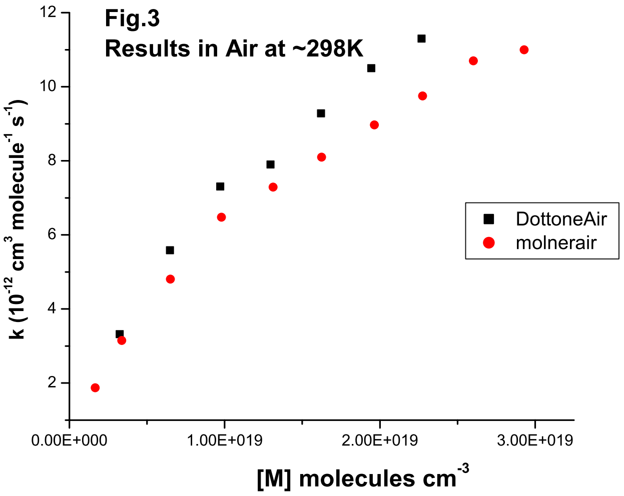

Fig. 4.

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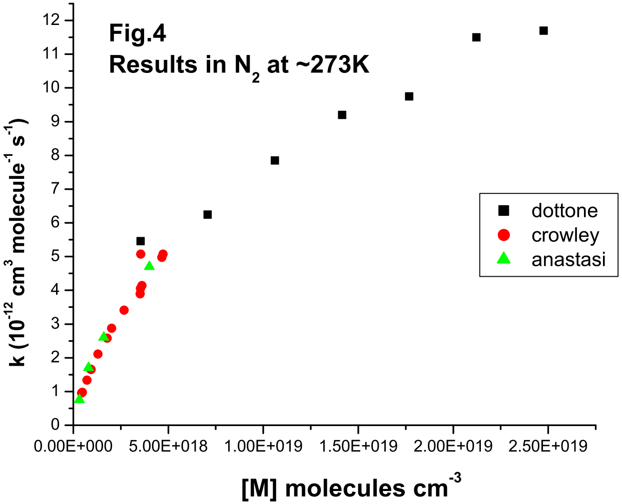

Fig. 5.

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