

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

Referee: Paul Seakins

Comment

This paper reports a very careful study on the reaction of the OH radical with nitric acid (HNO₃). Technically, this is a very difficult reaction to study, but it is important to generate precise and accurate rate coefficients as this reaction is vital in controlling HNO₃/NO_x ratios. Due to the atmospheric relevance, this material is appropriate for publication in ACP. I have no significant concerns about the paper, which I strongly recommend for publication, however, as well as some minor details listed below, there are a couple of issues that I would like the authors to consider for the final publication.

Reply

We thank Dr. Seakins for this careful review and very positive assessment of our manuscript

Comment

1. The reaction shows interesting temperature and pressure behaviour. Although ACP is not the vehicle for a detailed discussion of the fundamental mechanisms, I would ask the authors to consider including a brief rationale of the physical model for two reasons. Firstly, it would illustrate to potential users (modellers primarily?) the issues that need to be considered in laboratory studies, not just the technical issues as detailed here, but also the theoretical understanding. The importance of conveying such information to a wider audience was highlighted in a recent article by Burkholder et al. in ES&T. Secondly, and this is related to the next point, understanding the mechanism allows for a better assessment of whether the parameterizations are valid outside of the measurement regime.

Reply

The model used to parameterise the data was developed by Lamb et al. and is consistent with a reaction that proceeds via formation of an association complex, the fate of which is already described at the bottom of page 2. As this has been discussed many times in various publications dealing with the kinetics of this reaction (which are all cited) we see no real benefit in repeating this here. Note that we have modified the form of the equation (mathematically equivalent) to be consistent with its previous usage.

We have added text to encourage high level theoretical studies of this reaction that provide a working theoretical framework for confident prediction of coefficients outside of the experimentally accessible temperature range:

High-level theoretical studies of the title reaction and experimental studies at temperatures not accessible by standard methods (e.g. using Laval nozzle expansions) would be useful to provide a working theoretical framework and a more physical parameterisation of the data, which in turn allow for confident prediction of rate coefficients outside of the presently available temperature range.

Comment

2. As mentioned above, the data have been parameterized, which will be useful to modellers, but there is no mention of the uncertainty in the parameterization constants or on the validity of the parameterization outside the experimental range. The biggest differences in the ratio of rate coefficients reported in Fig 11 a are for 180 K, significantly below the current measurements and those of Brown et al. Uncertainties in parameterizations can be difficult to present as the parameters can be highly correlated and simple error ranges may underestimate the total uncertainty. However, some discussion needs to be presented on both of these issues (uncertainty and validity beyond experimental range).

Reply

Although 180 K is "only" 23 K cooler than the lowest temperature of Brown et al., this is a valid point. We have added text and a Figure that addresses the uncertainty of the parameterisation within and

outside the range of temperatures covered experimentally:

At low temperatures (for which the loss of HNO₃ by reaction with OH is most important) the parameters capture the pressure and temperature dependence reasonably well. The agreement is illustrated in Fig. S4 of the supplementary information which plots the measured and parameterised rate coefficient against each other. This plot has a slope of 0.99 ± 0.01 with $R^2 = 0.99$ and indicates only slight deviation from a linear relationship at the highest temperatures. The confidence limits of the fit-line are within the scatter of the experiments, suggesting that, between ≈ 200 and 290 K) the parameterisation does not introduce uncertainty beyond that associated with the experiments. We thus estimate an overall uncertainty of $\approx 15\%$ in the parameterised rate coefficients within the range of temperatures studied experimentally and those relevant for the OH-initiated removal of atmospheric HNO₃, i.e. 200 – 290 K. Extrapolation to temperatures lower than those covered experimentally may result in larger uncertainty as becomes apparent when comparing the new and old parameterisations.

Comment

1. Give values of k₅ in the abstract – at least room temperature and atms pressure.

Reply

Temperatures close to room temperature and 1 bar are found in the planetary boundary layer, where HNO₃ is lost by deposition and not (significantly) by reaction with OH. The focus of this paper is on the atmospherically important low temperature kinetics of the reaction and listing k₅ at room temperature and 1 bar in the abstract (conditions where none of the present experiments were conducted) would not provide useful information.

Comment

2. page 2 – Give an example of the magnitude of the measured:modelled HNO₃ concentrations and HNO₃:NO_x ratios.

Reply

The abundance of HNO₃ and the HNO₃:NO_x ratio is extremely variable. There are large horizontal and vertical gradients and great differences in e.g. the boundary layer, the lower troposphere and the stratosphere. There is no “typical” value and a single example (or even two or three) would not inform the interested reader. A discussion of this is covered in many papers that deal with the measurements of these trace gases in the atmosphere, several of which we already cite.

Comment

3. page 3 – Give typical laser fluence (or range of fluence) in mJ cm⁻² pulse⁻¹ .

Reply

This information is now given in section 2.2:

The exciplex laser fluence (2-4 mJ cm⁻² pulse⁻¹) was adjusted so that the [HNO₃]/[OH] ratio was always $> 10^4$ ensuring first-order conditions and suppressing interfering secondary OH chemistry (see section 3.3).

Comment

4. page 8, Section 3.3. I would suggest re-titling as Impurities and Secondary Reactions.

Reply

Section 3.3 has been re-titled:

3.3 Impurities and secondary chemistry

Comment

5. page 9 – Clarify the results of the air vs N₂ experiment. A difference within 4% is reported. My assumption would be that therefore no significant difference between k₅ reported in air vs N₂, but this should be clarified.

Reply

Correct. We have added:

Within experimental uncertainty and the temperature and pressure range studied, there is thus no significant dependence of k_5 on use of N_2 or air bath gases.

Comment

6. page 10, Terminology – k_0 is not the best term to describe the pressure independent term in k_5 . k_0 has a specific meaning within Lindemann-Hinshelwood theory and therefore there is potential for confusion.

Reply

We have replaced k_0 with k .

Comment

7. page 12, Fig 11 – The text at the top of p12 refers to differences between current parameterization and IUPAC and JPL, but only IUPAC data presented in the Figure.

Reply

AS both IUPAC and JPL adopt the same parameters, the recommendations are identical. We have modified Fig. 11 and the caption to mention both IUPAC and JPL.

Comment

8. p13 – The final sentence of section 3.5 needs expanding to make it clear why a 6% change is significant

Reply

We agree that this is a rather ambiguous statement. However, it is difficult to be more quantitative as no firm definition of what represents a significant change in e.g. the amounts of photochemically generated ozone exists. Instead we now indicate that, in terms of sensitivity to rate constant changes, the reaction between OH and HNO_3 is in the top ten reactions that impact on the global O₃ burden and cite a very recent paper (Newsome and Evans, 2017) in ACPD: Given the importance of HNO_3 to NO_x partitioning in governing rates of photochemical ozone production (Newsome and Evans, 2017) and the important role of the OH + HNO_3 reaction, the impact of the changes in k_5 are significant.

Comment

9. References – Jolly et al. CPL, should be Chem. Phys. Lett. Several references need correcting for subscripts and capitals (e.g. Uv)

Reply

Corrections made

Comment

10. Figures – Would suggest more use of colour for Figs 4 onwards. Because the authors have chosen symbols etc carefully, most figs work fine in b/w, but most could be enhanced with a bit of colour.

Reply

Figures 7 and 10 have now been reproduced with colour.

Comment

11. Figs 11 and 12 – Captions need a bit more detail. e.g. Fig 11 'change in rate coefficient k_5 ' – compared to what? Is it the new parameterization including this work and literature or just this work?

Reply

We have clarified this by writing (in the caption):

Figure 11

Lower panel: Change in rate coefficient k_5 (new) compared to previous IUPAC and JPL evaluations. The percentage change was calculated using annually and zonally averaged temperatures and

pressure in the EMAC model.

Figure 12

The contours indicate the percentage change in the predicted mixing ratios (zonal and annual average) of HNO₃ (upper panel) and NO_x (lower panel), which result from the new parameterization of k₅ compared to the IUPAC and JPL recommended values.

Referee 2

Comment

The authors report rate coefficients for the reaction of OH with HNO₃ over a wide range of temperature and pressure. The reaction is of atmospheric significance as it directly influences NO_x levels and the NO_x/HNO₃ ratio. This is an excellent paper, detailing a careful and thorough study of the reaction, and I have no hesitation in recommending its publication (subject to consideration of a few minor points made below). In particular, I applaud the efforts made by the authors to measure as best as possible in situ the HNO₃ concentrations, as well as the levels of numerous possible interferences, to provide what is a very reliable set of data.

Reply

We thank referee 2 for this careful review and very positive assessment of our manuscript

Comment

Page 4, line 20 – ‘concentration at the centre . . .’

Reply

Correction made

Comment

You might mention in some way in the caption to Figure 2 that the pathlengths for the two cells are different, so that the ratio of the OD's are not equal to the ratio of the cross sections obtained.

Reply

In the caption to Figure 2 we now write:

The inset shows the linear relation between optical densities (OD) at 184.95 nm (optical path-length = 43.8 cm) and 213.86 nm (optical path-length = 34.8 cm).

Comment

Again, I applaud the efforts made to quantify HNO₃ levels via TPEFS. But, is it not the case that the TPEFS is calibrated by measuring the [HNO₃] downstream, making the argument partially circular? I understand that the agreement over a large range of temperatures (with a small possible downturn at low T) is very re-assuring, but could it be that there is a little bit of loss occurring at all temperatures that puts some kind of systematic bias to the whole dataset? If I am correct in this assessment, maybe just one sentence to clarify assumptions made here would be warranted.

Reply

The point of the TPEFS is to look for gradients in HNO₃ concentrations across the diameter of the reactor and not to check the concentration in an absolute sense. Our kinetic data do not rely on calibrations of the TPEFS signal in any way. The only assumption made is that there is no gradient in HNO₃ concentrations at warmer temperatures where its partitioning to the reactor walls is less important.

Comment

Page 7, line 3 - missing a period after (1985).

Page 9, line 16 – ‘determinations’ should be plural.

Reply

Corrections made

Comment

Page 12 and Figure 11 – Can the authors say anything about why the difference between ‘old’ and ‘new’ suddenly increases at 180 K?

Reply

At the lowest temperatures (and pressures distinct from the low pressure limiting regime) the reaction will proceed mainly via the stabilised association complex and the rate coefficient is influenced most by the values of k_c at different temperatures. Indeed, the largest differences between the present recommendation and the IUPAC and JPL parameters (based on Brown et al., 1999) is found in the terms for k_c . k_c (new) = $8.46 \times 10^{-32} \exp(525/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$, and k_c (old) = $6.51 \times 10^{-34} \exp(1335/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$. We have added text to illustrate this:

At pressures (< 200 mbar) and temperatures (< 240 K) typically associated with the upper troposphere and lower stratosphere, the new parameterisation results in lower values of k_5 with a decrease in k_5 of up to 20% at 180 K, which is beyond the range of temperatures studied experimentally. As the parameters for k_Δ and k are similar to those previously recommended, the large difference at 180 K most likely reflects changes in the temperature dependence of k_c with the older value represented by $6.51 \times 10^{-34} \exp(1335/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ compared to the present value of $8.46 \times 10^{-32} \exp(525/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$.