

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

Editor's comments

Non-public comments to the Author:

Congratulations on a nice piece of experimental work on an important topic. We look forward to seeing a revised final version of the manuscript to be published in ACP.

We thank the editor for his positive assessment of our work.

Comments to the Author:

The revised version of the manuscript addresses most, but not all, of the comments from three reviewers, and one public comment. Overall there is consensus that the work is generally of high quality, and should ultimately be published. The authors are asked to provide revised files that address the following minor revisions. The Editor may decide to consult with reviewers, if needed, but the revisions are deemed straightforward. They aim to maximize transparency about sources of systematic bias, and the uncertainty over a wide range of temperatures for atmospheric modeling in air.

We have modified the manuscript in line with these comments. The comment of referee #1 regarding documentation of the data obtained using a lower repetition rate was indeed overlooked. We address this and the other comments below.

Minor revisions:

1) The authors agree with the error identified in their analysis of literature spectra noted in Frank Winiberg's comment. This error has been corrected, and does not affect the presented data or analysis, as the authors note. However, it is relevant since the implication of the smaller differences to the NO₂ literature data suggest that it is unlikely the only cause for the differences in rate constants determined here and earlier by Mollner et al 2010. As reviewer #3 correctly points out, "there are other possible sources of systematic error that affect the rate constant determinations although these are not particularly obvious."

The current response to reviewer #3 focuses exclusively on NO₂ calibrations. The response on this important point is certainly appropriate, but the lengthy discussion dilutes somewhat the broader point. In particular, the authors did not respond to reviewer #3's broader point: what other sources of systematic bias could there be?

The dominant (identified) source of potential systemic bias is the measurement of the NO₂ concentration. We already discuss other sources of bias that we identified including 1) secondary reactions of OH (hence the experiments in which the initial OH concentration and repetition rate were varied) and 2) the correction for NO₂ dimerization at low temperature / high concentrations (hence the experiments with LIF detection of NO₂). If we had been aware of a further potential causes of systematic bias, we would have mentioned it in the manuscript, thereby describing our efforts to eliminate / correct it. We have added extra details about the estimation of uncertainty associated with the values of k_5 we present and modified the rate coefficients listed in Table 1 to reflect total uncertainty:

The total uncertainty associated with each value of k_5 is listed in Table 1 and considers uncertainty in NO₂ concentrations measurement (i.e. uncertainty associated with NO₂ cross-

sections and the equilibrium constant for NO₂ dimerisation) as well as statistical error on the fits to derive k' (Fig. 6). The expression used to calculate the total overall uncertainty for each value of k_5 is given in the supplementary information and results in ~8% at T > 240 K and ~16% for measurements at 217 and 229 K.

In the SI, we write:

Calculation of uncertainty associated with determination of k_5

The total uncertainty stems from:

- 1) The statistical error of the linear fit of the plot of k' versus [NO₂] (σ_{meas})
- 2) The uncertainty associated with [NO₂] measurements using optical absorption ($\sigma_{[NO_2]} = 3\%$). This value was obtained from the spread in cross-sections of the different reference spectra.
- 3) the NO₂ concentration correction due to the N₂O₄ formation at low temperatures ($\sigma_{N_2O_4\ corr}$) which is a function of the magnitude of the correction, and the error associated with K_{eq} (which we conservatively derive from the difference in values of K_{eq} preferred by the NASA and IUPAC panels).

The formula used is:

$$\sigma_{k_5} = 2 \times k_5 \times \sqrt{\left(\frac{\sigma_{meas}}{k_5}\right)^2 + (\sigma_{[NO_2]})^2 + (\sigma_{N_2O_4\ corr})^2}$$

$$\text{where } \sigma_{N_2O_4\ corr} = \left(1 - \frac{[NO_2]_{ave}}{[NO_2]_0}\right) \times \sqrt{\left(\frac{\sigma_{[NO_2]_{ave}}}{[NO_2]_{ave}}\right)^2 + (\sigma_{K_{eq}})^2}$$

where $[NO_2]_{ave}$ is the average of the corrected [NO₂] using NASA and IUPAC equilibrium constant, $[NO_2]_0$ is the NO₂ concentration measured optically, $\sigma_{[NO_2]_{ave}}$ is the standard deviation of $[NO_2]_{ave}$ and $\sigma_{K_{eq}}$ is the uncertainty of the equilibrium constant which we set to 50%.

Please add a paragraph, ideally supported by a Table, that constructs a comprehensive error budget of the present work as it relates to air (!).

Related to this, reviewer #2 notes the need for "corrections for the lower third body efficiency in air". As the authors point out this correction is small at 293K. Is it a source of systematic bias in air? The temperature dependence is not well known. How much of an effect is expected at other temperatures?

Please make an effort to provide a concise summary to make systematic bias related to atmospheric use in air explicit.

The issue here appears to be the assumption that a parameterization, based on the temperature and pressure dependent data we obtained in N₂ and the (small) effect of replacing N₂ with air as bath gas at 293 K correctly takes the O₂ effect into account, i.e. does the effect of O₂ remain constant at different temperatures, or, more specifically, do $k_0(N_2)$ and $k_0(O_2)$ have the same temperature dependence (parameter m)?

First, we note that our results confirmed the two values of the relative O₂ / N₂ 3rd-body efficiency (~0.7) previously reported. This number is therefore robust.

Second, there is no reason to expect a difference in the temperature dependence of k_0 for different bath gases, that would be sufficiently large to reduce the accuracy of our rate coefficients over the small range of atmospheric temperatures. When comparing literature values of k_0 obtained in He, Ar and N₂ (which have vastly different 3rd-body efficiencies) we find very a similar temperature dependence in k_0 (Anderson, J. G., Margitan, J. J., and Kaufman, F., J. Chem. Phys., 60, 3310-3317, 1974.)

We do not expect that the assumption of no temperature dependence in the relative 3rd-body efficiency of N₂ and O₂ will increase the uncertainty of a fall-off parameterisation above that already quoted in the manuscript. We have added some text to mention this:

We have not investigated the temperature dependence of the low pressure rate coefficient (m) in O₂ but note that previous studies of k_5 close to the low pressure limit indicate the same values of m for He, N₂ and Ar even though the 3rd-body efficiencies of these three bath-gases are very different (Anderson et al., 1974). There is no reason to expect that this would be different for O₂ and therefore do not consider assumption of the same value of m for N₂ and O₂ to be a source of uncertainty in deriving rate coefficients for atmospheric conditions (i.e. a mixture of N₂ and O₂).

2) Reviewer #1 writes: ... the manuscript states "We additionally carried out some experiments at a lower repetition rate to rule out any influence of product build-up on the measured rate coefficient." I would like the authors to document these experiments (at least in the Supplementary Information). (end quote)

The response to this by the authors appears to be missing. At least from the provided files it is unclear if changes to the Supplementary Information have been made. Please add the requested information.

The rate coefficient obtained at low repetition rate was already listed in Table 1, but was not identified. We added a foot-note in the table to the rate coefficient that was measured at a lower repetition rate (5 Hz instead of 10 Hz) and added the text below at the bottom of Table 1.

Experiment performed at a laser repetition rate of 5 Hz (instead of the usual 10 Hz).

We now also mention this in section 2.1:

We additionally carried out some experiments at a lower repetition rate (5 Hz) to help rule out any influence of product build-up on the measured rate coefficient.

And in section 3.2:

Reducing the laser repetition rate from 10 Hz to 5 Hz had no discernible effect on the value of k_5 retrieved ($10.6 \pm 0.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 10 Hz and $10.7 \pm 0.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 5 Hz, see Table 1, rate coefficients at 293 K and 498.5 Torr).

3) Reviewer #2 writes: For use in atmospheric models "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."

The authors responses acknowledge that questions about HOONO vs HNO₃ branching ratios are beyond the scope of this paper, but this should also be stated in the final manuscript. Please add in the introduction on page 2, line 12 "...HOONO [, which are beyond the scope of this study]."

This has been done as suggested. We write:

The impact of the title reaction as a HO_x and NO_x sink thus depends on the relative efficiency of formation of HNO₃ and HOONO and the fate of HOONO, investigation of which are beyond the scope of this study.

We also write:

We emphasize that, for use in atmospheric models, both the lower third body of efficiency of air compared to N₂ and the branching ratio to HNO₃ or HOONO formation need to be considered.

The comment from reviewer #2 also relates to the paragraph on "Sources of systematic bias and atmospheric implications" to be added in the discussion (see above point #1).

We have added a detailed description of the uncertainties associated with our values of k_5 and also indicated that calculation of k_5 for the purpose of atmospheric modelling requires that the different third-body efficiency of N₂ and O₂ (presently ignored by IUPAC) needs to be taken into account.
