Kinetics of the OH + NO_2 reaction: effect of water vapour and new parameterization for global modelling

Damien Amedro, Matias Berasategui, Arne J. C. Bunkan, Andrea Pozzer, Jos Lelieveld, and John N. Crowley
Department of Atmospheric Chemistry, Max Planck Institute for Chemistry, 55128 Mainz, Germany

Correspondence: John N. Crowley (john.crowley@mpic.de)

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Abstract. The effect of water vapour on the rate coefficient for the atmospherically important, termolecular reaction between OH and NO_2 was determined in He–H_2O (277, 291, and 332 K) and N_2–H_2O bath gases (292 K). Combining pulsed-laser photolytic generation of OH and its detection by laser-induced fluorescence (PLP-LIF) with in situ, optical measurement of both NO_2 and H_2O, we were able to show that (in contrast to previous investigations) the presence of H_2O increases the rate coefficient significantly. We derive a rate coefficient for H_2O bath gas at the low-pressure limit (k_{H_2O}^0) of 1.59 \times 10^{-30} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}. This indicates that H_2O is a more efficient collisional quencher (by a factor of \approx 6) of the initially formed HO–NO_2 association complex than N_2, and it is a factor of \approx 8 more efficient than O_2. Ignoring the effect of water vapour will lead to an underestimation of the rate coefficient by up to 15%, e.g. in the tropical boundary layer. Combining the new experimental results from this study with those from our previous paper in which we report rate coefficients obtained in N_2 and O_2 bath gases (Amedro et al., 2019), we derive a new parameterization for atmospheric modelling of the OH + NO_2 reaction and use this in a chemical transport model (EMAC) to examine the impact of the new data on the global distribution of NO_2, HNO_3, and OH. Use of the new parameters (rather than those given in the IUPAC and NASA evaluations) results in significant changes in the HNO_3/NO_2 ratio and NO_2 concentrations (the sign of which depends on which evaluation is used as reference). The model predicts the presence of HOONO (formed along with HNO_3 in the title reaction) in concentrations similar to those of HO_2NO_2 at the tropical tropopause.

1 Introduction

In our recent study of the title reaction (Amedro et al., 2019), we reported extensive measurements of the rate constant (k_1) for the termolecular reaction between OH and NO_2 (Reaction R1) in N_2 and O_2 bath gas over a large range of temperatures and pressures.

\[
\text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M}, \quad \text{(R1a)}
\]
\[
\rightarrow \text{HOONO} + \text{M}. \quad \text{(R1b)}
\]

Reaction (R1) converts NO_2 to nitric acid (HNO_3) and peroxynitrous acid (HOONO), and its rate strongly influences the relative abundance of atmospheric NO_x (NO_2 + NO) and longer-lived “reservoirs” of NO_x, which include, for example, HNO_3 and organic nitrates. It also converts OH (the main initiator of atmospheric oxidation) to a long-lived reservoir (HNO_3). As the abundances of OH and NO_2 directly impact on photochemical ozone formation and the lifetimes of greenhouse gases, Reaction (R1) may be considered one of the most important gas-phase processes in atmospheric science (Newsome and Evans, 2017). As outlined by Amedro et al. (2019), the rate coefficients and product branching for this reaction are dependent on pressure and temperature and also on the bath-gas identity, i.e. the identity of the collision partner (M in Reaction R1). The efficiency per collision of energy transfer from the initially “hot” association complex to bath gas can vary considerably, with more complex bath gases possessing more degrees of freedom and bonds with similar vibrational frequencies to those in the association complex being generally more efficient. In this sense, we may expect H_2O to be better than N_2 or O_2 in quenching [HO–NO_2]_x.

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In this second part of our study of the reaction between OH and NO₂, we extend the experiments to H₂O and He bath gases. After N₂ (≈ 78 %) and O₂ (≈ 21 %), water vapour is the third most abundant gaseous species in the lower atmosphere. Its concentration is highly variable in time and space, varying in mixing ratio from a few percent at sea level to parts-per-million levels in the stratosphere. Most of the atmosphere’s water vapour is present in the planetary boundary layer where its average mixing ratio on the global scale is ≈ 1 % but which may exceed 5 % in tropical regions.

The effect of water vapour on gas-phase radical reactions has been the subject of numerous studies (Buszek et al., 2011) and is sometimes interpreted in terms of formation of H₂O-radical complexes leading, via a chaperone-type mechanism, to an increase in the rate constant. An important example of this is the HO₂ self-reaction for which the rate constant increases by a factor of up to 2 in the presence of water vapour due to formation of an HO₂–H₂O complex (Lii et al., 1981; Kircher and Sander, 1984). Theoretical calculations (Alldred et al., 2006; Sadanaga et al., 2006; Thomsen et al., 2012) suggest that, under experimental conditions, the fraction of OH and NO₂ clustered with H₂O is < 0.1 %, which is insufficient to significantly impact k₁.

On the other hand, the role of H₂O as a collision partner in termolecular, atmospheric reactions has rarely been reported though its potential impact has been highlighted (Troe, 2003). Indeed, water vapour is known to be a more efficient third-body collider, by up to an order of magnitude, compared to N₂ in termolecular reactions such as H + H + M, H + OH + M, and H + O₂ + M (Getzinger and Blair, 1969; Michael et al., 2002; Fernandes et al., 2008; Shao et al., 2019).

The conclusions of three previous experiments examining the role of H₂O in kinetic studies of Reaction (R1) are highly divergent, with the addition of H₂O found to (1) increase the rate coefficient (Simonaitis and Heicklen, 1972), (2) have no measurable effect (D’Ottone et al., 2001), or (3) even reduce it (Sadanaga et al., 2006). The overall aim of this research was to clarify these differences and provide quantitative data on the third-body efficiency of H₂O for the title reaction. Based on the kinetic data for the water-vapour effect reported in this paper and in N₂ and O₂ presented in the first part of this study (Amedro et al., 2019), we have generated a new parameterization for the overall rate coefficient, k₁, and examined its impact on atmospheric OH, NOₓ, and NO₃ in a global chemical transport model.

2 Experimental details

The details of the experimental set-up have been published previously (Wollenhaupt et al., 2000; Amedro et al., 2019), and only a brief description is given here.

### Table 1. Measurements of k₁ in He bath gas.

| T (K) | p (Torr) | M² | OH precursor | k₁ \(^{b}\) |
|-------|---------|----|--------------|-----------|
| 277   | 48.6    | 1.68 | H₂O₂        | 1.59 ± 0.14 |
|       |         |     | H₂O₂        | 0.75 ± 0.07 |
|       | 50.0    | 1.65 | H₂O₂        | 1.37 ± 0.08 |
|       | 75.1    | 2.47 | H₂O₂        | 1.88 ± 0.12 |
|       | 102.9   | 3.39 | HNO₃        | 2.32 ± 0.15 |
| 292   | 206.9   | 6.81 | HNO₃        | 3.73 ± 0.25 |
|       | 300.7   | 9.89 | HNO₃        | 4.64 ± 0.29 |
|       | 405.8   | 13.35| HNO₃        | 5.54 ± 0.37 |
|       | 495.6   | 16.30| HNO₃        | 6.29 ± 0.40 |
|       | 595.0   | 19.57| HNO₃        | 6.83 ± 0.42 |
|       | 689.1   | 22.67| HNO₃        | 7.46 ± 0.46 |
| 332   | 28.1    | 0.82 | H₂O₂        | 0.60 ± 0.06 |
|       | 56.8    | 1.65 | H₂O₂        | 0.99 ± 0.08 |
|       | 85.4    | 2.48 | H₂O₂        | 1.34 ± 0.10 |

| \(^{a}\) Molecular density M(He) in units of 10\(^{18}\) molecule cm\(^{-3}\), \(^{b}\) Units of 10\(^{-12}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\). The errors are 2\sigma total uncertainty. \(^{c}\) Concentration range of HNO₃ = 5–14 × 10\(^{13}\) molecule cm\(^{-3}\). \(^{d}\) Concentration range of HNO₃ = 5–9 × 10\(^{13}\) molecule cm\(^{-3}\). |

2.1 PLP-LIF technique

The experiments were carried out in a quartz reactor of 500 cm\(^3\) volume, which was thermostatted to the desired temperature by circulating a 60 : 40 mixture of ethylene glycol–water. The pressure in the reactor was monitored with 100 and 1000 Torr capacitance manometers. Flow rates were chosen so that a fresh gas sample was available for photolysis at each laser pulse (laser frequency, 10 Hz), thus preventing build-up of products. Pulses of 248 nm laser light (≈ 20 ns) for OH generation from HNO₃, H₂O₂, and O₃/H₂O precursors were provided by an excimer laser (Compex 205 F, Coherent) operated using KrF:

\[
\text{HNO}_3 + h\nu(248\text{ nm}) \rightarrow \text{OH} + \text{NO}_2, \quad (R2)
\]

\[
\text{H}_2\text{O}_2 + h\nu(248\text{ nm}) \rightarrow 2\text{OH}, \quad (R3)
\]

\[
\text{O}_3 + h\nu(248\text{ nm}) \rightarrow \text{O}(^1\text{D}) + \text{O}_2, \quad (R4)
\]

\[
\text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{OH}. \quad (R5)
\]

OH concentrations (10\(^{11}\) to 10\(^{12}\) molecule cm\(^{-3}\)) were similar to those reported by Amedro et al. (2019) and the same arguments, which rule out a significant influence of secondary reactions, apply. The concentration ranges of the H₂O₂, HNO₃, and O₃ precursors are listed in the notes to Tables 1 and 2.

OH was detected following excitation of the OH \( A^2\Sigma(v' = 1) \leftarrow X^2\Pi(v'' = 0) \) transition (Q(11) (1) at 281.997 nm using a YAG-pumped dye laser (Quantel Brilliant B and Lambda-Physik Scanmate)). OH fluorescence
As discussed by Amedro et al. (2019), the determination of the NO\textsubscript{2} concentration is critical for accurate measurement of \(k_1\). We therefore deployed in situ, broadband (405–440 nm), and single-wavelength (365 nm) optical absorption spectroscopy techniques. The former was located prior (in flow) to the quartz reactor; the latter was located behind the quartz reactor. Using the broadband cell, the NO\textsubscript{2} concentration was retrieved by least square fitting from 405 to 440 nm to a reference spectrum (Vandaele et al., 2002) and degraded to the resolution of our spectrometer. Simultaneously, we measured \(\text{NO}_2\) at 365 nm using the absorption cross section of \(5.89 \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1}\), which was determined previously by Amedro et al. (2019), who give a detailed description of the NO\textsubscript{2} concentration measurements and the choice of reference spectrum. For the temperatures used in this study, corrections to the NO\textsubscript{2} concentration due to formation of the N\textsubscript{2}O\textsubscript{4} dimer were not necessary.

For the present experiments, a third absorption cell \(l = 40 \text{ cm}\) was placed downstream of the quartz reactor to measure the NO\textsubscript{2} concentration at 184.95 nm. This set-up used a low-pressure mercury Pen-Ray lamp isolated with a 185 nm interference filter as light source. Optical extinction was converted to concentrations using a cross section of \(7.14 \times 10^{-20} \text{ cm}^2 \text{ molecule}^{-1}\) (Cantrell et al., 1997).

### 2.3 Chemicals

\(\text{N}_2\) and He (Westfalen, 99.999 \%) were used without further purification. \(\text{H}_2\text{O}_2\) (AppliChem, 50 wt \%) was concentrated to \(>90\%\) wt by vacuum distillation. Anhydrous nitric acid was prepared by mixing KNO\textsubscript{3} (Sigma Aldrich, 99 \%) and \(\text{H}_2\text{SO}_4\) (Roth, 98 \%) and condensing HNO\textsubscript{3} vapour into a liquid-nitrogen trap. NO (Air Liquide, 3.5 \%) was purified of other nitrogen oxides by fractional vacuum distillation and then converted to NO\textsubscript{2} via reaction with a large excess of O\textsubscript{2}. The NO\textsubscript{2} thus made was trapped in liquid N\textsubscript{2}, and the excess O\textsubscript{2} was pumped out. The resulting NO\textsubscript{2} was stored as a mixture of \(\sim 0.5\%\) NO\textsubscript{2} in \(\text{N}_2\) or \(\sim 5.5\%\) NO\textsubscript{2} in He. Distilled H\textsubscript{2}O (Merck, liquid chromatography grade) was degassed before use and kept at constant temperature.

### 3 Results and discussion

#### 3.1 Measurements of \(k_1\) in He bath gas and comparison with literature

Our study of the role of H\textsubscript{2}O as collision partner in Reaction (R1) was carried out in mixtures of \(\text{He–H}_2\text{O}\) and \(\text{N}_2–\text{H}_2\text{O}\). In order to separate the effects of H\textsubscript{2}O and He, we also required accurate rate coefficients for pure He bath gas, which we describe below. As for the \(\text{N}_2\) and O\textsubscript{2} bath-gas datasets (Amedro et al., 2019), the experiments were carried out under pseudo-first-order conditions ([NO\textsubscript{2}] \(\gg\) [OH]) so that Eqs. (1)–(2) describe the decay of OH and the derivation of the bimolecular rate coefficient \(k_1\).

\[
[\text{OH}] = [\text{OH}]_0 \exp(-k't),
\]

where [OH]\textsubscript{0} is the concentration (molecule cm\textsuperscript{-3}) at time \(t\) after the laser pulse. \(k'\) is the pseudo-first-order rate coefficient and is defined as

\[
k' = k_1[\text{NO}_2] + k_d,
\]

where \(k_d\) (s\textsuperscript{-1}) accounts for OH loss due to diffusion out of the reaction zone and reaction with its photolytic precursors such as HNO\textsubscript{3} or H\textsubscript{2}O\textsubscript{2}.
An exemplary dataset illustrating OH decays and a plot of $k'$ versus $[\text{NO}_2]$ is given in Fig. S1 of the Supplement.

Values of $k_1$ obtained in He bath gas (25–690 Torr, 292 K) are summarized in Figs. 1 and 2 and listed in Table 1. The kinetics of termolecular reactions can be described by the Lindemann–Hinshelwood mechanism, whereby the rate constant at the low-pressure limit ($k_0$, units of cm$^6$ molecule$^{-2}$ s$^{-1}$) is proportional to the pressure, and at the high-pressure limit ($k_\infty$, units of cm$^3$ molecule$^{-1}$ s$^{-1}$) is independent of pressure. In the intermediate pressure range, the fall-off regime, the rate coefficient is a function of both low-pressure ($k_0$) and high-pressure ($k_\infty$) rate coefficients and the (reaction-partner-dependent) broadening factor $F$, which accounts for the lower rate constant measured in the fall-off regime than predicted by the Lindemann–Hinshelwood mechanism reactions (Troe, 1983). Under the conditions of temperature and pressure relevant for atmospheric chemistry, the title reaction is in the fall-off regime.

$$k = \frac{k_0 [M] k_\infty}{k_0 [M] + k_\infty F}$$  \hspace{1cm} (3)

The solid lines in Figs. 1 and 2 are fits according to the Troe formalism for termolecular reactions (Troe, 1983) as adopted by the IUPAC panel in their evaluation of atmospheric reactions:

$$k(PT) = \frac{k_0 \left( \frac{T}{T_0} \right)^{-m} [M] k_\infty \left( \frac{T}{T_0} \right)^{-n} F}{k_0 \left( \frac{T}{T_0} \right)^{-m} [M] + k_\infty \left( \frac{T}{T_0} \right)^{-n}}$$  \hspace{1cm} (4)

where $T$ is the temperature in kelvin, $[M]$ is the bath-gas concentration (molecule cm$^{-3}$), and $m$ and $n$ are dimensionless temperature exponents.

The broadening factor, $F$, is

$$\log F = \frac{\log F_c}{1 + \left[ \log \left( \frac{k_0 \left( \frac{T}{T_0} \right)^{-m} [M]}{k_\infty \left( \frac{T}{T_0} \right)^{-n}} \right) / N \right]^2},$$  \hspace{1cm} (5)

where $N = (0.75–1.27 \log F_c)$ and $F_c$ is the broadening factor at the centre of the fall-off curve.

As discussed in some detail in the first part of our studies of the title reaction (Amedro et al., 2019), the low- and high-pressure rate constants for the title reaction ($k_0$ and $k_\infty$) are not well defined by existing datasets, which do not deliver sufficiently accurate rate coefficient at very low pressures (< 1 mbar) or at very high pressures (> 500 bar). Studies in which $k_\infty$ has been derived from rates of vibrational relaxation of OH (Smith and Williams, 1985; D’Ottone et al., 2005) return values of $k_\infty$ that provide some constraint on its value, but the associated uncertainty is too large to consider this parameter well defined.

In our previous paper, Amedro et al. (2019) describe highly accurate measurements of $k_1$ over a wide range of temperatures and pressures in the fall-off regime. From measurements of $k_1$ in N$_2$ bath gas, we retrieved values for $k_0$ and $k_\infty$ of 2.6 $\times$ 10$^{-30}$ cm$^6$ molecule$^{-2}$ s$^{-1}$ and 6.3 $\times$ 10$^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, respectively, by fixing $F_c$ to a value of 0.39, which has a theoretical basis (Cobos and Troe, 2003). The reasons for choosing this value of $F_c$ are dis-
cussed in Amedro et al. (2019). Note that whereas \( k_0 \) is
dependent on the bath gas used, at the high-pressure limit,
\( k_{SC} \) should be the same in \( N_2, O_2, He, \) or \( H_2O \) bath
gases.

In Fig. 1 we display pressure-dependent rate coefficients
(solid, black squares) obtained in \( He \) bath gas at 292 K.
The black line is a fit (Eq. 4) to our data with \( k_{WC} \) fixed to
\( 6.3 \times 10^{-11} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1} \) and \( n = 0 \) as derived from
an extensive dataset obtained using \( N_2 \) bath gas (Amedro et al.,
2019). For this dataset, the best fit is obtained with \( F_c = 0.32, \) and \( k_{He} = 1.4 \times 10^{-30} \text{cm}^6\text{molecule}^{-2}\text{s}^{-1} \). When using
\( F_c = 0.39 \) (i.e. same value as that obtained in \( N_2 \) bath
gas), the fit slightly overestimates (~5%) the measurements
at pressures above ~300 Torr, whereas it underestimates by
10% at lower pressures (Fig. S2). We note that using a
higher \( F_c = 0.39 \) resulted in a lower value of \( k_{He} \) equal to
\( 1.0 \times 10^{-30} \text{cm}^6\text{molecule}^{-2}\text{s}^{-1} \). The \( T \)-dependence factor
in \( He, m(He) \), was determined to be 3.1 over the tempera-
ture range from 277 to 332 K (Table 1 and Fig. S6).

The high precision of our measurements in \( He \) and \( N_2 \) indi-
cates that different broadening factors \( (F_c) \) are required to
interpret the pressure dependence of \( k_1 \) obtained in \( N_2 \) and
\( He \). This can be rationalized by considering that \( F_c \) is the
product of strong-collision \( (F_c^{SC}) \) and weak-collision \( (F_c^{WC}) \)
components (Eqs. 6–8) (Gilbert et al., 1983; Troe, 1983; Troe
and Ushakov, 2011):

\[
F_c \approx F_c^{SC} F_c^{WC},
\]
\[
F_c^{SC} \approx S_K^{-0.62} \approx \left(1 + \frac{r}{2}\right)^{-0.62},
\]
\[
F_c^{WC} \approx \beta_c^{0.14}.
\]

Here, \( S_K \) is the Kassel parameter, \( r \) is the total number of
external rotational modes of the reactants (equal to 5 in the
reaction between \( OH \) and \( NO_2 \)), and \( \beta_c \) is the collision
efficiency. While the strong collision component is independent
of bath gas \( (F_c^{SC} \approx 0.46 \text{ for the title reaction}) \) a change in
\( F_c^{WC} \) due to a lower collision efficiency \( (\beta_c) \) of \( He \) relative to
\( N_2 \) is likely.

The collision efficiency for \( N_2 \), which was used to calcu-
late \( F_c = 0.39 \), was \( \beta_c(N_2) \approx 0.3 \) (Troe, 2001). The value of
\( F_c = 0.32 \) from our \( He \) data implies \( \beta_c(He) \approx 0.08 \), a factor
of 3.7 times lower than \( \beta_c(N_2) \). A large difference in collision
efficiency between \( N_2 \) and \( He \) is consistent with theoretical
calculations (Glanzer and Troe, 1974; Troe, 2001; Golden et
al., 2003).

In Fig. 1, we also compare our measurements of \( k_1 \) in \( He \)
with data collected in the same pressure range using similar
techniques. The three first measurements (Morley and Smith,
1972; Anastasi and Smith, 1976; Wine et al., 1979) used
flash photolysis of \( H_2O \) as a \( OH \) precursor with detection of
\( OH \) by resonance fluorescence. Morley and Smith (1972) re-
ported rate coefficients at pressures of 20 to 280 Torr at room
temperature with the \( NO_2 \) concentration calculated mano-
metrically. Our parametrization agrees within the combined
uncertainty of both measurements (Fig. S3). Anastasi and
Smith (1976) reported one value of \( k_1 \) at 25 Torr of \( He \), which
is \( \approx 20\% \) lower than our measurement. Wine et al. (1979)
presented values of \( k_1 \) at three pressures of \( He \). The agree-
ment with our parameterization at the lowest two pressures is
excellent but a deviation of \( \approx 20\% \) is observed at the highest
pressure (Fig. S4). As both studies measured \( NO_2 \) concen-
trations using optical absorption at 365 nm, the \( \approx 20\% \) dif-
fERENCE is significant. Most recently, D’Ottone et al. (2001)
reported rate coefficients from 30 to 600 Torr of \( He \) using a
very similar approach to ours, i.e. PLP-LIF technique with in-
situ measurements of \( NO_2 \) by absorption at 365 nm. The dis-
agreement (up to 40%) between our measurements and theirs
exceeded the combined reported uncertainty (Fig. S5). While it
is unclear what could have caused the discrepancy, we note
that the data of D’Ottone et al. (2001) are significantly more
scattered and do not describe a smooth increase in rate coeffi-
cient with pressure as expected from termolecular reactions
in the fall-off regime. This would appear to indicate an un-
derestimation of the total uncertainty in their study.

Figure 2 extends the pressure range to additionally display
data obtained in low-pressure flow tubes (Westenberg and
Dehaas, 1972; Anderson et al., 1974; Erler et al., 1977;
Anderson, 1980) and the high-pressure measurements by Hip-
pler et al. (2006). At low pressures our data are in excellent
agreement (within 10%) with the data of Erler et al. (1977),
but they predict values \( \approx 40\% \) lower than those reported
by Westenberg and Dehaas (1972) and Anderson (1980).

The data of Anderson et al. (1974) display a large intercept
\( (4.9 \times 10^{-14} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}) \) at zero pressure, which
is attributed to a second-order heterogeneous removal rate
constant. As indicated in a critical assessment of the low-
pressure data by Amedro et al. (2019), it is unclear whether
one can simply subtract a constant value equal to the inter-
cept (obtained from a linear fit) to each data point. If we
were to do so, the work by Anderson et al. (1974) would
be in very good agreement with the low-pressure study by
Erler et al. (1977) as well as with our parameterization ex-
tended to low pressures. Additionally, Amedro et al. (2019)
demonstrated that, owing to the large asymmetric broaden-
ing of fall-off for this reaction, the assumption that the rate
coefficient is in the low-pressure limit at \( N_2 \) pressures of
\( 0.5 \text{Torr} < p < 10 \text{Torr} \) is invalid and leads to underestima-
tion of \( k_0 \). This observation is still true of datasets obtained
at low pressures of \( He \), so that while very good agreement
is observed between our parameterization and individual rate
coefficients obtained between 3 and 8 Torr of \( He \), reported
values of \( k_{He} \) are \( 40\% \) lower than our values obtained from
the fall-off analysis. As indicated in Fig. 2, our parameteri-
zation of \( k_1 \) in \( He \) is in very good agreement with the high-
pressure data reported by Hippler et al. (2006).

3.2 Influence of \( H_2O \) on \( k_1 \)
As mentioned above, the effect of water vapour on \( k_1 \) was
determined in mixtures of \( H_2O \) with both \( N_2 \) and \( He \). This
is because the vapour pressure of H$_2$O at room temperature ($\approx 17$ Torr at 293 K) is too low to enable experiments in pure H$_2$O bath gas to be conducted using our instrument. The measurements were performed at low density ([M] = $1.6 \times 10^{18}$ molecule cm$^{-3}$; 50 Torr at 293 K) where the relative increase in $k_1$ in the presence of H$_2$O is pronounced, resulting in greater accuracy in the determination of $k_0$. Experimental data on the influence of H$_2$O on $k_1$ were obtained in N$_2$–H$_2$O and He–H$_2$O mixtures by varying the H$_2$O mixing ratio, $x_{H_2O}$, from 0.05 to 0.27 ([H$_2$O] = 0.9–4.5 $\times 10^{17}$ molecule cm$^{-3}$) while keeping the total pressure constant at 50 Torr. Under these conditions, the addition of H$_2$O resulted in an increase in $k_1$ up to a factor of 2 as illustrated by the datasets of Fig. 3 in which the increase in slope as more water vapour is added is proportional to the increase in $k_1$ (Eq. 2). At the highest concentration of water vapour (4.5 $\times 10^{17}$ molecule cm$^{-3}$) the rate coefficient in He–H$_2$O increased by a factor of $>3$ compared to that obtained in pure He (see Table 1).

In order to determine the temperature dependence of the enhancement in $k_1$ caused by the presence of water, the experiments in He were carried out at three different temperatures (277, 291, and 332 K). The values of $k_1$ obtained from these experiments are plotted versus the mole fraction of H$_2$O in Fig. 4b. At the pressures used in our experiments, $k_1$ displays fall-off, precluding a direct measurement of $k_0$.

The total rate constant measured in, for example, a H$_2$O–N$_2$ bath gas is not equal to the sum of the individual rate constants calculated from the mixing ratios of N$_2$ and H$_2$O; i.e. $k_{N_2–H_2O} \neq k_{N_2} + k_{H_2O}$; $k_{N_2–H_2O}$ is only equal to the sum of $k_{N_2}$ and $k_{H_2O}$ at the low-pressure limit ($\ll 1$ Torr in the case of the OH reaction with NO$_2$) and under certain conditions where gas mixtures are composed of strong colliders and/or have similar collision efficiencies (Troe, 1980; Burke and Song, 2017). Additionally, at the high-pressure end of the fall-off curve, the rate coefficient is independent of bath gas composition. To be able to make a reasonable prediction of this effect under atmospheric conditions, where the mole fraction of water vapour ($x_{H_2O}$) can be as large as 0.05, we analysed our measurements using two different approaches to determine $k_{H_2O}$. In the first case, the low-pressure rate constant in a N$_2$–H$_2$O mixture is defined as the sum of two individual low-pressure-limit rate constants,

$$k(p, T) = \left( x_{N_2} k_0 N_2 \left( \frac{T}{300} \right)^{-m} + x_{H_2O} k_0 H_2O \left( \frac{T}{300} \right)^{-o} \right) [M] k_\infty \left( \frac{T}{300} \right)^{-n} F,$$

where $x_{N_2}$ and $x_{H_2O}$ are the mixing ratio for N$_2$ and H$_2$O, respectively; $k_0 N_2$ and $k_0 H_2O$ are low-pressure-limiting rate constants (units of cm$^3$ molecule$^{-2}$ s$^{-1}$) for pure N$_2$ and H$_2$O; $k_\infty$ is the high-pressure limit rate constant (units of cm$^3$ molecule$^{-1}$ s$^{-1}$); $T$ is the temperature in kelvin; [M] is the molecular density (molecule cm$^{-3}$); and $m$, $n$, and $o$ are dimensionless temperature exponents.

The broadening factor, $F$, is

$$\log F = \frac{\log F_c}{1 + \left[ \log \left( \frac{\left( x_{N_2} k_0 N_2 \left( \frac{T}{300} \right)^{-m} + x_{H_2O} k_0 H_2O \left( \frac{T}{300} \right)^{-o} \right) [M]}{k_\infty \left( \frac{T}{300} \right)^{-n}} \right) / F_c \right]^2},$$

where $N = (0.75–1.27 \log F_c)$ and $F_c$ is the broadening factor at the centre of the fall-off curve.

In the second approach, we follow Burke and Song (2017), where, in addition to the low-pressure limiting rate coefficients, the broadening factors for each bath gas are also...
mixed linearly and log $F^{N_2-H_2O}$ is defined as

$$
\log F^{N_2-H_2O} = X_{N_2} \log F^{N_2} + X_{H_2O} \log F^{H_2O},
$$

where

$$
X_{N_2} = \frac{x_{N_2} k^{N_2} (T_{300})^{-m}[M]}{x_{N_2} k^{N_2} (T_{300})^{-m} + x_{H_2O} k^{H_2O} (T_{300})^{-o}[M]},
$$

$$
X_{H_2O} = \frac{x_{H_2O} k^{H_2O} (T_{300})^{-m} + x_{H_2O} k^{H_2O} (T_{300})^{-o}[M]}{x_{N_2} k^{N_2} (T_{300})^{-m} + x_{H_2O} k^{H_2O} (T_{300})^{-o}[M]};
$$

$$
\log F^{N_2} = \frac{\log F^{N_2}}{1 + \left[ \log \left( \frac{\left( n_{N_2} (T_{300})^{-m} \right)^{-n} + n_{H_2O} (T_{300})^{-o}}{k_{N_2}(T_{300})^{-o}} \right) \right] [M] \left( 0.75 - 1.27 \log F^{N_2} \right)};
$$

$$
\log F^{H_2O} = \frac{\log F^{H_2O}}{1 + \left[ \log \left( \frac{\left( n_{N_2} (T_{300})^{-m} \right)^{-n} + n_{H_2O} (T_{300})^{-o}}{k_{N_2}(T_{300})^{-o}} \right) \right] [M] \left( 0.75 - 1.27 \log F^{H_2O} \right)};
$$

where $F^{N_2}_c$ and $F^{H_2O}_c$ are the broadening factors at the centre of the fall-off curve for $N_2$ and $H_2O$.

In the case where two bath gases have identical (or very similar) values of $F_c$, the two approaches result in identical predictions and the first approach will be preferred for its simplicity. This is the case for $N_2$ and $H_2O$ bath gases. However, when two bath gases have significantly different values of $F_c$ (as is the case for He–$H_2O$ mixtures; see below) the second approach provides a more accurate parameterization.

### 3.2.1 Parameterization of $k_1$ from data obtained in $N_2$–$H_2O$ and He–$H_2O$ bath gases

Values of $k_1$ obtained in $N_2$–$H_2O$ and He–$H_2O$ bath gases are listed in Table 2. Each rate coefficient obtained in $N_2$–$H_2O$ bath gas was defined by five parameters: the mixing ratio of $N_2$ and $H_2O$ ($x_{N_2}$ and $x_{H_2O}$), the overall rate coefficient ($k_1$), the molecular density [M], and the temperature $T$. We performed a multivariate fit of the $N_2$–$H_2O$ dataset with $k_0^{H_2O}$ as variable and all other parameters fixed with $k_0^{N_2} = 6.3 \times 10^{-11}$ cm$^3$ molecule$^{-2}$ s$^{-1}$, $k_0^{He} = 1.4 \times 10^{-30}$ cm$^6$ molecule$^{-2}$ s$^{-1}$, $F_0^{H_2O} = 2.6 \times 10^{-30}$ cm$^6$ molecule$^{-2}$ s$^{-1}$, and $m = 3.6$ as derived in Amedro et al. (2019); $o$ was fixed to 3.4 (see below) and $F_c$ was held at 0.39, making the assumption that the broadening factors at the centre of the fall-off curve for $N_2$ and $H_2O$ were identical. The fit to the data returned $k_0^{H_2O} = (15.9 \pm 0.7) \times 10^{-30}$ cm$^6$ molecule$^{-2}$ s$^{-1}$ where the uncertainty is $2\sigma$ (statistical only). The solid black line in Fig. 4a represents the parameterization for a varying fraction of $H_2O$ in $N_2$ at a total pressure of 50 Torr using the parameters given above. Equating $F_0^{H_2O}$ and $F_0^{N_2}$ simplifies the analysis, though it is likely that $F_0^{H_2O} > F_0^{N_2}$ as the collision...
efficiency ($\beta_c$) is likely to be larger for H$_2$O than for N$_2$. We found that the He–H$_2$O data cannot be modelled by assuming the same $F_c$ for both He and H$_2$O bath gas, and the approach of Burke and Song (2017) was therefore preferred. In order to analyse the data, we fixed the following parameters: $k_{0\text{H}_2\text{O}}$ = $15.9 \times 10^{-30}$ cm$^6$ molecule$^{-2}$ s$^{-1}$, $F_{c\text{H}_2\text{O}}$ = 0.39, $F_{c\text{He}}$ = 0.32, $k_{0\text{He}}$ = $1.4 \times 10^{-30}$ cm$^6$ molecule$^{-2}$ s$^{-1}$, and $m$ = 3.1 to derive $\sigma$ = $3.4 \pm 0.8$ (2$\sigma$, statistical only), which describes the temperature dependence of the low-pressure limit in H$_2$O as depicted in Fig. 4b.

There is clearly some uncertainty related to the arbitrary use of $F_{c\text{H}_2\text{O}}$ = 0.39. For example, if we were to analyse the data in N$_2$–H$_2$O using $F_{c\text{H}_2\text{O}}$ = 0.6 and the linear mixing method, we would retrieve $k_{0\text{H}_2\text{O}}$ = $10 \times 10^{-30}$ cm$^6$ molecule$^{-2}$ s$^{-1}$, which is $\approx 50\%$ lower than our preferred value. The effect of the different analyses can be assessed by comparing the predicted impact of H$_2$O on $k_1$ at 80% relative humidity, 1000 mobar, and 313 K. If we set $F_{c\text{H}_2\text{O}}$ = 0.39, we predict that the effect of H$_2$O is to increase $k_1$ by 15%, while choosing $F_{c\text{H}_2\text{O}}$ = 0.6 results in an increase of 20%. Theoretical calculation of the relative values of $F_c$ in N$_2$, O$_2$, and H$_2$O bath gases input would be useful to reduce this uncertainty. Our data indicate a significant positive trend in $k_1$ when adding H$_2$O. As discussed above, more efficient energy transfer from [HO–NO$_2$] in collision with H$_2$O compared to N$_2$ is intuitively and supported by the present data set as well as that of Simonaitis and Heicklen (1972), who derived $k_{0\text{H}_2\text{O}}$ = $11 \times 10^{-30}$ cm$^6$ molecule$^{-2}$ s$^{-1}$, given the complexity of the analysis, this may be considered to be in good agreement. This result is, however, not consistent with the observations of D’Ottone et al. (2001), who report no significant change in $k_1$ in 150 Torr of He when adding either 10 or 20 Torr of H$_2$O and is completely at odds with the conclusions of Sadanaga et al. (2006), who report a reduction in $k_1$ (by 18%) when adding 29.1 mbar of H$_2$O at atmospheric pressure. If our value for $k_{0\text{H}_2\text{O}}$ is correct, D’Ottone et al. (2001) should have seen an increase in $k_1$ of $\approx 55\%$ and Sadanaga et al. (2006) should have observed an increase of $\approx 5\%$.

A potential explanation for the very divergent observations of the effect of H$_2$O is the heterogeneous loss of NO$_2$ when adding H$_2$O. We tested for NO$_2$ loss in a set of experiments in which NO$_2$ and H$_2$O were monitored simultaneously while systematically varying the amount of H$_2$O. Our results indicated a reduction in the concentration of NO$_2$ by up to $\approx 20\%$ as we increased the concentration of H$_2$O up to $4.5 \times 10^{17}$ molecule cm$^{-3}$. Unless NO$_2$ is monitored in situ (as in our experiments), $20\%$ loss of NO$_2$ would lead to a smaller size reduction in the OH decay constant and thus an underestimation of the rate coefficient. A fractional loss of NO$_2$ of this magnitude would explain why Sadanaga et al. (2006) found an apparent reduction in $k_1$ when adding H$_2$O.

However, the situation becomes more complex if NO$_2$ is converted to trace gases that are reactive towards OH. For this reason, we performed an additional experiment to investigate whether NO$_2$ was converted via reaction with H$_2$O on surfaces to HONO and/or HNO$_3$. Note that conversion of NO$_2$ to HONO at low pressures (e.g. 50 Torr) would result in an increase in the OH decay constant ($k_{\text{OH}+\text{HONO}} > k_{\text{OH}+\text{NO}_2}$), whereas conversion of NO$_2$ to HNO$_3$ would result in a decrease ($k_{\text{OH}+\text{HNO}_3} < k_{\text{OH}+\text{NO}_2}$).

In order to test for the presence of HONO, we modified the broadband absorption set-up by replacing the halogen lamp with a deuterium lamp, allowing us to detect HONO around 350 nm as well as NO$_2$. The optical absorption of NO$_2$ and HONO (340–380 nm) was monitored in a flow of NO$_2$ (1.7 $\times 10^{15}$ cm$^{-3}$) at 50 Torr of He in the absence and presence of H$_2$O ([H$_2$O] = $4.5 \times 10^{17}$ molecule cm$^{-3}$, the maximum concentration used in this work). A depletion in NO$_2$ of 21% ($3.7 \times 10^{14}$ molecule cm$^{-3}$) was observed when H$_2$O was added. An analysis of the spectra with and without H$_2$O (Fig. S7) enabled us to establish an upper limit to the HONO concentration of $\approx 1 \times 10^{13}$ molecule cm$^{-3}$, which would correspond to just 3% of the NO$_2$ lost. At this concentration, HONO does not significantly increase the loss rate of OH ($<3\%$ using a rate coefficient for reaction of OH with HONO of $6.0 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (IU-PAC, 2019). In the same experiment, we also recorded the optical density at 185 nm, where H$_2$O, NO$_2$, and HNO$_3$ all absorb. Despite the large HNO$_3$ absorption cross section at this wavelength ($1.6 \times 10^{-17}$ cm$^2$ molecule$^{-1}$; Dulitz et al., 2018) we found no evidence for HNO$_3$ formation, indicating that the NO$_2$ lost was not converted to gas-phase HNO$_3$. Given its great affinity for glass in the presence of H$_2$O, we expect that any HNO$_3$ formed is strongly partitioned to the walls of the reactor. The tests indicate that, on the timescales of our experiments, NO$_2$ is lost irreversibly on the humidified walls of our experiment. The maximum concentration of H$_2$O used in this experiment, $4.5 \times 10^{17}$ molecule cm$^{-3}$, corresponds to a relative humidity of 80% (at 292 K) so that H$_2$O condensation is not expected.

It is difficult to establish whether our observations of significant NO$_2$ loss can explain the result of D’Ottone et al. (2001), who did not observe an enhancement in $k_1$. D’Ottone et al. (2001) did not state whether, in their experiments, NO$_2$ and H$_2$O were monitored simultaneously. Also, our observed loss of NO$_2$ is not necessarily transferable to other studies as the heterogeneous loss of NO$_2$ will vary from one experimental set-up to the next, as residence times and surface areas may vary substantially.

A very simple calculation serves to illustrate the role of water vapour as a third-body quencher for the title reaction. We consider, for example, the tropical boundary layer with a temperature of 30°C and a relative humidity of 80% at a total pressure of 1 bar. The pressure of water vapour is 34 mbar, and those of O$_2$ and N$_2$ are then 210 and 756 mbar, respectively. A rough contribution of each quenching gas to the overall rate coefficient can be calculated from the respective low-pressure rate coefficients. For N$_2$, O$_2$, and H$_2$O these
are (in units of $10^{-30}$ cm$^3$ molecule$^{-1}$ s$^{-1}$) 2.6, 2.0, and 15.9. Water vapour is therefore a factor of $\approx 8$ more efficient than O$_2$, and a factor of $\approx 6$ more efficient than N$_2$ as a quencher of the HO–NO$_2$ intermediate, which is qualitatively consistent with known strong binding (40 kJ mol$^{-1}$) in the HNO$_3$–H$_2$O complex (Tao et al., 1996).

For our tropical boundary layer case study, in which the O$_2$ pressure is only a factor of 6 greater than that of H$_2$O, we calculate that H$_2$O contributes more to the rate coefficient of the title reaction than O$_2$ does. Clearly, the neglect of including the quenching effect of H$_2$O leads to an underestimation (in the boundary layer) of the rate coefficient for this centrally important atmospheric reaction.

In order to assess both the effect of H$_2$O (this work) and the new parameterization for $k_1$ in N$_2$ and O$_2$ bath gases presented in the first part of this study (Amedro et al., 2019), we have used a 3-D chemical transport model (EMAC; see below) to explore the impact on a global scale.

### 3.3 Atmospheric modelling of the OH + NO$_2$ reaction including the effect of water vapour

The EMAC (ECHAM/MESSy Atmospheric Chemistry) model employed is a numerical chemistry and climate simulation system (Jöckel et al., 2006, 2010) using the fifth-generation ECMWF Hamburg general circulation model (ECHAM5; Roeckner et al., 2006) as core atmospheric general circulation model. For the present study, we applied EMAC (ECHAM5 version 5.3.02, MESSy version 2.53.0) in the T42L47MA resolution, i.e. with a spherical truncation of T42 (corresponding to a quadratic Gaussian grid of approx. 2.8° by 2.8° in latitude and longitude) with 47 vertical hybrid pressure levels up to 0.01 hPa. The model has been weakly nudged in spectral space, nudging temperature, vorticity, divergence, and surface pressure (Jeuken et al., 1996).

The chemical mechanism scheme adopted (MOM: Mainz Organic Mechanism) includes oxidation of isoprene and saturated and unsaturated hydrocarbons, including terpenes and aromatics (Sander et al., 2019). Further, tracer emissions and model set-up are similar to the one presented in Lelieveld et al. (2016). EMAC model predictions have been evaluated against observations on several occasions (Pozzer et al., 2010; de Meij et al., 2012; Elshorbany et al., 2014; Yoon and Pozzer, 2014): for additional references, see http://www.messy-interface.org (last access: November 2019). For this study, EMAC was used in a chemical transport model (CTM mode) (Deckert et al., 2011), i.e. by disabling feedbacks from photochemistry on radiation and dynamics. Two years were simulated (2009–2010), with the first year used as spin-up time.

| Bath gas | $k_0^n$ | $T$ dependence of $k_0$ | $k_{\infty}^n$ | $F_c$ |
|----------|---------|-------------------------|--------------|-------|
| N$_2$    | $2.6 \times 10^{-30}$ | 3.6 (m) | 6.3 $\times 10^{-11}$ | 0.39 |
| O$_2$    | $2.0 \times 10^{-30}$ | 3.6 (q) |               |       |
| H$_2$O   | $15.9 \times 10^{-30}$ | 3.4 (a) |               |       |

*Units of cm$^6$ molecule$^{-2}$ s$^{-1}$. b Units of cm$^3$ molecule$^{-1}$ s$^{-1}$. Note that $k_{\infty}$ is independent of temperature ($n = 0$).

The following parameterization of $k_1$ was implemented in EMAC; values of each parameter are listed in Table 3.

$$k_1(p, T) = \frac{M_{k_1}(T)}{M_{k_1}(T_0)}$$ \quad (15)

The broadening factor, log $F$, is

$$\log F = \frac{\log F_c}{1 + \left[\log \left(\frac{M_{k_1}(T)}{M_{k_1}(T_0)}\right)\right] / \text{[6.75 – 1.27 log $F_c$]}}$$ \quad (16)

As described in Sect. 1, the reaction between OH and NO$_2$ forms not only HNO$_3$ but also HOONO. HOONO decomposes rapidly at typical boundary layer temperatures, but it is long lived with respect to thermal dissociation at the temperatures found in the upper troposphere and lower stratosphere (UTLS).

$$\text{HOONO} + \text{M} \rightarrow \text{OH} + \text{NO}_2$$ \quad (R6)

The rate constant ($k_6$) for thermal decomposition of HOONO was calculated from the channel-specific rate coefficient for its formation ($k_1(\alpha)$) and an equilibrium coefficient:

$k_6 = k_1(\alpha) / K_{eq}$, where $K_{eq} = 3.5 \times 10^{-27} \exp(10135 / T)$ (Burkholder et al., 2015; IUPAC, 2019) based on the analysis of Golden et al. (2003). The branching ratio to HOONO formation ($\alpha$) was adapted from the present IUPAC recommendations for $k_{1a}$ and $k_{1b}$, which were derived from experimental work (Hippler et al., 2006; Mollner et al., 2010) and theoretical analysis (Troe, 2012). The IUPAC recommendations were augmented with a pressure-independent HOONO yield of 0.035 to better represent the dataset of Mollner et al. (2010), who detected HOONO directly at room temperature. We assume $\alpha$ is independent of water vapour. The expression used and a plot of $\alpha$ at different temperatures and pressures is given in Fig. S8.

In the absence of experimental data on the reactions of HOONO with OH or on its photolysis, we follow the approach of Golden and Smith (2000) and set these equal to those for H$_2$O(NO$_2$):

$$\text{HOONO} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{NO}_3,$$ \quad (R7)
HOONO + hv → HO + NO₂.  

(R8)

In Fig. 5, we illustrate the global impact (annual average) of H₂O vapour on the rate coefficient. We plot the fractional reduction in k₁ at the Earth’s surface when setting x₁H₂O to zero rather than using the EMAC global water-vapour fields. We focus on the boundary layer as the H₂O concentration is largest here and decreases rapidly with altitude.

As expected, the greatest effect is found in warm, tropical regions where neglecting the impact of water vapour results in an average underestimation of the rate coefficient by up to ≈ 8%. At higher or lower latitudes the effect is diminished and water vapour accounts for only 3%–4% of the overall rate coefficient at 40° N or S. The presence of water vapour does not impact on values of k₁ above the boundary layer.

Our experimental data do not give insight into whether the H₂O-induced enhancement in k₁ is accompanied by a change in the branching ratio to favour either HNO₃ or HOONO. However, as the formation of HOONO is favoured at high pressures (more effective collisional deactivation), it is possible that the HOONO yield may be enhanced relative to HNO₃ in the presence of H₂O. If this is the case, the increase in rate coefficient at high water-vapour levels (e.g. in the tropical lower troposphere) may be to some extent offset by the subsequent thermal dissociation of HOONO in these warm regions.

As described by Amedro et al. (2019) (Fig. 1 of that paper), two expert panels (IUPAC, NASA) evaluating kinetic data for use in atmospheric modelling fail to reach consensus for the title reaction, with the preferred rate coefficients differing by as much as 50% in the cold UTLS. For this reason, we have calculated values of k₁ (this work) and k₁ (IUPAC last evaluated in 2017; IUPAC, 2019) and NASA (k₁ (NASA last evaluation published in 2015; Burkholder et al., 2015). As displayed in Fig. 6, values of k₁ (this work) and k₁ (IUPAC) vary greatly with pressure and temperature and thus altitude. The NASA recommendations are always slightly lower but in good agreement (≤ 10%) for most of the troposphere, with larger differences (≤ 15%) always < 1) only observed in the lower and mid-stratosphere. At altitudes above ≈ 30 km the ratio decreases to ≈ 0.8.
comparison with the rate coefficient derived from the IUPAC parameterization shows that $\frac{1}{k_{\text{IUPAC}}}$ varies from $\approx 0.9$ at the surface to $\approx 1.1$ at the tropopause but increases to $>1.3$ at the low pressures and temperatures that reign at 30 km and above. At high altitudes (low pressure and temperature) the rate coefficients that the evaluation panels recommend are strongly biased by choice of the rate coefficient (and its temperature dependence) at the low-pressure limit. As discussed by Amedro et al. (2019) the available experimental data at low pressures and temperatures are not of sufficient accuracy to use as basis for recommendation of $k_0$, and this is reflected in the highly divergent values of $k_1$ under these conditions.

As mentioned above, the atmospheric HNO$_3$/NO$_2$ ratio is expected to be highly sensitive to the rate coefficient $k_1$, with an increase in $k_1$ resulting in an increase in the HNO$_3$/NO$_2$ ratio and vice versa. The HNO$_3$/NO$_2$ ratio also depends on the concentration of OH, and thus the effect of using different values of $k_1$ will be most apparent in regions where the greatest OH concentrations are found, i.e. at low latitudes. At higher latitudes, especially in winter months where solar insolation is weak and OH levels are relatively low, the HNO$_3$/NO$_2$ ratio will also be impacted by night-time conversion of NO$_2$ to N$_2$O$_5$ and finally, via heterogeneous hydrolysis, to HNO$_3$. In Fig. 7 we plot zonally and yearly averaged model values of $\frac{\text{HNO}_3}{\text{NO}_2}$ (IUPAC)/$\frac{\text{HNO}_3}{\text{NO}_2}$ (this work) in the upper panel (Fig. 7a) and $\frac{\text{HNO}_3}{\text{NO}_2}$ (NASA)/$\frac{\text{HNO}_3}{\text{NO}_2}$ (this work) in the lower panel (Fig. 7b). Compared to the present parameterization of $k_1$, the IUPAC evaluation returns HNO$_3$/NO$_2$ ratios that are between 0.9 and 1 throughout most of the lower and free troposphere (up to $\approx 5$ km) and larger HNO$_3$/NO$_2$ ratios (factor of 1.1 to 1.15) above $\approx 10$ km especially at the tropical tropopause. The divergence between the HNO$_3$/NO$_2$ ratios increases as we move further into the stratosphere with $\frac{\text{HNO}_3}{\text{NO}_2}$ (IUPAC)/$\frac{\text{HNO}_3}{\text{NO}_2}$ (this work) values as large as 1.2 to 1.3 above 25 km. At the same time, NO$_x$ levels (NO$_x$ = NO + NO$_2$) decrease by a factor of $\approx 0.95$ (see Fig. S9). When we compare our parameterization with that of the NASA panel, the picture is largely reversed (lower panel, Fig. 7b). Again, we find reasonable agreement in the HNO$_3$/NO$_2$ ratio in the lowermost atmosphere, but in this case lower values (0.8 to 0.9) in the lower stratosphere, which are accompanied by a factor of 1.06 change in NO$_x$ concentrations (Fig. S9). For both the NASA and IUPAC parameterizations, the largest differences in the HNO$_3$/NO$_2$ ratio compared to the present study are found higher in the atmosphere. The modelling studies confirm the simple calculation of Amedro et al. (2019; see Fig. 1 of their paper), showing that the IUPAC and NASA parameterizations result in very different values of $k_1$ in some parts of the atmosphere, and they will result in divergent predictions of partitioning of reactive nitrogen between NO$_x$ and NO$_2$. Use of the parameterization based on the present dataset lies roughly between the two evaluations, with best agreement observed with NASA for the lower atmosphere. However, as previous laboratory studies had not identified the important role of H$_2$O in the title reaction, which could therefore not be incorporated in either of the previous parameterizations, any agreement at better than the 10% level is fortuitous, reflecting random cancelling of systematic bias.

As reaction with OH is the predominant sink for most atmospheric trace gases, its concentration largely defines the oxidizing power of the atmosphere (Lelieveld et al., 2004, 2008, 2016) and even changes of a few percent in its concentration are significant. An increase in the rate coefficient of the title reaction will reduce the atmospheric abundance of this centrally important radical. In Fig. S10 we illustrate the impact of using the parameterization of $k_1$ from the present

**Figure 7.** Effect of different parameterizations of $k_1$ on the global (zonal and yearly averaged) HNO$_3$ to NO$_2$ ratio. (a) $\frac{\text{HNO}_3}{\text{NO}_2}$ (IUPAC)/$\frac{\text{HNO}_3}{\text{NO}_2}$ (this work). (b) $\frac{\text{HNO}_3}{\text{NO}_2}$ (NASA)/$\frac{\text{HNO}_3}{\text{NO}_2}$ (this work). The black line represents the model tropopause.
study compared to the IUPAC and NASA recommendations. The upper panel in Fig. S10 plots the ratio of OH concentrations obtained when using the IUPAC parameterization and that from the present study, OH(IUPAC)/OH(this work). Throughout the troposphere OH(IUPAC)/OH(this work) deviates by only a few percent, with a value of 1.02 at the surface and 0.96 at the tropical tropopause. OH(NASA)/OH(this work) is also 1.02 at the surface but increases to 1.04 at the tropical tropopause as the NASA-derived value of \( k_1 \) is lower at the temperatures and pressures encountered in this part of the atmosphere. The weak effect of changing \( k_1 \) on OH at the surface reflects the fact that many reactions apart from that with NO2 contribute to the overall sink term for OH in the lower troposphere.

Although our experiments do not give insight into the branching between formation of HOONO and HNO3 in the title reaction, previous work predicts a significant yield of HOONO especially at low temperatures (see Fig. S8). As the lifetime of HOONO with respect to re-dissociation to reactants is short at, for example, boundary layer temperatures (\( \approx 1 \) s at 298 K and 1 bar pressure), its formation may be seen as an effective reduction in the rate coefficient for OH + NO2 (Golden and Smith, 2000). However, its lifetime increases to several days at temperature and pressure conditions typical of the tropical tropopause (100 mbar, 220 K).

As HOONO formation and loss are now parameterized (see above) in EMAC, we can explore its potential contribution to odd-nitrogen species in the atmosphere. The reaction between OH and NO2 to form HOONO converts short-lived HOx \((\text{HO} = \text{OH} + \text{HO}_2)\) and NOx \((\text{NO} = \text{NO} + \text{NO}_2)\) into a longer-lived “reservoir” species, and in this sense it is similar to the reaction between HO2 and NO2 to form HO2NO2:

\[
\text{HO}_2 + \text{NO}_2 + \text{M} \rightarrow \text{HO}_2\text{NO}_2 + \text{M},
\]

(R9)

which is also thermally unstable, dissociating to reform HO2 and NO2. Unlike HOONO, for which there are no atmospheric measurements, much effort has been made to measure concentrations of HO2NO2 in colder regions of the atmosphere, and it is considered an important component of the NOy budget at high altitudes (Nault et al., 2016). We therefore compared EMAC predictions of HOONO concentrations with those of HO2NO2. The results are displayed in Fig. 8, in which we plot the zonally averaged HOONO/NO2NO2 ratio. Immediately apparent from Fig. 8 is that, compared to HO2NO2, HOONO is a minor component of NOy in the warm, lower atmosphere. This reflects the difference in the thermal decomposition rate constant of the two trace gases, i.e. that of HO2NO2 being \( \approx 4 \times 10^{-5} \) s\(^{-1}\) in, for example, the middle troposphere at 400 mbar and 250 K, whereas HOONO decomposes a 10 times faster so that its lifetime is only \( \approx 1000 \) s. In the UTLS region, the ratio increases further (HO2NO2 is a factor of 50 more long lived with respect to thermal decomposition at 100 mbar and 220 K), but the lifetimes of both gases under these conditions are sufficiently long that their concentrations are largely determined by their production rates and their losses due to photolysis and reaction with OH. The maximum ratio of HOONO to HO2NO2 is found at the tropical tropopause, where concentrations become comparable. As the modelled loss processes of HOONO and HO2NO2 (rate constants for photolysis and reaction with OH) are assumed to be identical, the occurrence of the maximum HOONO to HO2NO2 ratio at the tropical tropopause is related to the ratio of the (temperature-dependent) rate coefficients responsible for their formation (at 220 K and 100 mbar this favours HOONO formation by a factor of \( \approx 2 \)) and the model OH/NO2 ratio. Whilst this result indicates that HOONO could be an important reservoir of NOx under certain conditions, we must bear in mind that there is great uncertainty associated not only with the branching ratio to HOONO formation in Reaction (R1b) but also with its loss processes (reaction with OH, photolysis), which remain unexplored experimentally. OH reacts with HO2NO2 via H abstraction from the HO—O2 group (IUPAC, 2019), and a similar mechanism is likely for HOONO. As the H—O2 bond strength is likely to be greater in HOONO than in HO2NO2 (larger electron density around the peroxo bond), we may expect the rate coefficient to be lower for HOONO. A significantly lower rate coefficient for reaction with OH (or photolysis rate constant) could greatly increase the abundance of HOONO. If this were the case, airborne instruments that measure NO2 would likely also measure some fraction of HOONO following its rapid decomposition in warm inlet lines, as has been observed for HO2NO2 and CH32NO2 (Nault et al., 2015; Silvern et al., 2018). Clearly, more experimental or theoretical data that better constrain the yield of HOONO and its atmospheric loss processes as well as atmospheric measurements are necessary in order to improve our understanding of the role of the reaction between OH and NO2 throughout the atmosphere.

4 Conclusions

We have made very precise and accurate measurements for the overall rate coefficient, \( k_1 \), of the reaction between OH and NO2, which is of critical importance in atmospheric chemistry. Our experiments demonstrate clearly that the presence of H2O increases significantly the overall rate coefficient (\( k_1 \)) of the reaction between OH and NO2. H2O is found to be a more efficient collisional quencher (by a factor of \( \approx 6 \)) of the initially formed HO–NO2 association complex than N2 and a factor of \( \approx 8 \) more efficient than O2. A new parameterization of the rate coefficient for the title reaction that considers the roles of N2, O2, and H2O as third-body quenchers (also using data from our previous paper: Amedro et al., 2019) has been incorporated into a global chemistry transport model to assess its impact on, for example, the HNO3/NO2 ratio as well as NOx and OH levels. Compared to existing evaluations of the kinetic data, use of the new parameters will result in significant changes (5%–10%).
in the partitioning of NO$_x$ and NO$_y$, the direction of the bias depending on which evaluation is used as reference and on region of the atmosphere. This work highlights the continuing importance of obtaining accurate laboratory kinetic data for those reactions that are central to our understanding of atmospheric chemistry and which provide anchor-points in chemical transport models.

Though the result is associated with great uncertainty owing to missing kinetic parameters for HOONO, the global model predicts the presence of HOONO in concentrations similar to those of HO$_2$NO$_2$ at the tropical tropopause. The present dataset addresses only the overall rate coefficient ($k_1$). Detailed experimental studies of the formation of HOONO (e.g. its yield at various temperatures and in the presence of H$_2$O) and on the fate of HOONO (OH kinetics, photolysis) are required to better assess its role as an NO$_x$ and HO$_x$ reservoir in cold parts of the atmosphere.

Data availability. The rate coefficients measured during this experimental study are listed in Table 1.

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