

11 January 1999

Chemical Physics Letters 299 (1999) 277-284

CHEMICAL PHYSICS LETTERS

# Rate constants for the reaction $OH + NO_2 + M \rightarrow HNO_3 + M$ under atmospheric conditions

Steven S. Brown <sup>a, \*</sup>, Ranajit K. Talukdar <sup>a,b</sup>, A.R. Ravishankara <sup>a,b,c</sup>

<sup>a</sup> Aeronomy Laboratory, NOAA, 325 Broadway, Boulder, CO 80303, USA

<sup>b</sup> Cooperative Institute for Research in the Environmental Sciences, University of Colorado, Boulder, CO 80309, USA <sup>c</sup> Department of Chemistry, University of Colorado, Boulder, CO 80309, USA

Received 22 October 1998; in final form 3 November 1998

### Abstract

We present rate constants for the title reaction,  $k_1$ , measured using a pulsed photolysis-laser induced fluorescence technique between 220 and 250 K in 20–250 Torr of N<sub>2</sub> and 20–50 Torr of O<sub>2</sub>. Our measured  $k_1$  agree with literature values at low temperatures but show that the current recommendations for atmospheric modeling overestimate  $k_1$  by 10–30% in the falloff region below 250 K. The revised values of  $k_1$  help to better define the role of NO<sub>2</sub> in the stratosphere. © 1999 Elsevier Science B.V. All rights reserved.

## 1. Introduction

Nitrogen dioxide is central to the chemistry of the atmosphere. In the stratosphere it directly participates in catalytic ozone destruction, suppresses ozone destruction due to other chemical cycles by forming reservoir species (e.g., CIONO<sub>2</sub>, HONO<sub>2</sub>, HO<sub>2</sub>NO<sub>2</sub>) and directly affects the partitioning of compounds within different chemical families. In the troposphere, one of its key roles is to photochemically produce ozone. The determining factor for NO<sub>2</sub> chemistry is the fraction of the total nitrogen oxides present in the active form of NO and NO<sub>2</sub>, collectively referred to as NO<sub>x</sub>, compared to the fraction present in inactive forms (e.g., HNO<sub>3</sub>). One of the

most important reactions that converts  $NO_x$  into its reservoir is that of hydroxyl radicals with  $NO_2$ .

$$OH + NO_2 + M \rightarrow HNO_3 + M.$$
(1)

The pressure dependence of the rate constant for this association reaction  $(k_1)$  lies in the falloff region between second- and third-order kinetics over the pressure and temperature range encountered in the troposphere and stratosphere. Accurate characterization of the rate constant behavior under atmospheric conditions thus requires extensive measurements as a function of both pressure and temperature in N<sub>2</sub> and O<sub>2</sub>.

Surprisingly, the database for reaction (1) is quite limited over the temperature and pressure range characteristic of the lower stratosphere and upper troposphere (200–250 K, 10–300 mbar), and the fits that come from the NASA/JPL [1] and IUPAC [2] recommendations for atmospheric modeling are

<sup>\*</sup> Corresponding author. Fax: +1-303-497-5822; e-mail: sbrown@al.noaa.gov

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heavily weighted with rate constant data at higher temperatures. The low-temperature database for  $M = N_2$  consists of two studies, that of Anastasi and Smith [3] at 220 and 238 K and that of Wine et al. [4] at 247 K. Both of these studies measured rate constants in a variety of bath gases, including  $N_2$ , but neither made measurements with  $M = O_2$  at low temperatures. Numerous other studies [5–10] of reaction (1) have examined rate constants at temperatures closer to 298 K and/or in the low- and high-pressure limits, and in bath gases other than  $N_2$ .

The atmospheric significance of reaction (1) and the lack of data under the conditions of interest, in addition to recent discrepancies between calculated and observed NO<sub>x</sub> concentrations in the atmosphere [11], warrant further study of  $k_1$  at low temperatures and sub-atmospheric pressures in N<sub>2</sub> and O<sub>2</sub>. We report rate constant measurements over the pressure range 20–250 Torr in N<sub>2</sub> and O<sub>2</sub> bath gases and at temperatures from 220 to 250 K and at room temperature.

#### 2. Experiments and data analysis

The pulsed-photolysis laser-induced fluorescence (LIF) apparatus has been extensively used in previous OH kinetic studies in this laboratory [12,13]. We briefly describe the apparatus here to emphasize some of the features and changes made to accurately measure  $k_1$ . Photolysis of either HNO<sub>3</sub> or H<sub>2</sub>O<sub>2</sub> at 248 nm (KrF excimer laser) produced an initial OH concentration, [OH]<sub>0</sub>, of typically 10<sup>11</sup> cm<sup>-3</sup>, and we monitored the OH decay over 2–3 orders of magnitude via LIF. We measured  $k_1$  under pseudo-first-order conditions in OH, i.e., [M]  $\gg$  [NO<sub>2</sub>]  $\gg$  [OH]<sub>0</sub>, with the minimum NO<sub>2</sub> concentration approximately two orders of magnitude larger than [OH]<sub>0</sub>. At a fixed pressure, [M], the OH temporal profile is given by:

$$\ln \frac{[\text{OH}]}{[\text{OH}]} = \ln \frac{S_t}{S_0} = -(k_1[\text{NO}_2] + k_d)t = -k't,$$
(2)

$$k' = k_1 [NO_2] + k_d$$
, (3)

where S refers to the OH LIF signal and k' is the pseudo-first-order OH loss rate constant. A linear fit

to a plot of k' vs. [NO<sub>2</sub>] gives the effective bimolecular rate constant at a fixed pressure,  $k_1$ , as the slope, and the first-order loss rate constant in the absence of NO<sub>2</sub>,  $k_{\rm d}$ , as the intercept. The reaction of OH with  $HNO_3$  or  $H_2O_2$  is the most important contribution to  $k_{\rm d}$  in these experiments. Nitric acid was the OH precursor for all rate constant measurements reported here: however, we checked that the measured rate constants were invariant to the OH source by also using H<sub>2</sub>O<sub>2</sub> photolysis as an OH source at 250 and 296 K. In all cases,  $k_d$  was ~ 150-250 s<sup>-1</sup>, while the estimated first-order loss rate constant due to diffusion and flow out of the reaction zone was  $20-50 \text{ s}^{-1}$ . The linear gas flow velocity through the 150  $\text{cm}^3$  reaction cell was 7–8  $cm s^{-1}$ , enough to refresh the gas mixture in the reaction zone every 1-2 laser shots at 10 Hz. A factor of two variation in the linear flow velocity produced no change in the measured rate constants. We measured nitric acid concentrations by absorption at 185 nm ( $\sigma = 1.63 \times 10^{-17}$  cm<sup>2</sup> [14]) in a 100 cm external absorption cell using a mercury lamp and a solar blind photodiode and verified that the nitric acid concentrations, which were typically  $\sim 5$  $\times 10^{14}$  cm<sup>-3</sup>, were consistent with the observed values of  $k_d$  [13]. The first-order loss rate constants due to reaction with HNO<sub>3</sub> remained the same before and after measurement of a series of k' values.

Nitrogen and oxygen bath gases were from Scott Specialty Gases and had stated purities of 99.9995% and 99.99%, respectively. We used them without further purification. We synthesized NO<sub>2</sub> from the reaction of NO with excess O<sub>2</sub> and purified the product by repeated freeze-pump-thaw cycles at 77 K. We made bulbs of 0.2-1% NO<sub>2</sub> in He and measured the concentration of the mixtures via absorption near 365 nm using an Hg lamp, a 100 cm cell, and a bandpass filter centered at 365 nm with a FWHM of  $\pm 10$  nm. We took the NO<sub>2</sub> absorption cross-section at the pair of Hg emission lines near 365 from the work of Wine et al. [4]:  $\sigma = 5.75 \times$  $10^{-19}$  cm<sup>2</sup> (±3% accuracy). The absorption measurement agreed with a manometric measurement of the NO<sub>2</sub> concentration to within the cross-section uncertainty. We determined  $[NO_2]$  in the reaction cell by measuring the  $NO_2$ /He flow relative to the total flow using calibrated electronic mass flow meters. At the highest [NO<sub>2</sub>] measurable using the 10 SCCM (standard cubic centimeters per minute) flow meter for the  $He/NO_2$  mixture, we checked the flow measurement by absorption. The absorption and flow measurement gave the same  $[NO_2]$ , although the flow measurement had significantly higher precision because of the small  $NO_2$  absorbances.

Dimerization of NO<sub>2</sub> to form N<sub>2</sub>O<sub>4</sub> is important at low temperatures [1]. The extent of this equilibrium limited the maximum NO<sub>2</sub> concentrations and thus the maximum measurable first-order OH loss rate constant. To demonstrate the effect of this equilibrium and the resulting correction to obtain  $k_1$ , we carried out measurements at high [NO<sub>2</sub>] (Fig. 1). The maximum [NO<sub>2</sub>] in the figure is more than an order of magnitude larger than that actually used to measure  $k_1$  (Table 1). According to the equilibrium,  $2NO_2 \rightleftharpoons N_2O_4$ , the following expression gives the NO<sub>2</sub> concentration:

$$[NO_{2}] = \frac{\left(\sqrt{8[NO_{2}]_{0}K_{eq} + 1}\right) - 1}{4K_{eq}}, \qquad (4)$$

where  $[NO_2]_0$  is the measured NO<sub>2</sub> concentration in the absence of the N<sub>2</sub>O<sub>4</sub> equilibrium (i.e., from the

flow measurement alone), [NO<sub>2</sub>] is the actual concentration in the low-temperature reaction cell and  $K_{eq}$  is the equilibrium constant at the reaction cell temperature. The solid points in Fig. 1 are the firstorder OH loss rate constants vs.  $[NO_2]_0$ , and the solid line is a fit to Eq. (3) with  $[NO_2]$  coming from Eq. (4). The value of  $K_{eq}$  is fixed at its literature value, [1] and  $k_1$  and  $k_d$  are varied to produce the fit. The open circles are the first-order OH loss rate constants vs. the corrected NO<sub>2</sub> concentration given by Eq. (4), and the dashed line is the resulting linear fit to Eq. (3). The agreement of the calculated line with the measured  $k_1$  in Fig. 1 shows that  $N_2O_4$ does not react as rapidly with OH as NO<sub>2</sub> and that the correction for  $N_2O_4$  can be carried out quite accurately. The straight line fit in Fig. 1 reproduces the value for  $k_1$  in Table 1 for identical temperature and pressure (220 K, 50 Torr N<sub>2</sub>) but much lower  $[NO_2]$  to within 3%, a deviation smaller than the experimental uncertainty. For the rate constants in Table 1, the correction due to the  $N_2O_4$  equilibrium was < 10% at 220 K and significantly smaller at higher temperatures. Therefore, any error introduced by the correction is negligibly small.



Fig. 1. Effect of the  $N_2O_4$  equilibrium at 220 K on the first-order OH loss rate constant, k'. Solid points are k' vs.  $[NO_2]$  as measured by mass flow outside the low-temperature reactor (i.e., uncorrected for the  $N_2O_4$  equilibrium), and the solid line is a non-linear least-squares fit to the equation shown in the figure. Open circles are for k' vs. the calculated NO<sub>2</sub> concentration in the reactor (after accounting for  $N_2O_4$ ), and the dashed line is a least-squares fit to Eq. (3).

Table 1 Measured  $OH + NO_2$  rate constants

T (K)	P (Torr)	$k (10^{12} \text{ cm}^3 \text{ s}^{-1})$		
		$M = N_2$	$M = O_2$	
220	20	$3.30 \pm 0.26$	$2.44\pm0.16$	
	30	$4.52\pm0.28$	$3.53 \pm 0.21$	
	50	$6.02\pm0.37$	$4.92 \pm 0.30$	
	75	$7.81 \pm 0.47$		
	100	$8.69 \pm 0.58$		
	170	$11.37 \pm 0.75$		
	250	$13.28\pm0.99$		
230	20	$2.86 \pm 0.20$	$2.47 \pm 0.15$	
	30	$3.98 \pm 0.24$	$3.28 \pm 0.20$	
	50	$5.20 \pm 0.32$	$4.26 \pm 0.25$	
	75	$6.91 \pm 0.42$		
	100	$7.56 \pm 0.48$		
	170	$10.54 \pm 0.65$		
	250	$12.15\pm0.89$		
240	20	$2.49 \pm 0.15$	$1.87 \pm 0.11$	
	30	$3.24 \pm 0.20$	$2.59 \pm 0.16$	
	50	$4.84 \pm 0.29$	$3.53 \pm 0.21$	
	75	$5.87 \pm 0.36$		
	100	$7.06 \pm 0.44$		
	170	$9.12 \pm 0.62$		
	250	$10.23 \pm 1.11$		
250	20	$2.33 \pm 0.15$	$1.86 \pm 0.11$	
	40	$3.62\pm0.22$	$2.90 \pm 0.17$	
	70	$4.90 \pm 0.34$		
	135	$7.48 \pm 0.46$		
	250	$9.26 \pm 0.79$		
296	20	$1.12\pm0.08$	$0.93 \pm 0.08$	
	50	$2.11\pm0.14$	$1.72\pm0.12$	
	100	$3.24 \pm 0.21$		
	200	$4.48 \pm 0.73$		

The error bars are at the 95% confidence limit and include the estimated systematic errors described in the text.

Additional potential error sources include the reaction of OH with the photolysis products of NO<sub>2</sub> (O and NO). The NO<sub>2</sub> absorption cross-section has a minimum at the photolysis laser wavelength, 248 nm, having a room-temperature value of  $1 \times 10^{-20}$ cm<sup>2</sup> [15]. At a typical maximum NO<sub>2</sub> concentration (2 × 10<sup>14</sup> cm<sup>-3</sup>) and 248 nm excimer laser fluence (7.5 mJ cm<sup>-2</sup>), the concentration of photolysis products is approximately [O] = [NO] =  $3.5 \times 10^{10}$  cm<sup>-3</sup>. Reaction with NO<sub>2</sub> converts the O atoms rapidly into NO; however, the resulting NO concentration is still less than [OH]<sub>0</sub>, and reaction with NO remains an insignificant contributor to the observed OH loss rate constants. To verify the lack of any secondary chemistry arising from NO<sub>2</sub> photolysis products, we varied the excimer laser fluence by a factor of 4 and observed that it did not influence the measured rate constants. In experiments using  $H_2O_2$  as an OH precursor, OH regeneration can occur through the reaction of NO with HO<sub>2</sub>, generated from reaction of OH with  $H_2O_2$ . This reaction sequence can regenerate at most 1% of  $[OH]_0$ , and much less under most experimental conditions. The regeneration would be significant if there were appreciable (> 0.1%) NO impurity in the NO<sub>2</sub>, but the observation of identical rate constants using HNO<sub>3</sub> and  $H_2O_2$  precursors indicates that this is not the case.

## 3. Results and discussion

Table 1 presents the OH + NO<sub>2</sub> effective bimolecular rate constants  $(k_1)$  in 20–250 Torr of N<sub>2</sub> and 20–50 Torr of O<sub>2</sub> at temperatures between 220 and 296 K. Each rate constant is an average of 2–3 individual measurements of  $k_1$ . The quoted errors are the averages of the 2 $\sigma$  precision from the slopes of the k' plots combined with the uncertainties in the NO<sub>2</sub> concentration measurements arising from the 3% uncertainty in the 365 nm NO<sub>2</sub> absorption cross-section and the 5% uncertainty associated with mass flow meter calibrations. The temperatures in Table 1 are accurate to ±0.5 K, and the uncertainty in the pressures varies between ±1 and 0.4% from 20 to 250 Torr.

Fig. 2 compares our measured rate constants at 220, 240, 250 and 296 K to the literature data available at these temperatures and to the current NASA/JPL recommendation [1] for the pressure falloff of  $k_1$ . At 296 K (Fig. 2a), our data in N<sub>2</sub> agree within the experimental uncertainty with all other measurements, including those of Anastasi and Smith [3], Wine et al. [4] and the recent, extensive, room-temperature measurements of Donahue et al. [10]. (For clarity we have displayed only the fit resulting from the latter study as the dashed line.) Our limited 298 K measurements are intended only to show the agreement with the large room-temperature data set. Interestingly, however, the



Fig. 2. Comparison of our measurement of the pressure falloff of  $k_1$  with literature data at: (a) 296 K; (b) 250 K; (c) 240 K; and (d) 220 K.

rate constants in  $O_2$  between 20 and 50 Torr are 20% smaller than those in  $N_2$ , despite the similar molecular weights of the two gases. The only literature data point with which we can compare the lower efficiency of  $O_2$  is the 25 Torr point of Anastasi and Smith at room temperature, where the rate constant in  $O_2$  is similarly smaller relative to  $N_2$ . Burrows et al. [8] measured the third-order, low-pressure limiting rate constant to be very slightly smaller in  $O_2$  than in  $N_2$ , but not outside the uncertainties in the rate constants.

The smaller rate constants with  $M = O_2$  do not appear to result from an experimental artifact since there is no apparent mechanism for OH regeneration in O<sub>2</sub>. The 248 nm photolysis light is not energetic enough to photolyze ground state O<sub>2</sub>, and the O<sub>2</sub> absorption cross-section is too small ( $< 10^{-24}$  cm<sup>2</sup>) to yield significant quantities of O atoms even at the highest [O<sub>2</sub>] [1]. Furthermore, the lack of any measurable dependence of  $k_1$  in O<sub>2</sub> on the photolysis laser fluence ruled out any multiphoton dissociation of O<sub>2</sub>. Photolysis of HNO<sub>3</sub> at 248 nm produces < 0.2% H atoms [16], so OH regeneration via production of HO<sub>2</sub> is not significant.

Our measurements at 250 K also agree to within the combined uncertainty with those of Wine et al.

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Table 2

Fit parameters for rate constant data (Eqs. (5) and (6))		
$k_0^{300}$	$2.47 \times 10^{-30}$	
n	2.97	
$k_{\infty}^{300}$	$1.45 \times 10^{-11}$	
т	2.77	
$\beta(N_2)$	1	
$\beta(O_2)$	0.70	
$\beta(air)$	0.94	

These parameters fit the data in Table 1 to within  $\pm 8\%$  at the 95% confidence level.

[4] at 247 K (Fig. 2b). Once again the rate constants in  $O_2$  are ~ 20% smaller than those in  $N_2$ . The NASA/JPL recommendation [1] at this temperature appears to be a slight overestimate of the measured rate constants in N<sub>2</sub>. This trend continues as the temperature decreases, as Fig. 2c shows. At 240 K, our data for  $M = N_2$  agree with Anastasi and Smith but differ from the NASA/JPL recommendation by 10–20% at the low end of the pressure range. At 220 K, the agreement between our measurements and Anastasi and Smith is not as good, although our data lie within their  $\pm 18\%$  error limits. Our measurements for  $M = N_2$  are 15–25% smaller than the NASA/JPL recommendation.

The present study greatly increases the database for reaction (1) in the falloff region relevant for the atmosphere below 250 K. To provide a rate constant expression that is useful for lower stratospheric chemical models, we have fit our data for  $M = N_2$ 



Fig. 3. Comparison of the pressure falloff in air (Eq. (5)) of our data and selected literature data (solid lines) to the current NASA recommendation (dashed lines) at four different temperatures. Data from this work for  $M = N_2$  and  $O_2$  appear as closed and open points, respectively. The  $N_2$  and  $O_2$  data are plotted against  $\beta_i[M]$ , where  $\beta_i$  is the collisional efficiency for each gas relative to air, which is taken as unity in this plot.

and  $O_2$  in the falloff region along with data for  $M = N_2$  from Wine et al. [4], Donahue et al. at 298 K [10], and Anastasi and Smith at 238 K and above [3]. The fit does not include any data in the high- or low-pressure limits but does encompass the temperature range 220–358 K. The fit function is the semi-empirical formula to describe the pressure falloff [1].

$$k = \left(\frac{k_0(T)\beta[M]}{1 + k_0(T)\beta[M]/k_{\infty}(T)}\right) \times 0.6^{\left(1 + \left[\log_{10}(k_0(T)\beta[M]/k_{\infty})\right]^2\right]^{-1}}, \qquad (5)$$
$$k_0(T) = k_0^{300} \left(\frac{T}{300}\right)^{-n}, \quad k_{\infty}(T) = k_{\infty}^{300} \left(\frac{T}{300}\right)^{-m}. \qquad (6)$$

Eq. (5) is identical to the fit function from the NASA/JPL recommendation [1] except for the parameter  $\beta$ , which we have introduced in order to account for the difference in collisional stabilization efficiency between N<sub>2</sub> and O<sub>2</sub>. We first fit the much larger data set for M = N<sub>2</sub>, fixing  $\beta$  at unity. We then fit the limited data for M = O<sub>2</sub> using the N<sub>2</sub> coefficients but allowing  $\beta$  for O<sub>2</sub> to vary. Table 2 lists the fit parameters. We find the collisional efficiency for O<sub>2</sub> relative to N<sub>2</sub> to be 0.70 ± 0.04. The collisional efficiency of air as a third body is the average of  $\beta$ (N<sub>2</sub>) and  $\beta$ (O<sub>2</sub>) weighted by their relative abundances (0.80 and 0.20, respectively), or  $\beta$ (air) = 0.94 ± 0.01. Table 2 presents all of the coefficients resulting from the fit.

Fig. 3 compares the pressure falloff curves from our fit for dry air as the third body to the current NASA/JPL recommendation [1] at 200, 220, 240 and 296 K. Our data for  $M = N_2$  and  $O_2$  also appear with their associated number densities scaled to a collisional efficiency of unity for air (i.e., with  $\beta(N_2) = 1/0.94 = 1.06$  and  $\beta(O_2) = 0.70/0.94 =$ 0.74). The NASA/JPL recommendation agrees closely with our fit at room temperature, but overestimates the rate constants by 33% at 10 Torr and 200 K and by 14% at 100 Torr at this temperature. The solid line at 200 K in Fig. 3 is an extrapolation since there are no measurements at this temperature. The fit presented in Table 2 and Fig. 3 is an empirical one intended to be useful for atmospheric modeling of the upper troposphere and lower stratosphere. We do not anticipate that it will accurately recover the

high- or low-pressure limits for reaction (1), but we do expect it to be valid over the pressure and temperature range of interest in the lower and middle atmosphere.

The amount of NO<sub>x</sub> present in the atmosphere depends on the relative rates for formation and destruction of reservoir species such as HNO<sub>2</sub>. Reaction (1) is the most important gas-phase reaction that converts NO<sub>x</sub> into HNO<sub>3</sub>. Additional reactions involving formation and heterogeneous hydrolysis of  $N_2O_5$  also contribute [17]. The results of this work, combined with recent measurements of the rate constant for reaction of OH with HNO<sub>3</sub> [13], an important gas-phase process for NO<sub>x</sub> regeneration from the nitric acid reservoir, have increased the calculated ratio of NO<sub>x</sub> to total odd nitrogen species and have brought atmospheric models into better agreement with observations [11]. The new  $OH + NO_2$ and OH + HNO<sub>3</sub> rate constants also influence calculated ozone loss rates. In conjunction with new measurements of rate constants in the NO<sub>x</sub> catalytic ozone destruction [18], they have resulted in a reevaluation of the role of NO<sub>x</sub> in the lower stratosphere [19].

Note added in proof: While this manuscript was in preparation, we became aware of rate constants for this reaction in 50–150 Torr of  $N_2$  from 212.5 to 310 K measured recently by Dransfield et al. [20]. Their data, within the quoted uncertainties, agree with our fits.

## Acknowledgements

We thank Jim Burkholder for providing samples of  $NO_2$  and assisting in checking their purity. SSB thanks the National Research Council for a postdoctoral research fellowship during this work. This work was funded in part by the NOAA Climate and Global Change research program.

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