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# Temperature Dependence of the Reaction $NO_3 + NO_2 \rightarrow NO + NO_2 + O_2$ in the Range from 296 to 332 K

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The temperature dependence of the  $[NO]/[NO_2]$  ratio in  $N_2O_5/NO_2/N_2$  gas mixtures has been determined in the range 296 K  $\leq$  T  $\leq$  332 K. The experiments were made at 50 mbar in a static reactor. Tunable diode laser spectroscopy was used to measure [NO] while  $[NO_2]$  and  $[N_2O_3]$  were determined by FTIR spectroscopy. The use of a steady-state assumption for NO in the gas mixtures leads to the expression  $k_1/k_2 = [NO]/[NO_2]$  where  $k_1$  and  $k_2$  are the rate coefficients for the title reaction and the reaction NO + NO<sub>3</sub>  $\rightarrow$  2NO<sub>2</sub>, respectively. The relation  $k_1/k_2 = 3.3 \times 10^{-3} \exp(-1598/T)$  was found to describe the experimental data. The present result, in conjunction with a recently reported value for  $k_2$  [J. Phys. Chem. 1991, 95, 4381], yields  $k_1 = 5.4 \times 10^{-14} \exp(-1488/T)$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. The estimated accuracy at the 95% confidence level is  $\pm 29\%$ . The error in activation energy of  $k_1$  due to the functional dependence on  $k_2$  is expected to be small due to the low activation energy of the latter.

#### Introduction

The importance of the nitrate radical, NO<sub>3</sub>, for atmospheric chemistry has been increasingly evident ever since this species began to attract attention some 20 years ago.<sup>1-3</sup> The nitrate radical is formed in the atmosphere by the reaction between ozone and nitrogen dioxide, and the radical normally exists in thermal equilibrium with nitrogen dioxide and dinitrogen pentoxide. Due to its high absorption cross section<sup>1</sup> in parts of the visible spectrum, the nitrate radical is easily photolyzed and may therefore be present in significant concentrations only at night. Unsaturated organic compounds, e.g., alkenes, isoprene, and a variety of terpenes, as well as several reduced sulfur compounds may react at high rates with the nitrate radical during the dark hours.<sup>1,2</sup> In some cases, the turnover of unsaturated hydrocarbons by nitrate radicals at night is expected to exceed that by hydroxyl radicals during daytime.4

Channels which compete with the title reaction for NO<sub>3</sub> radicals in the atmosphere are reaction with NO and with unsaturated hydrocarbons.<sup>1,2</sup> Disappearance of NO<sub>3</sub> via N<sub>2</sub>O<sub>5</sub> hydrolysis on wet aerosols could also be important.<sup>5</sup> The natural lifetime may be used to make an estimate of the importance of the various processes. Assuming an NO<sub>2</sub> concentration of  $1.2 \times 10^{12}$  molecules cm<sup>-3</sup> (50 ppb) and using  $k_1 = 6.3 \times 10^{-16}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298 K<sup>1</sup> gives an NO<sub>3</sub> lifetime of about 22 min with respect to reaction 1. The rate coefficient for the reaction between NO and NO<sub>3</sub> is roughly 5 orders of magnitude larger than  $k_1$ , and if NO is present in concentrations above  $3 \times 10^{7}$  molecules cm<sup>-3</sup> this path will dominate over reaction 1. Values of NO<sub>3</sub>-alkene rate coefficients of 10<sup>-15</sup> and 10<sup>-12</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> may be taken as typical for a small, slowly reacting alkene and a larger, branched alkene, respectively. A 22-min lifetime with respect to the NO<sub>3</sub>-alkene reaction then corresponds to an alkene concentration of  $7.5 \times 10^{11}$  (30 ppb) and  $7.5 \times 10^8$  (30 ppt), respectively. Higher concentrations would proportionally reduce the lifetime. If the NO<sub>2</sub> concentration is assumed to be constant, then loss of the NO<sub>3</sub>

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storage compound N<sub>2</sub>O<sub>5</sub> would result in a corresponding reduction in NO<sub>3</sub>. Mozurkewich and Calvert<sup>5</sup> have shown that wet aerosols scavenge N<sub>2</sub>O<sub>5</sub> and that lifetimes between 30 s and 2 h may be expected, depending on relative humidity and specific surface of the aerosol. Thus, the title reaction may play a small but in some cases significant role in the nighttime destruction of NO<sub>3</sub> in the atmosphere. Conditions which would increase the relative importance of reaction 1 are high concentrations of O<sub>3</sub> and NO<sub>2</sub> which promotes NO<sub>3</sub> production and, at the same time, reduces the NO concentration. The relative importance of (1) is also enhanced by low aerosol loading and low relative humidity, which reduces N<sub>2</sub>O<sub>5</sub> losses on wet aerosols, and by low concentrations of reactive hydrocarbons.

The transformation of dinitrogen pentoxide into oxygen and nitrogen dioxide was an early example of a gas-phase process with first-order behavior. The reaction later proved to be rather more complex than a simple unimolecular gas-phase decomposition.<sup>6</sup>

$$NO_2 + NO_3 \rightarrow NO_2 + NO + O_2 \tag{1}$$

$$NO + NO_3 \rightarrow 2NO_2$$
 (2)

$$NO_2 + NO_3 + M \rightarrow N_2O_5 + M \tag{3}$$

$$N_2O_5 + M \rightarrow NO_2 + NO_3 + M \qquad (-3)$$

$$2N_2O_5 \rightarrow 4NO_2 + O_2 \tag{4}$$

The NO molecule resulting from the destruction of one NO<sub>3</sub> in reaction 1 will, in effect, destroy another NO<sub>3</sub> molecule in reaction 2.  $N_2O_5$  is then decomposed in (-3) to maintain the (3/-3) equilibrium. The resulting overall reaction is described by (4). Reaction 4 is first order for a range of conditions, both in the gas phase and in liquids. However, it is the title reaction (1) which determines the rate of irreversible destruction of  $N_2O_5$ , and this reaction has to be coupled to reaction 2 and 3/-3 to give a complete description of the decomposition.

The only direct measurement, so far, of  $k_1$  was made at elevated temperatures by Schott and Davidson,<sup>7</sup> who made shock tube experiments with N<sub>2</sub>O<sub>5</sub> in the temperature range 750–934 K and followed [NO<sub>2</sub>] and [NO<sub>3</sub>] by UV-vis spectroscopy. At temperatures above 600 K N<sub>2</sub>O<sub>5</sub> is completely dissociated into NO<sub>2</sub> and NO<sub>3</sub>, and the decay of NO<sub>3</sub> was assumed to be due to reaction 1 followed by reaction 2 and to the self-reaction

$$2NO_3 \rightarrow 2NO_2 + O_2 \tag{5}$$

The analysis of the NO<sub>3</sub> decay led to two different expressions for  $k_1$ , which give  $k_1 = 1.3 \times 10^{-18}$  and  $2.3 \times 10^{-16}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, respectively, when extrapolated to 296 K. The latter value is calculated from the  $k_1$  expression that, according to the authors, corresponds to the most reliable data set.

At room temperatures reaction 2 and the equilibrium 3/-3, characterized by the equilibrium constant  $K_3$ , are fast compared with reaction 1. The rate of reaction 1 can then be related to the rate of N<sub>2</sub>O<sub>5</sub> decomposition as shown by

$$-\frac{d[N_2O_5]}{dt} = 2k_4[N_2O_5] = 2k_1[NO_2][NO_3] = 2\frac{k_1}{K_3}[N_2O_5]$$
(I)

Identification shows that  $k_4 = k_1/K_3$ , and thus  $k_1$  may be determined indirectly from  $k_4$  and  $K_3$ . By combining literature values of  $k_4^8$  with measurements of  $K_3$ , Graham and Johnston<sup>9</sup> arrived at the expression

$$k_1 = (2.5 \pm 0.5) \times 10^{-14} \exp[(-1230 \pm 100)/T]$$
 cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (II)

which is valid from 338 to 396 K. The  $k_1$  value calculated for 296 K from this expression is  $3.9 \times 10^{-16}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, in fair agreement with the higher value from Schott and Davidson discussed above. On the other hand, if eq II is used to calculate  $k_1$  in the temperature range between 750 and 934 K, then values which are much lower than those determined by Schott and Davidson accounted for by Johnston et al.<sup>3</sup> in terms of a contribution from

the thermal decomposition of NO<sub>3</sub> according to

$$NO_3 \rightarrow NO + O_2$$
 (6)

The Arrhenius expression for reaction 6

$$k_6 = 2.5 \times 10^6 \exp(-6100/T) \, \mathrm{s}^{-1}$$
 (III)

was derived from a reinterpretation of data from Schott and Davidson<sup>7</sup> and three other studies made at room temperature.<sup>3</sup>

Cantrell et al.<sup>10</sup> remeasured  $k_4$ , and when combining  $k_4$  with their own measurement of  $K_3$ , they obtained

$$k_1 = 9.5 \times 10^{-14} \exp(-1414/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
 (IV)

The accuracy of expression IV was reported to be  $\pm 35\%$  at the 95% confidence level. At 296 K expression IV gives a value of  $8.0 \times 10^{-16}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, which in comparison with the value from Graham and Johnston<sup>9</sup> differs by a factor of 2. The discrepancy is mainly due to the difference between the values of  $K_3$  which were used.  $K_3$  has been determined by several investigators, but its value is still a matter of debate.<sup>1</sup>

Hjorth et al.<sup>11</sup> devised another indirect way of determining  $k_1$ . The expression

$$k_1[NO_3][NO_2] + k_6[NO_3] = k_2[NO][NO_3]$$
 (V)

was obtained from the equation for the NO balance in an inert gas mixture containing  $N_2O_5$  and using a steady-state assumption for NO. The equation may be rearranged to give

$$k_1 = k_2 \frac{[\text{NO}]}{[\text{NO}_2]} - \frac{k_6}{[\text{NO}_2]}$$
 (VI)

If  $k_2[NO] \gg k_6$ , the influence from reaction 6 is small and

$$k_1 = k_2 \frac{[\text{NO}]}{[\text{NO}_2]} \tag{VII}$$

This method relies on  $k_2$ , which is independent of both  $k_4$  and  $K_3$ , and thus allows another indirect way of establishing  $k_1$ . Hjorth et al.<sup>11</sup> used FTIR spectroscopy to determine [NO<sub>2</sub>] and tunable diode laser spectroscopy to measure [NO] in mixtures of N<sub>2</sub>O<sub>5</sub> and NO<sub>2</sub>. The experiments resulted in an [NO]/[NO<sub>2</sub>] ratio of  $1.6 \times 10^{-5}$  at 296 K and, when combined with the rate coefficient  $k_2$  from ref 12, gave a value of  $k_1$  of  $5.1 \times 10^{-16}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. This value falls in between the value of Graham and Johnston<sup>9</sup> of  $3.9 \times 10^{-16}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and that of Cantrell et al.<sup>10</sup> of  $8.0 \times 10^{-16}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 296 K.

Cantrell and co-workers<sup>13</sup> determined the temperature dependence of the  $k_1/k_2$  ratio using a stainless steel flow reactor. Long-path UV spectroscopy was used to measure NO<sub>2</sub> while NO was determined by passing the flow through an NO chemiluminescence instrument. Nitrogen passed over thermostated, solid N<sub>2</sub>O<sub>5</sub> served as the N<sub>2</sub>O<sub>5</sub> source, and addition of NO<sub>2</sub> in nitrogen was used to control the absolute NO<sub>2</sub> concentration in the reaction mixture. In the temperature range 273 K  $\leq T \leq 313$  K the expression

$$\frac{[\text{NO}]}{[\text{NO}_2]} = \frac{k_1}{k_2} = 2.58 \times 10^{-3} \exp(-1375/T) \quad \text{(VIII)}$$

was obtained with the overall uncertainty estimated to be 25% at the 95% confidence level. This ratio at 296 K,  $2.5 \times 10^{-5}$ , differs significantly from that determined by Hjorth et al.<sup>11</sup> of  $1.6 \times 10^{-5}$ . When combined with the rate coefficients of  $k_2$  from Hammer et al.,<sup>14</sup> the following expressions were obtained

$$k_1 = 4.00 \times 10^{-14} \exp(-1180/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
  $T < 300 \text{ K}$  (IX)

$$k_1 = 7.62 \times 10^{-14} \exp(-1375/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
 T > 300 K (X)

The value of  $k_1$  at 296 K calculated from (IX) is 7.4 × 10<sup>-16</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, and it compares favorably with the earlier value from Cantrell et al.<sup>10</sup>



Figure 1. Experimental setup.

In the present work we have used the in-situ steady-state method employed by Hjorth et al.<sup>11</sup> to determine the temperature behavior of reaction 1.

# **Experimental Setup and Procedure**

The experimental setup consists of a cylindrical reactor, 2 m long and of 0.3 m in diameter, made of a borosilicate glass tube with the ends sealed by stainless steel plates. The reactor is thermally insulated and can be thermostated between 273 and  $353 \pm 1$  K. The reactor is equipped with White optics giving 80-m optical path length. The optical system is connected to a Mattson Polaris FTIR spectrometer or, alternatively, via a flip mirror to a tunable diode laser (TDL) system. Both infrared beams are focused on an Hg-Cd-Te detector. The detector signal is preamplified and coupled to the FTIR spectrometer or to a lock-in amplifier, the latter a part of the TDL signal processing system. The details of the experimental setup are shown in Figure 1. The FTIR instrument was used to measure the concentration of NO<sub>2</sub> and N<sub>2</sub>O<sub>5</sub> while the TDL system was used to measure the much lower NO concentration.

In order to determine the NO<sub>2</sub> absorption cross section, commercial liquid NO<sub>2</sub> was distilled twice and kept in a small glass container equipped with a teflon valve. Known amounts, determined by weighing the container, of NO<sub>2</sub>/N<sub>2</sub>O<sub>4</sub> mixture were introduced into a vacuum line connected to the reactor. The aliquots were in the range 0.17–1.9 g and determined with an accuracy of 0.1 mg. A known fraction of the NO<sub>2</sub>/N<sub>2</sub>O<sub>4</sub> mixture was then introduced into the reactor with N<sub>2</sub> as carrier gas. Since high concentrations of NO<sub>2</sub> were to be measured, the absorption at 2914 cm<sup>-1</sup> in the relatively weak  $v_1 + v_3$  band was used. FTIR spectra with 1-cm<sup>-1</sup> resolution were taken at 296 K with NO<sub>2</sub> concentrations from  $1.7 \times 10^{15}$  to  $1.4 \times 10^{16}$  molecules cm<sup>-3</sup> at a total pressure of 50 mbar. This resulted in a nonlinear calibration curve described by the relation

$$[NO_2] = (-1.96 \times 10^{19} + 2.25 \times 10^{20}A - 4.10 \times 10^{20}A^2 + 7.03 \times 10^{20}A^3 \pm 1.4 \times 10^{18})/l \text{ molecule cm}^{-3} \text{ (XI)}$$

 $A = \log (I_0/I)$  (base 10) and *l* is the path length in centimeters. The uncertainty was calculated by *t*-statistics at the 95% confidence level. The absorbance was also measured at 332 K and found to be about 7% larger than at 296 K. In order to correct for the intermediate temperatures, a linear dependency was assumed.

The TDL system consisted of a tunable  $PbS_{1-x}Se_x$  diode laser (Spectra-Physics) with the spectral range 1885–1915 cm<sup>-1</sup>, housed in a closed cycle cryo-cooled laser head (MDS 1100 Mütek). The diode was powered by a bias supply and frequency modulated via a current ramp. The diode laser was in this way scanned over the strong unresolved double peak R(6.5) for the  $X^2\Pi_{3/2}$  state at 1900.52 cm<sup>-1</sup>. The 2*f* technique<sup>15</sup> was utilized by superimposing a small sinusoidal 2-kHz current on the current ramp. The 2*f* signal from the lock-in amplifier was digitized at 1-kHz sampling rate and stored by a personal computer. At the low NO concentrations used, the ratio (2*f* signal)/ $I_0$ , where  $I_0$  is the emitted laser intensity at the absorption line, is directly proportional to



Figure 2. S vs [NO]l where  $S = (2f \text{ signal})/I_0$ , [NO] is expressed in molecules cm<sup>-3</sup>, and l is the path length in cm. A least-squares fit to the data gave the expression  $S = (2.017 \pm 0.085) \times 10^{-18} [NO]l$ . The precision given is calculated at the 95% confidence level.

the NO concentration. Since  $I_0$  could vary slightly between measurements, this quantity was always determined in conjunction with the 2*f* measurements. The  $I_0$  measurements were made by modulation of the laser beam by a rotating chopper at 325 Hz followed by lock-in detection. The resulting transmittance signal was digitized and stored by the computer. A Ge etalon with a free spectral range of 0.05 cm<sup>-1</sup> was used to check the single-mode behavior of the diode during the scan.

To convert the  $(2f \text{ signal})/I_0$  to NO concentrations, the following calibration was made. A commercial gas mixture containing 193.2 ± 1.1 ppm NO in N<sub>2</sub> was filled in calibrated volumes in the vacuum line, and the pressure was determined by a Barocel 600 capacitance pressure gauge. The gas sample was then flushed into the reactor with N<sub>2</sub> as the carrier gas to give a total pressure of 50 mbar. The laser intensity at the 2f signal were then measured by averaging 60 scans. The  $(2f \text{ signal})/I_0$  as a function of NO concentrations measured in the range from  $7.7 \times 10^{10}$  to  $5.0 \times 10^{11}$  molecules cm<sup>-3</sup> gave a straight line with a near-zero intercept as is shown in Figure 2. The precision of the slope as calculated by *t*-statistics was ±4.2% at the 95% confidence level. This calibration was made at 296 K, and correction of the absorption strength at elevated temperatures was made assuming a Boltzmann distribution of the rotational states.

Before each experiment, the reactor was thermostated to the desired temperature and evacuated. Then  $NO_2$  and  $O_3$ , the latter produced by a silent discharge ozone generator, were mixed in the reactor, producing  $NO_3$  radicals according to reaction 7 which,

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \tag{7}$$

in turn, formed  $N_2O_5$  via reaction 3. Subsequently,  $N_2$  was added in order to mix the gas species. The pressure was then reduced to 50 mbar. The large excess of  $NO_2$  gave an instant removal of the ozone, and the equilibrium (3/-3) was rapidly established. Initial concentrations of  $N_2O_5$  were typically around 7.5  $\times$  10<sup>13</sup> molecules  $cm^{-3}$ . The experiments at temperatures below 332 K normally started with an FTIR measurement to determine NO<sub>2</sub> and  $N_2O_5$  concentrations. The flip mirror was then altered, and the NO concentration was determined by the TDL. The NO concentration was determined by the same procedure as for the calibration, except that 4-6 measurements, each containing the average of 60 scans, were taken over 10-20 min. At the end of the experiments another  $NO_2$  determination was made, but no significant difference between the initial and final NO<sub>2</sub> measurement was ever seen. At 332 K the decomposition of  $N_2O_5$ was rapid, and it was necessary to start the TDL measurements at quickly as possible. Thus, in these experiments only one  $NO_2$ and  $N_2O_5$  measurement was made.

# **Results and Discussion**

In order to estimate the time needed to reach steady state with respect to NO, a series of simulations at temperatures from 277 to 332 K were made using the FACSIMILE computer program.<sup>16</sup> Reactions 1, 2, 3, -3, 7, and 8 were included in the calculations,

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{8}$$

and the rate coefficients were taken from Wayne et al.<sup>1</sup> The  $NO_2$  used in the experiments contained approximately 0.02% NO as an impurity, and this was taken into account in the calculations.

 $NO_3 + NO_2 \rightarrow NO + NO_2 + O_2$  Reaction

temp	$[NO] \times 10^{-11}$	$[NO_{2}] \times 10^{-15}$	
(K)	(molecules cm <sup>-3</sup> )	(molecules cm <sup>-3</sup> )	$[NO]/[NO_2] \times 10^5$
296	1.28	7.52	1.70
296	0.74	4.87	1.52
296	1.34	8.20	1.64
296	2.21	13.7	1.61
296	1.11	7.33	1.51
296	0.76	5.81	1.31
296	0.27	2.44	1.12
296	1.46	10.2	1.42
296	0.80	5.04	1.59
296	1.37	9.40	1.46
296	0.85	5.15	1.66
313	1.77	8.25	2.14
313	1.16	5.83	2.00
313	1.49	8.47	1.76
313	0.57	2.60	2.20
313	2.32	12.7	1.82
313	1.51	8.56	1.76
323	2.05	8.66	2.37
323	1.04	4.54	2.28
323	0.51	2.34	2.19
323	2.63	11.8	2.23
323	1.43	5.96	2.39
332	1.74	5.80	3.00
332	1.99	8.19	2.43
332	1.68	5.82	2.89
332	2.40	8.68	2.76
332	2.65	10.1	2.62
332	1.18	4.40	2.68
332	1.90	7.16	2.66

As expected, this initial amount of NO was, in most cases, rapidly converted to  $NO_2$  through reaction 8. The simulations also showed a temperature dependence of the relaxation time since the equilibrium constant  $K_3$  has a strong temperature dependence. The NO<sub>3</sub> concentration was close to the ratio  $[N_2O_5]/K_3[NO_2]$ ; thus, at low temperatures, the NO3 concentration is low and consequently the buildup of NO through reaction 1 will be slow. However, under some conditions with high  $NO_2$  concentration, significant amounts of the initially introduced NO could remain after the ozone concentration had become negligible. In this case the time to reach steady state was dependent on the removal of NO through reaction 2. The calculated relaxation times spanned from a few seconds to 7 min depending on temperature and initial  $[N_2O_5]/[NO_2]$  ratio. At 332 K the relaxation times were less than 30 s at all  $[N_2O_5]/[NO_2]$  ratios, but the rapid  $N_2O_5$  decomposition limited the steady-state situation to about 10 min. These results were experimentally verified by monitoring the NO concentrations in the reactor.

Equation VII is based on the assumption that the influence from homogeneous and/or heterogeneous decay of NO<sub>3</sub> radicals according to reaction 6 is small. In order to ascertain that this was the case, the measured steady-state concentration of NO from different runs at each temperature was plotted against the corresponding NO<sub>2</sub> concentration. According to expression VI this should give a slope of  $k_1/k_2$  and an intercept equal to  $k_6/k_2$  as is shown by the equation

$$[NO] = \frac{k_1}{k_2}[NO_2] + \frac{k_6}{k_2}$$
(XII)

Small positive intercepts were actually seen from the experiments at 313 and 332 K, but the values could not be shown to be significant in a statistical analysis. This is consistent with the ratio  $k_6/k_2$ , calculated from literature values,<sup>1</sup> always being less than 1% of the measured NO concentration at our experimental conditions.

The rate coefficient ratio  $k_1/k_2$  was measured at 296, 313, 323, and 332 K. A number of experiments with different NO<sub>2</sub> concentrations were made at each temperature. The measured NO<sub>2</sub> and NO concentrations and the calculated  $k_1/k_2$  rate coefficient ratio from each experiment are given in Table I. In Table II, the averages of the  $k_1/k_2$  ratios at each temperature are presented.

TABLE II: Average  $k_1/k_2$  Rate Coefficient Ratios with Errors Limits at the 95% Confidence Level



Figure 3. Temperature dependence of  $k_1/k_2$  rate coefficient ratios. (a) This work; error bars show errors at the 95% confidence level. (b) The result from Cantrell et al.<sup>13</sup> The open circle represents the result from Hjorth et al.<sup>11</sup> at 296 K.

The value obtained at 296 K is  $(1.5 \pm 0.1) \times 10^{-5}$ , which can be compared with  $(1.6 \pm 0.1) \times 10^{-5}$  from the study by Hjorth et al.<sup>11</sup> and to  $2.5 \times 10^{-5}$  from Cantrell et al.<sup>13</sup> The agreement between our value and that of Hjorth et al.<sup>11</sup> is within the statistical errors calculated at the 95% confidence limit. Our temperature dependence of  $k_1/k_2$  between 296 and 332 K is shown by an Arrhenius plot in Figure 3. The results from Hjorth et al.<sup>11</sup> and Cantrell et al.<sup>13</sup> are also included. The present data are described by the expression

$$k_1/k_2 = 3.3 \times 10^{-3} \exp(-1598/T)$$
 (XIII)

The overall accuracy was estimated to  $\pm 12\%$ . The statistical error calculated from the precision of NO and  $NO_2$  calibrations gave  $\pm 6.0\%$ . The estimated systematic errors included were those in the concentrations of the NO and NO<sub>2</sub> standards (1% each), NO and  $NO_2$  calibrations due to volume/pressure determinations (2%), and other possible errors (2%). The precision of the Arrhenius slope calculated from all the individual  $k_1/k_2$  data is ±15.1% at the 95% confidence level. The exponential term in eq XIII is only 16% higher than that from Cantrell et al.<sup>13</sup> The agreement between the two studies is, in this respect, good and within the stated accuracy. However, the  $k_1/k_2$  ratios from eq XIII give values which are only 60% of those from Cantrell et al.<sup>13</sup> This may be caused by unaccounted errors in one or both of the two different methods applied. The reproducibility between our data and that from Hjorth et al.,<sup>11</sup> who also made in-situ, steady-state, IR measurements in a static reactor, is good as pointed out above. In the paper by Cantrell et al.<sup>13</sup> the discrepancy between their  $k_1/k_2$  ratio and that by Hjorth et al.<sup>11</sup> is discussed. Cantrell et al.<sup>13</sup> show that it is possible to underestimate NO steady-state concentrations due to NO loss caused by adsorbed O<sub>3</sub> on the reactor walls. These authors found a temporary decrease of up to 50% in NO concentration after their system had been conditioned by high  $O_3$  concentrations (>10<sup>16</sup> molecules cm<sup>-3</sup>). Although our reactor walls are made of glass, in contrast to the stainless steel flow reactor used by Cantrell et al.,13 such adsorption is conceivable also in our case. The  $O_3$  concentrations used in the present work were, however, about 2 orders of magnitude smaller and the NO concentrations an order of magnitude greater than those used by Cantrell et al.<sup>13</sup> Thus, such removal of NO is not likely to be important in the present case. It is however possible to overestimate the  $k_1/k_2$  ratio. As discussed above, the  $NO_2$  used in the present investigation was seen to contain 0.02% NO, most of which was rapidly destroyed by O<sub>3</sub> long before the NO/NO<sub>2</sub> measurements were started. Even a smaller NO contamination of the NO<sub>2</sub> could certainly lead to an overestimate of the NO steady-state concentration, when used in a flow system with short residence times. Whether or not this may be a problem in the work of Cantrell et al.<sup>13</sup> is not known since no statement



Figure 4. Arrhenius plot for the reaction  $NO_2 + NO_3 \rightarrow NO + NO_2 + O_2$ : (a) this work with  $k_2$  from Tyndall et al.<sup>17</sup> (b) this work with  $k_2$  from Hammer et al.<sup>14</sup> (c) Cantrell et al.<sup>13</sup> with  $k_2$  from Hammer et al.<sup>14</sup> (d) Cantrell et al.<sup>10</sup> (e) Graham and Johnston<sup>9</sup> The open circle represents the result from Hjorth et al.<sup>11</sup> at 296 K with a  $k_2$  from DeMore et al.12

about the possible presence of impurities was made.

The rate coefficient  $k_1$  as a function of temperature was obtained by combining eq XIII with rate coefficients for reaction 2 from Hammer et al.<sup>14</sup> and from Tyndall et al.<sup>17</sup> The results are shown in Figure 4 together with previous results from Graham and Johnston,<sup>9</sup> Cantrell et al.,<sup>10</sup> Hjorth et al.,<sup>11</sup> and Cantrell et al.<sup>13</sup> It is clear that the main discrepancy between the present result and the result from Cantrell et al.<sup>13</sup> is due to different  $k_1/k_2$ ratios, but the calculated  $k_1$  values are also dependent on the choice of  $k_2$  value as is seen in Figure 4. The rate of reaction 2 as a function of temperature has been the subject of three direct studies. Hammer et al.<sup>14</sup> measured  $k_2$  between 209 and 414 K in a flow tube system. They found a weak negative temperature dependence below 300 K and a temperature-independent rate coefficient above 300 K. In a flash photolysis investigation by Sander and Kircher,<sup>18</sup> a 20-25% lower  $k_2$  value than that of Hammer et al. was obtained. The experiment covered a temperature range from 224 to 328 K and showed a weaker temperature dependence than that found by Hammer et al.<sup>11</sup> In order to reconcile earlier results, Tyndall et al.<sup>17</sup> performed an extensive direct study of the temperature dependence of  $k_2$  in the range 223-400 K, using flow tube technique with detection of NO<sub>3</sub> by laser-induced fluorescence or NO detection by chemiluminescence. Their result is in excellent agreement with the flash photolysis determination made by Sander and Kircher.<sup>18</sup> The two studies gave results which are identical within the limits of error and the equation

$$k_2 = (1.65 \pm 0.35) \times 10^{-11} \exp[(110 \pm 25)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (\text{XIV})$$

recommended by Tyndall et al.<sup>17</sup> is a combination of the two. The error in the preexponential factor includes precision  $(2\sigma)$  and an estimated 10% from systematic errors, while the error in the exponential term represents statistical uncertainty. We consider the rate coefficient expression given Tyndall et al.<sup>17</sup> as the most reliable at present. Expression XIV was therefore preferred when calculating  $k_1$ . The resulting equation is

$$k_1 = 5.4 \times 10^{-14} \exp(-1488/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
 (XV)

The estimated total accuracy is 29%, based on a propagation of error calculation using the uncertainty from our determination together with that given for  $k_2$ . Since the temperature dependence of  $k_2$  is very low, its contribution to the temperature dependence of (XV) is less than 8%. The exponential term in the resulting Arrhenius expression will therefore, to the greater part, be determined by eq XIII while the preexponential term also relies on  $k_2$ . The activation energy for reaction 1 derived from this work is 12.4 kJ mol<sup>-1</sup>, which may be compared with 10.2 kJ mol<sup>-1</sup> from Graham and Johnston,<sup>9</sup> 11.8 kJ mol<sup>-1</sup> from Cantrell et al.,<sup>10</sup> and 9.8 or 11.4 kJ mol<sup>-1</sup> from Cantrell et al.<sup>13</sup> Although the present activation energy is higher than those previously determined, the agreement is remarkably good, especially between our value and that by Cantrell et al.<sup>10</sup> and the higher value from Cantrell et al.<sup>13</sup> As is shown in Figure 4, the difference between published  $k_1$ expressions may be greater than a factor of 2 in the region of temperature overlap. For the  $k_1$  determinations which are  $K_3/k_4$ 

TABLE III: The  $NO_2 + NO_3 \implies N_2O_5$  Equilibrium

temp range (K)	$K_3(T)$ (cm <sup>3</sup> molecule <sup>-1</sup> )	$K_3(298 \text{ K}) \times 10^{11}$ (cm <sup>3</sup> molecule <sup>-1</sup> )	ref
450-550	$1.78 \times 10^{-26} \exp(10115/T)$	0.98	7
298-329	$1.19 \times 10^{-27} \exp(11180/T)$	2.34	9
200-300	$1.33 \times 10^{-27} (T/300)^{0.32}$ exp(11080/T)	1.86	20
300500	$1.33 \times 10^{-27} (T/300)^{1.12}$ exp(11080/T)	1.85	20
262-384	$3.14 \times 10^{-30}(T)$ exp(11349/T)	3.24	21
275-315	$8.13 \times 10^{-29} \exp(11960/T)$	2.19	22ª
243-397	$7.69 \times 10^{-27} \exp(10815/T)$	4.44	10 <sup>a</sup>
273-300 300-313	$3.25 \times 10^{-27} \exp(11050/T)$ $6.21 \times 10^{-27} \exp(10855/T)$	4.12	13 13
296-332	$4.39 \times 10^{-27} \exp(10742/T)$	1.98	this work

<sup>a</sup> Determinations made by direct methods.

dependent, the discrepancy is mainly due to the  $K_3$  values used. This is the case since these  $k_1$  values are based on essentially the same, well-established first-order N<sub>2</sub>O<sub>5</sub> decomposition rate  $k_4$ .

The uncertainty regarding the value of  $K_3$  probably reflects experimental difficulties involved in making direct measurements of this quantity. In contrast, in a reinvestigation of  $k_4$ , the first-order decay of N<sub>2</sub>O<sub>5</sub>, Cantrell et al.<sup>10</sup> found an excellent agreement with previous results from Daniels and Johnston<sup>19</sup> and Johnston and Tao.<sup>8</sup> The resulting expression, when all data were put together, is given by

$$k_4 = 1.23 \times 10^{13} \exp(-12230/T) \, \mathrm{s}^{-1}$$
 (XVI)

The error limits were estimated to  $\pm 15\%$  at the 95% confidence level. The equilibrium constant  $K_3$  may be calculated from  $k_1$ and  $k_4$ . In Table III the expression for  $K_3$  based on our  $k_1$  and  $k_4$  from Cantrell et al.<sup>10</sup> is compared with other directly or indirectly determined expressions for  $K_3$ . This work gives a value which falls in the low end. The agreement regarding the temperature dependencies is good. Our temperature dependence is very close to that of Cantrell et al.<sup>10</sup> which covers the most extensive temperature range. It must, however, be stressed that the temperature dependence in the derived expression for  $K_3$  is to a large extent due to that of  $k_4$ .

#### Conclusions

The value of  $k_1$ , calculated using a recent  $k_2$  value by Tyndall et al.<sup>17</sup> giving the Arrhenius expression  $k_1 = 5.4 \times 10^{-14} \exp(-10^{-14} \exp(-10^{-14}$ 1488/T) cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, falls in the low end of the determinations available in the literature. The reproducibility of the rate coefficient ratio  $k_1/k_2$  determined by identical methods in different laboratories appears to be good. The significant difference in the  $k_1/k_2$  ratio using the same underlying theory but different experimental setups is still unresolved and needs further work. The equilibrium constant for the reaction  $NO_2 + NO_3 =$ N<sub>2</sub>O<sub>5</sub> was calculated from  $k_1$  and found to be  $K_3 = 4.39 \times 10^{-27}$  $\exp(10742/T)$  cm<sup>3</sup> molecule<sup>-1</sup>.

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# A Study of the Reactions of $H_3^+$ , $H_2D^+$ , $HD_2^+$ , and $D_3^+$ with $H_2$ , HD, and $D_2$ Using a Variable-Temperature Selected Ion Flow Tube

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The reactions of  $H_3^+$  with  $H_2$  in all possible deuterated combinations (i.e.,  $H_3^+$ ,  $H_2D^+$ ,  $HD_2^+$ , and  $D_3^+$  variously with  $H_2$ , HD, and  $D_2$ ) have been studied at both 300 and 80 K using a VT-SIFT apparatus. The experimentally determined equilibrium constants are compared with those calculated using statistical mechanics. In general, the experimental and calculated equilibrium constants are in agreement at 300 K but differ significantly at 80 K. The discrepancy is considered in terms of nonequilibration of the reactant species at temperatures below 300 K in the VT-SIFT.

#### Introduction

The process of H/D isotope exchange in gas-phase ion-molecule reactions has been well studied from a fundamental standpoint<sup>1-12</sup> and toward gaining an understanding of heavy isotope enrichment in certain interstellar molecules.<sup>13-26</sup>

The process of H/D isotope exchange can be represented by the reaction

$$XH^{+} + YD + \frac{k_{t}}{k_{t}}XD^{+} + YH - \Delta H$$
(1)

where  $\Delta H$  is the enthalpy change for the reaction and  $k_f$  and  $k_r$ are the forward (exothermic) and reverse (endothermic) rate coefficients, respectively. Since such a reaction only involves the interchange of isotopes, it is near thermoneutral and  $\Delta H$  is essentially the difference between the zero-point vibrational energies of the products and reactants.

The equilibrium constant,  $K_{ec}$ , for reaction 1 is given by<sup>27</sup>

$$K_{\rm eq} = k_{\rm f}/k_{\rm r} \tag{2}$$

By using standard thermodynamic relationships,  $K_{eq}$  can be related to the enthalpy and entropy changes in a reaction by<sup>28</sup>

$$\ln\left(\frac{k_{\rm f}}{k_{\rm r}}\right) = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{3}$$

Hence,  $\Delta H$  and  $\Delta S$  for a reaction can be determined by measuring  $k_f$  and  $k_r$  as a function of temperature. A plot of  $\ln (k_f/k_r)$  versus  $T^{-1}$  (a van't Hoff plot) yields  $\Delta H$  from the gradient and  $\Delta S$  from the intercept, assuming that  $\Delta H$  and  $\Delta S$  are essentially temperature invariant over the range studied.

The variation of the equilibrium constant with temperature can also be determined using statistical mechanics. It is readily shown for ground electronic and vibrational state species that<sup>16,29</sup>

$$K_{\rm eq} = \left(\frac{\mu_{\rm p}}{\mu_{\rm r}}\right)^{3/2} \left(\frac{q_{\rm p1}q_{\rm p2}}{q_{\rm r1}q_{\rm r2}}\right) \exp\left(\frac{\Delta E}{k_{\rm B}T}\right) \tag{4}$$

where  $\mu$  is the reduced mass and q the rotational partition function (including nuclear spin contributions) where the subscripts p and r refer to the products and reactants, respectively, and 1 and 2 distinguish the two products or reactants.  $\Delta E$  is the zero-point energy released in the reaction ( $\Delta E/k_{\rm B} = -\Delta H/R$ ).

From expressions 3 and 4 it is apparent that at high temperatures, i.e., when  $-\Delta H \ll RT$ , the ratio  $k_l/k_r$  will be determined by the entropy change in the reaction. At lower temperatures, i.e.,  $-\Delta H > RT$ , the enthalpy effects in the reaction become dominant; indeed, even at room temperature for a large  $-\Delta H$  the reverse reaction can be significantly inhibited, favoring the incorporation of the heavy isotope into the ion. This effect is greatest for H/D exchange reactions due to the large mass difference between the isotopes (and hence large zero-point energy differences).

An interesting system in this context is the reaction of  $H_3^+$  with  $H_2$ , in all of its deuterated analogues, since it is the simplest system without a chemical reaction channel in which multiple isotope labeling of both the ion and the neutral is possible. A particularly important reaction is

$$H_3^+ + HD \rightleftharpoons H_2D^+ + H_2 - \Delta H \tag{5}$$

since this is a first step toward producing deuterated interstellar molecules. We have previously studied this reaction as a function of temperature using a variable-temperature selected ion flow tube apparatus (VT-SIFT).<sup>13,17</sup> Using expression 3, a  $\Delta H/R = -(90 \pm 10)$  K was determined at 80 K. Using expression 4, Herbst calculated the variation of the equilibrium constant for this reaction as a function of temperature.<sup>16</sup> Good agreement was obtained between his calculated values of  $K_{eq}$  at 300 and 200 K and those determined experimentally. However, the calculated  $K_{eq}$  at 80 K was larger than the experimentally determined value. This discrepancy was explained by the fact that the species H<sub>3</sub><sup>+</sup>, H<sub>2</sub>D<sup>+</sup>,

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