

## Determination of the $\text{NO}_3 + \text{NO}_2 \rightarrow \text{NO} + \text{O}_2 + \text{NO}_2$ Rate Constant by Infrared Diode Laser and Fourier Transform Spectroscopy

J. Hjorth,\* F. Cappellani, C. J. Nielsen,<sup>†</sup> and G. Restelli

Commission of the European Communities, Joint Research Centre—Ispra Establishment, I-21020 Ispra (VA), Italy (Received: August 24, 1988; In Final Form: February 8, 1989)

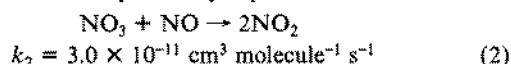
The rate constant,  $k_1$ , at 296 K for the reaction  $\text{NO}_3 + \text{NO}_2 \rightarrow \text{NO} + \text{NO}_2 + \text{O}_2$  has been determined relative to the rate constant,  $k_2$ , for the reaction  $\text{NO}_3 + \text{NO} \rightarrow 2\text{NO}_2$  by direct measurement of  $[\text{NO}]$  and  $[\text{NO}_2]$  in a steady-state situation where the effect of the thermal decomposition of  $\text{NO}_3$  was negligible.  $\text{NO}_3$  was generated in the presence of a large excess of  $\text{NO}_2$ . The  $[\text{NO}_2]$  was determined by FTIR while the  $[\text{NO}]$  was measured with a tunable diode laser spectrometer operated in second-harmonic detection mode. From a series of 18 experiments performed at 50- and 15-Torr total pressures, the rate constant  $k_1$  was calculated at 296 K as  $k_1 = ((1.5 \pm 0.28) \times 10^{-26})/k_2 \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Assuming the rate constant  $k_2 = (3.0 \pm 0.9) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , a  $k_1$  value at 296 K equal to  $(5.1 \pm 1.8) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  is calculated.

### Introduction

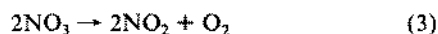
One of the reactions that destroys  $\text{NO}_3$  in the troposphere at night is



Although this reaction is not the most important sink for  $\text{NO}_3$ , it is far from negligible. An extensive review of the  $\text{N}_2\text{O}_5/\text{NO}_3$  kinetics has been published in ref 1. The first attempt to evaluate the rate constant,  $k_1$ , was made by Schott and Davidson,<sup>2</sup> who performed shock tube experiments in the temperature range 750–934 K. In these experiments,  $\text{N}_2\text{O}_5$  was completely dissociated into equal concentrations of  $\text{NO}_2$  and  $\text{NO}_3$  and the rate of decrease of  $[\text{NO}_3]$  and increase of  $[\text{NO}_2]$  was measured. The decay of  $\text{NO}_3$  under these conditions was assumed to be due either to reaction 1 followed by the very rapid reaction



or to the self-reaction



This leads to the following expression for the  $\text{NO}_3$  decay:

$$-d[\text{NO}_3]/dt = 2k_1[\text{NO}_2][\text{NO}_3] + 2k_3[\text{NO}_3]^2 \quad (a)$$

As previously mentioned, the concentrations of  $\text{NO}_3$  and  $\text{NO}_2$  were initially equal ( $t = 0$ ) while the final concentration of  $\text{NO}_3$  approached zero with a corresponding increase in the  $\text{NO}_2$  concentration ( $t = \infty$ ). Applying eq a to the results extrapolated to  $t = 0$  yielded

$$k_1 + k_3 = 3.63 \times 10^{-12} \exp(-3231/T)$$

At long reaction times ( $t = \infty$ ) when  $[\text{NO}_3]$  approaches zero, the contribution of reaction 3 becomes negligible and  $k_1$  is estimated as

$$k_1 = 6.4 \times 10^{-12} \exp(-4562/T)$$

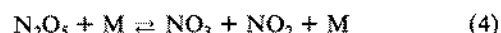
Further, the concentration ratio  $[\text{NO}_3]/[\text{NO}_2]$  was varied between 0.1 and 1 by adding  $\text{NO}_2$  to  $\text{N}_2\text{O}_5$  before it was decomposed by the shock wave. Extrapolating these results to  $t = 0$  and the contribution of reaction 3 to zero resulted in

$$k_1 = 4.28 \times 10^{-13} \exp(-2222/T)$$

Very different values are obtained for  $k_1$  from the two expressions above when the results are extrapolated to tropospheric temperatures, e.g., at 296 K:

$$\begin{aligned} k_1 &= 1.29 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (t = 0) \\ k_1 &= 2.35 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (t = \infty) \end{aligned}$$

Graham and Johnston<sup>4</sup> derived the equilibrium constant,  $K$ , for the reaction



from an analysis of the  $\text{N}_2\text{O}_5/\text{O}_3$  system kinetics. The temperature dependence of  $K$  was found as

$$K = (8.4 \pm 1.8) \times 10^{26} \exp[(-11180 \pm 100)/T]$$

Prior to these studies, Johnston and Tao<sup>5</sup> had determined the value for the product  $Kk_1$  in the temperature range 338–396 K by measuring the conversion of  $\text{N}_2\text{O}_5$  to  $\text{NO}_2$ . By combining the results from these studies,  $k_1$  was determined as<sup>4</sup>

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

At 296 K,  $k_1$  is calculated as  $3.92 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . As recently shown by Johnston et al.<sup>1</sup> a strong discrepancy appears when this expression is used to calculate  $k_1$  in the temperature range investigated by Schott and Davidson.<sup>2</sup> This discrepancy has been, however, discussed and accounted for<sup>1</sup> by the contribution of the thermal unimolecular decomposition of  $\text{NO}_3$  in the system



In the present study,  $k_1$  was evaluated from a simultaneous determination of  $[\text{NO}]$  and  $[\text{NO}_2]$  in a steady-state situation after mixing  $\text{NO}_2$  and  $\text{N}_2\text{O}_5$  in a large reaction chamber. The steady-state condition for  $\text{NO}$  is given by

$$k_5[\text{NO}_3] + k_1[\text{NO}_2][\text{NO}_3] = k_2[\text{NO}][\text{NO}_3] \quad (b)$$

A comparison between  $k_5$  as evaluated in ref 1 and the product  $k_1[\text{NO}_2]$  under our experimental conditions shows that with  $k_1 \approx 5 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  reaction 5 has negligible (<1%) influence on the concentration of  $\text{NO}$ . The rate constant  $k_1$  can then be derived from

$$k_1 = k_2[\text{NO}]/[\text{NO}_2] \quad (c)$$

and its determination will depend upon the knowledge of  $k_2$  and the accuracy with which  $[\text{NO}]$  and  $[\text{NO}_2]$  in the system can be measured. The  $[\text{NO}_2]$  can be determined accurately by IR

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<sup>†</sup> On leave from the Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, N-0315 Oslo 3, Norway.

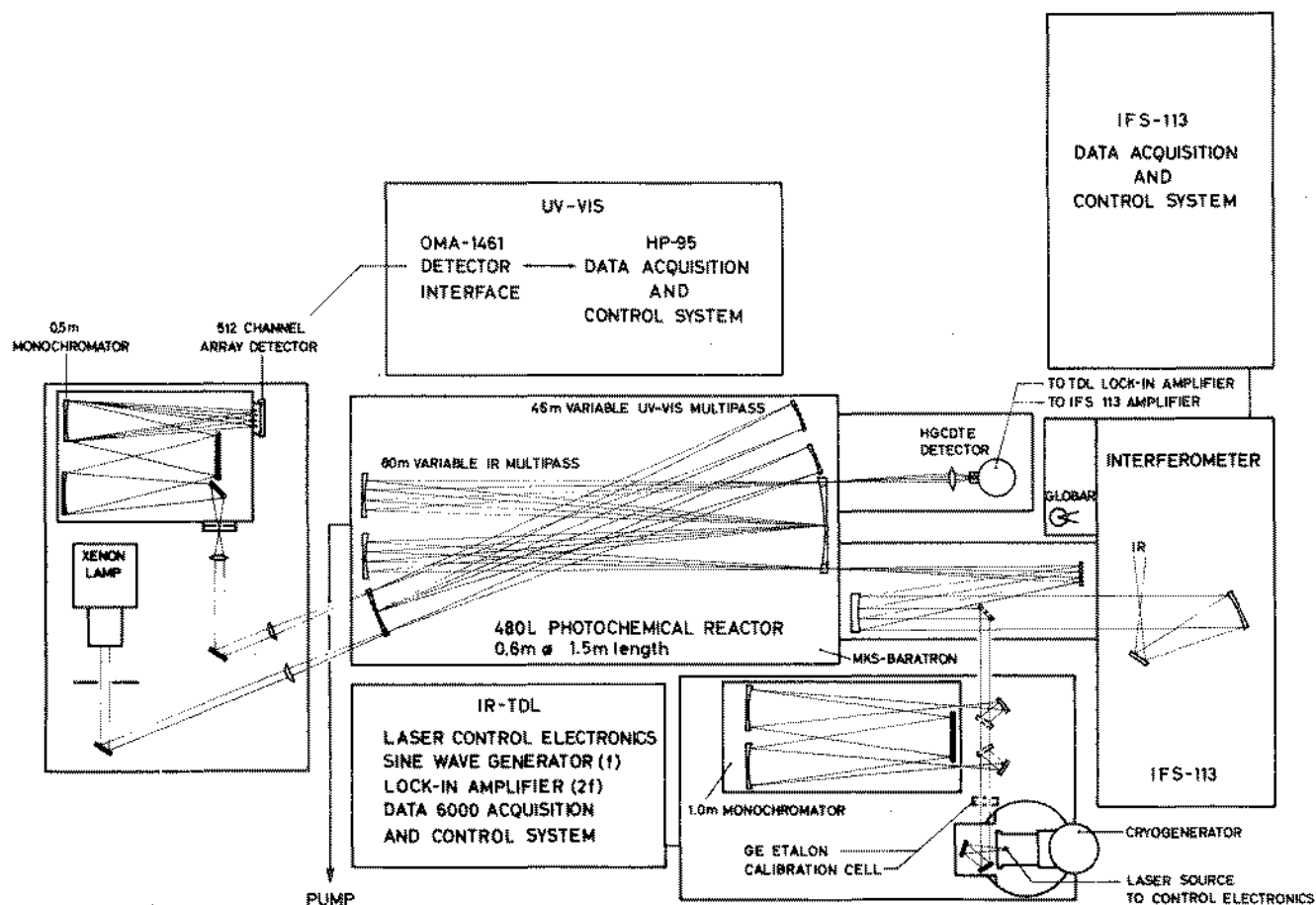


Figure 1. Experimental setup: 480L reactor with FTIR and TDL spectrometers.

spectroscopy with an FT spectrometer. The obviously low  $\text{NO}$  concentration can conveniently be measured by a tunable infrared diode laser absorption spectrometer, operating in second-harmonic mode.

We consider it an advantage of the method outlined that  $k_2$  has been determined by procedures that do not require the equilibrium constant  $K$  for reaction 4. The value of  $K$  is in fact still an unsettled question, as determinations in literature vary within a factor of 2 (see ref 6).

### Experimental Section

The chemical experiments were carried out under dark conditions at 50- and 15-Torr total pressures in a 480-L cylindrical cell made of a 60-cm-diameter 150-cm-length Teflon-coated DURAN glass tube closed by Teflon-coated aluminum flanges. The reaction chamber included a three-mirror White-type multiple-reflection system with an externally variable path length that was set during the experiments to a total beam path of 80 m. The multipass system was coupled via transfer optics to a Bruker IFS-113V interferometer (FTS) or by a remotely operated flip mirror to an infrared tunable diode laser (TDL) spectrometer as shown in Figure 1. The FTS or the TDL infrared beams were focused on the same  $\text{HgCdTe}$  detector alternatively connected to the FTS or the TDL signal electronics and data acquisition systems. The FTS was used to record the spectrum in the  $4000\text{--}600\text{-cm}^{-1}$  region and in particular to measure the concentrations of  $\text{NO}_2$ ,  $\text{N}_2\text{O}_5$ , and  $\text{HNO}_3$ , while the TDL spectrometer was used to analyze the  $\text{NO}$  concentration.

$\text{NO}_2$  was added to dry zero air in the reaction chamber at 296 K; the concentration was preliminarily estimated from IR spectra. Small quantities of  $\text{O}_3$  from a silent discharge generator were then added, and the formation and equilibration of  $\text{N}_2\text{O}_5$  were followed

by continuously recording infrared spectra. After this initial phase, the  $\text{N}_2\text{O}_5$  concentration was stable with a half-life at 50 Torr longer than 60 min; only a very small amount of  $\text{HNO}_3$  was in fact observed to build during the experiment. Dry zero air was then added up to 100–200-Torr total pressure to mix the gas system. The pressure was subsequently reduced to 50 or 15 Torr, and the  $\text{NO}$  absorption was followed by the TDL spectrometer until it reached a steady value. At this point, a series of measurements were performed to determine the  $\text{NO}$  concentration; then, the system was switched to the FTS for the determination of the  $\text{NO}_2$  concentration.

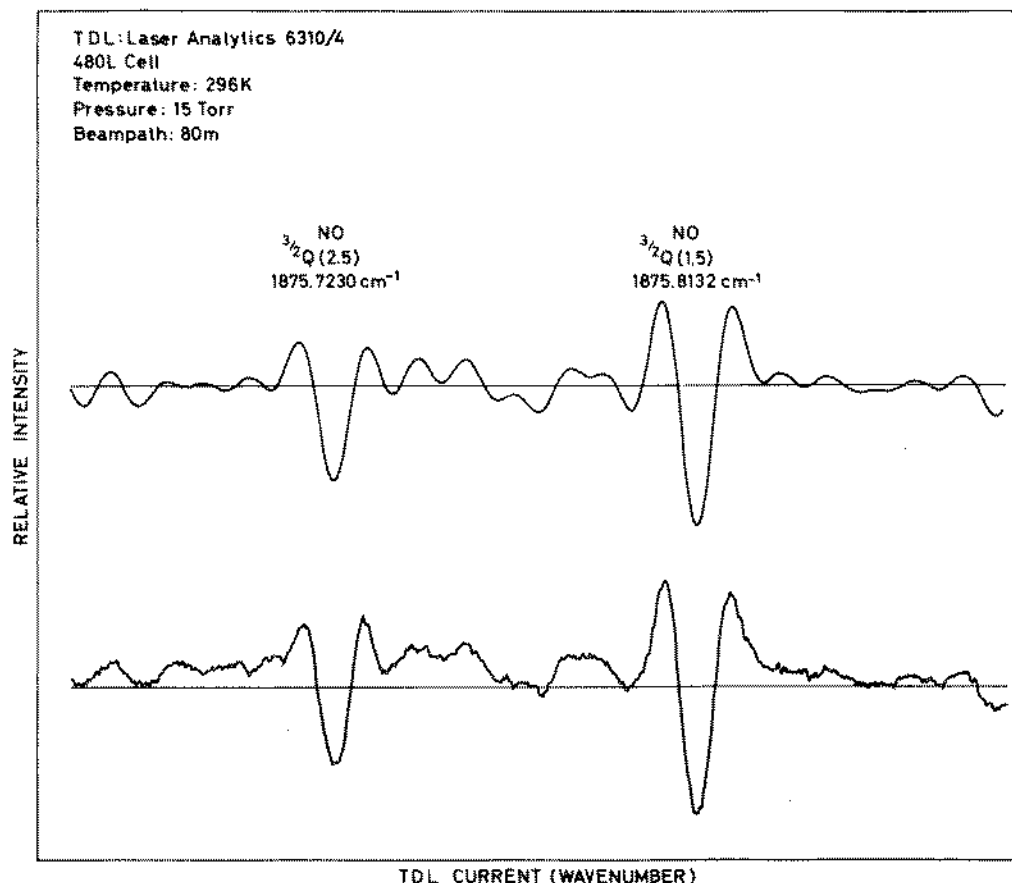
The possibility of having significant amounts of  $\text{O}_3$  remaining in the gas system could be excluded for the range of  $\text{NO}_2$  and  $\text{N}_2\text{O}_5$  concentrations used. In fact, in 10 min, the minimum time that elapsed between the addition of  $\text{O}_3$  and the measurement of  $\text{NO}$  in the steady state, the initial concentration of  $\text{O}_3$  was calculated to be reduced by a factor of more than  $10^9$ .

In order to be able to use a single calibration curve for the  $[\text{NO}_2]$ , the pressure in the cell was eventually brought to 300 Torr by adding dry zero air. The effect of the heterogeneous decomposition of  $\text{N}_2\text{O}_5$  possibly contributing to the  $\text{NO}_2$  concentration was found negligible by comparison of the  $\text{N}_2\text{O}_5$  spectrum before and after the admission of zero air.

The diode laser (Laser Analytics) emission around  $1870\text{ cm}^{-1}$  was previously examined in order to select the best operating conditions in terms of wavelength emission, laser intensity, mode structure, and stability with an insertable 1-m monochromator that was subsequently removed during the experiments. Spectra were recorded with the TDL in the second-harmonic detection mode. In this way, the measurements of very low optical densities are facilitated and the chances of overlap between adjacent absorption lines strongly reduced.<sup>7</sup> To this end, the laser emission

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**Figure 2.** TDL spectrum recorded in the second-harmonic detection mode, showing absorptions due to  $3.0 \times 10^{10}$  molecules  $\text{cm}^{-3}$  of NO. Spectrum averaged over eight scans (lower spectrum). Same spectrum after "cleaning" by Fourier transform analysis (upper spectrum).

was wavelength modulated at a frequency  $f = 2$  kHz by superposing a small sinusoidal current to the laser injection current, which was slowly varied to scan one or more NO absorption lines. The wavelength-modulated absorption signal was synchronously detected by a lock-in amplifier tuned at  $2f$  and digitized for multiscan averaging and postdetection signal handling.<sup>8</sup> The noise level was determined by the optical fringes resulting from the various optical components in the spectrometer and gas cell modulating the laser intensity.

Figure 2 shows the  $2f$  spectrum recorded as described above of a spectral region encompassing the  $3/2Q(2, 5)$  unresolved doublet and the  $3/2Q(1, 5)$  transition at 1875.7230 and 1875.8132  $\text{cm}^{-1}$ , respectively. These two transitions are characterized by their high line strengths ( $S = 0.212 \times 10^{-19}$  and  $0.344 \times 10^{-19}$   $\text{cm molecule}^{-1}$ , respectively) and by the absence of interfering lines from other molecules present in the system. The line positions and intensities are taken from ref 9.

The quantitative determination of NO was based upon the analysis of the most intense absorption at 1875.8132  $\text{cm}^{-1}$ . However, both of the above-mentioned lines were always recorded because their relative intensities could be used to test the laser emission mode stability between calibrations and experiments.

The NO concentrations were derived from a set of at least five consecutive measurements, each consisting of four averaged scans. Before and after each run, a calibration cell with a fixed concentration of NO was inserted in the optical path to check the stability of the laser emission intensity and of the electronic chain.

A calibration plot,  $2f$  signal versus NO concentration, was obtained in the following way. The exact NO concentration in a commercial  $\text{NO}/\text{N}_2$  mixture was first determined from the

integrated absorptions of individual NO lines, measured by FTS at 0.06- $\text{cm}^{-1}$  resolution. From the compiled line strengths of ref 9, the concentration was calculated as  $492 \pm 9$  ppm. However, to account for the uncertainties in the line strengths, the accuracy was estimated as only  $\pm 5\%$ .

Known volumes at pressures accurately measured by an MKS Baratron capacitance manometer were transferred from the bottle to the evacuated reaction chamber, the total volume of which was previously determined. Zero air was used to transfer the calibration sample and to bring the total pressure in the cell to the same value as chosen for the experiments, 15 or 50 Torr. The calibration points covered the range  $(5-50) \times 10^{10}$  NO molecules  $\text{cm}^{-3}$ , and a linear relationship, constrained to include the origin, resulted in a maximum spread of  $\pm 5\%$ . This led to a global systematic error in the NO calibration equal to  $\pm 7\%$ .

The  $\text{NO}_2$  concentration was measured from the integrated intensity of the  $\nu_1 + \nu_3$  band centered at about 2906  $\text{cm}^{-1}$ . The spectra were recorded at 1- $\text{cm}^{-1}$  resolution, coadding 100 scans. The 2906- $\text{cm}^{-1}$  band was used instead of the most intense  $\nu_3$  band at 1617  $\text{cm}^{-1}$ , which was too strongly absorbing at the experimental conditions applied. The relationship between  $[\text{NO}_2]$  and the integrated band absorbance (2828–2938  $\text{cm}^{-1}$ ) was established from a series of measurements carried out at 300-Torr total pressure. The  $\text{NO}_2$  concentrations used for calibration were in the same range as those in the experiments and were obtained by adding known volumes of a certified (0.835%  $\text{NO}_2$  in nitrogen) standard gas mixture to the cell. This procedure was estimated to give an overall uncertainty in the  $\text{NO}_2$  calibration of  $\pm 7\%$ .

$\text{N}_2\text{O}_5$  concentrations were determined from the 1225–1270- $\text{cm}^{-1}$  band. Since this molecule does not exhibit rotational fine structure even at reduced pressure, an estimate of the concentration was derived with the value for the absolute band intensity of  $10^{10} 3.8 \times 10^{-17}$   $\text{cm molecule}^{-1}$ .

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TABLE I: Experimental Conditions, 296 K, and Rate Constant Estimates<sup>a</sup>

run no.	$P_{\text{total}}$ , Torr	$[\text{NO}_2] \times 10^{-13}$ , molecules $\text{cm}^{-3}$	$[\text{NO}] \times 10^{-10}$ , molecules $\text{cm}^{-3}$	$k_1 \times 10^{-16}$ , $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
1	50	2.05	4.3	6.65
2	50	3.76	6.4	5.40
3	50	1.99	3.6	5.74
4	50	4.36	7.2	5.23
5	50	1.74	3.0	5.47
6	50	5.47	11.1	6.44
7	50	2.80	3.5	3.97
8	50	2.99	3.6	3.82
9	50	1.75	2.6	4.72
10	50	2.08	3.3	5.03
11	50	1.13	2.2	6.17
12	50	1.10	1.8	5.20
13	15	2.30	3.7	5.11
14	15	1.87	2.8	4.75
15	15	1.60	2.3	4.56
16	15	1.74	3.0	5.47
17	15	2.20	2.8	4.04
18	15	1.58	2.2	4.44
av at 50 Torr				5.32 ± 0.46
av at 15 Torr				4.72 ± 0.42
av				5.12 ± 0.33

<sup>a</sup>  $[\text{N}_2\text{O}_5]$  was in the range from  $5 \times 10^{13}$  to  $3 \times 10^{14}$  molecules  $\text{cm}^{-3}$ .

### Results and Discussion

Although the steady-state NO concentration according to eq c is expected to be independent of  $[\text{N}_2\text{O}_5]$  and  $[\text{NO}_3]$ , these concentrations do however influence the relaxation time needed to reach the steady-state situation. In order to ascertain that the steady state was reached when the NO and NO<sub>2</sub> measurements were carried out, the kinetics of the experiment was simulated by use of the FACSIMILE<sup>11</sup> computer program, assuming various initial conditions. For the conditions applied in the experiments, the steady-state situation was essentially reached within a few minutes.

The hypothesis of a heterogeneously catalyzed decay of NO<sub>3</sub> to NO + O<sub>2</sub> on the walls of the reactor must also be taken into consideration, in particular because these experiments were carried out at reduced pressure. There is however some evidence against the relevance of this hypothesis.

Johnston et al.<sup>1</sup> in their study of the homogeneous thermal decay of NO<sub>3</sub> to NO + O<sub>2</sub> exclude any significant contribution from heterogeneous reactions. This conclusion was based on a comparison of kinetic data for experiments performed at atmospheric pressure in reactors of volumes over a 100-fold range (37–3700 L).

In the present study, a dependence of the  $k_1$  value on the ratio of  $[\text{NO}_2]$  to  $[\text{N}_2\text{O}_5]$  should appear if the heterogeneous reactions were of significant importance. This was not observed.

Finally, an attempt was made to estimate an upper limit for this heterogeneous contribution to NO formation by measuring the formation of NO<sub>2</sub> during the decay of N<sub>2</sub>O<sub>5</sub>, as NO would react rapidly with NO<sub>3</sub> to form NO<sub>2</sub>. Measurements were performed on the formation of NO<sub>2</sub> at 50 Torr and 296 K in the usual experimental setup but with a much smaller NO<sub>2</sub> to N<sub>2</sub>O<sub>5</sub> ratio than by the  $k_1$  determinations. It was found that this reaction would contribute less than 10% to the production of NO at the experimental conditions applied by the determination of  $k_1$ . Note also that the heterogeneous decay of HNO<sub>3</sub>,<sup>12</sup> which is formed from N<sub>2</sub>O<sub>5</sub>, contributes to the formation of NO<sub>2</sub> as shown by a correlation between the rate of NO<sub>2</sub> formation and the buildup of HNO<sub>3</sub> in the reactor.

The rate constant  $k_1$  was calculated from the results of 18 experimental runs by use of eq c; the experimental details and the results are shown in Table I, where the confidence limits have been evaluated on the basis of the random error only. Although the average value obtained from the experiments performed at 15 Torr is somewhat lower than that calculated from the ex-

TABLE II: Reported Values of the Equilibrium Constant for the Reaction  $\text{N}_2\text{O}_5 + \text{M} \rightleftharpoons \text{NO}_3 + \text{NO}_2 + \text{M}$  Calculated at 296 K

equil const., 10 <sup>10</sup> molecules $\text{cm}^{-3}$		ref	equil const., 10 <sup>10</sup> molecules $\text{cm}^{-3}$		ref
3.52		4 <sup>a</sup>	3.48		18
4.18		16	1.76		15
2.37		17			

<sup>a</sup> The value of ref 4 has been corrected for a new value of the rate constant for the reaction  $\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2$ , as discussed in ref 6.

periments at 50 Torr, the confidence intervals are overlapping. Thus, a pressure dependence was not demonstrated. The rate constant was then evaluated as an average of all the individual determinations carried out.

The uncertainty limits were calculated by *t*-statistics for a 90% confidence level. However, the determination of  $k_1$  is affected by systematic errors in the NO and NO<sub>2</sub> calibrations and by the uncertainty in the rate constant  $k_2$ . The NO and NO<sub>2</sub> concentrations were estimated to be accurate within ±7% while the uncertainty attributed to  $k_2$  in ref 3 is as high as ±30%.

The combined effects of random and systematic errors lead to the final expression for  $k_1$  at 296 K:

$$k_1 = ((1.54 \pm 0.28) \times 10^{-26}) / k_2 \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

From the value for  $k_2$  recommended in the 1985 JPL compilation, derived from the analysis of the evaluation of ref 13 and 14 and confirmed in the 1987 JPL compilation ( $k_2 = (3.0 \pm 0.9) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ), a value for  $k_1 = (5.12 \pm 1.79) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  is calculated.

Johnston et al.<sup>1</sup> give an expression for the rate constant  $k_1$  derived from a study of the apparent first-order thermal decay of N<sub>2</sub>O<sub>5</sub> to NO<sub>2</sub>:

$$k_1 = (2.05 \times 10^{13} \exp(-12400/T)) / K$$

This result has recently been confirmed by Cantrell et al.,<sup>15</sup> who find agreement within 6% between their own data and those of Johnston and Tao<sup>5</sup> over the range of temperatures where the measurements overlap and within 10% when extrapolated to 298 K.

The value of  $k_1$  obtained from the expression above is quite dependent on the value selected for the equilibrium constant  $K$  of reaction 4. As shown in Table II, the values of  $K$  reported in the literature vary by more than a factor of 2 corresponding to a range of  $k_1$  values from  $3.32 \times 10^{-16}$  to  $7.96 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Our determination of  $k_1$ ,  $(5.12 \pm 1.79) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , lies approximately in the middle of this range.

On the other hand, it is of interest to derive the equilibrium constant  $K$  from the  $k_1$  values of this study and the expression given above. When this procedure, which is the reverse of that used as previously discussed to derive  $k_1$ , is applied, a value for  $K$  at 296 K of  $2.56 \times 10^{10} \text{ molecule cm}^{-3}$  is obtained. However, the uncertainty in  $k_2$ , which in turn determines the uncertainty in the value of  $k_1$  used for this comparison, precludes any definite conclusion.

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**Registry No.** NO<sub>3</sub>, 12033-49-7; NO<sub>2</sub>, 10102-44-0.

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