



## The equilibrium constant for N2O5NO2+NO3: Absolute determination by direct measurement from 243 to 397 K

C. A. Cantrell, J. A. Davidson, A. H. McDaniel, R. E. Shetter, and J. G. Calvert

Citation: The Journal of Chemical Physics **88**, 4997 (1988); doi: 10.1063/1.454679 View online: http://dx.doi.org/10.1063/1.454679 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/88/8?ver=pdfcov Published by the AIP Publishing

### Articles you may be interested in

Temperaturejump measurements on the kinetics of association and dissociation in weakly bound systems: N2O4+M=NO2+NO2+M J. Chem. Phys. **97**, 5472 (1992); 10.1063/1.463780

Rate constants for the reactions of O2 +, NO2 +, NO+, H3O+, CO3 , NO2 , and halide ions with N2O5 at 300 K  $\sim$ 

J. Chem. Phys. 68, 2085 (1978); 10.1063/1.436032

Evaluation of the Equilibrium Constant for the N2O4 (g)=2NO2 (g) Reaction at 298.16°K from Light Transmission Measurements J. Chem. Phys. **47**, 1703 (1967); 10.1063/1.1712153

Experimental Determination of the Heat of Dissociation of N2O42NO2 from the Temperature Dependence of Absolute Infrared Intensities J. Chem. Phys. **36**, 98 (1962); 10.1063/1.1732326

Nuclear Magnetic N14 Resonance Spectra, Molecular Structures, and Exchange Reactions in the System N2O5–NO2 +–NO3 —–H2O J. Chem. Phys. **25**, 1285 (1956); 10.1063/1.1743205



# The equilibrium constant for $N_2O_5 \approx NO_2 + NO_3$ : Absolute determination by direct measurement from 243 to 397 K

C. A. Cantrell, J. A. Davidson, A. H. McDaniel, R. E. Shetter, and J. G. Calvert *National Center for Atmospheric Research*,<sup>a)</sup> *Boulder, Colorado* 80307

(Received 4 November 1987; accepted 29 December 1987)

The equilibrium constant for  $N_2O_5 \neq NO_2 + NO_3$  [reaction (1)], has been determined through direct concentration measurements of  $N_2O_5$ ,  $NO_2$ , and  $NO_3$  in a temperature controlled long path cell, using absorption spectroscopy in the infrared and visible regions from 243 to 397 K. The results give  $K_{1C} = 1.30 \times 10^{26} \exp(-21490/RT)$  molecules cm<sup>-3</sup> with an estimated overall uncertainty of 30% at the 95% confidence level. This results in an equilibrium constant near room temperature approximately one-half that of previously accepted values. Using the temperature dependence of the equilibrium constant and new data for the enthalpy of formation of gaseous  $N_2O_5$  yields an enthalpy of formation for  $NO_3$  of  $15.39 \pm 0.72$  kcal mol<sup>-1</sup>. In additional experiments the temperature dependent first order decay rates of  $N_2O_5$  were determined from which a value for the product of the equilibrium constant ( $K_{1C}$ ) and the rate constant for reaction (2):  $NO_2 + NO_3 \rightarrow NO + NO_2 + O_2$  was obtained for temperatures from 298 to 396 K:  $K_1 k_2 = 1.23 \times 10^{13} \exp(-24300/RT) \text{ s}^{-1}$ . When this is combined with the equilibrium constant of the present study the following expression is obtained for  $k_2$ :  $9.5 \times 10^{-14} \exp(-2810/RT) \text{ cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup>.

### I. INTRODUCTION

The chemistry of dinitrogen pentoxide  $(N_2O_5)$  and associated oxides of nitrogen has been the subject of considerable study for several years (see review in Ref. 1). A parameter very critical to the understanding of the  $N_2O_5$  chemical system is the value of the equilibrium constant for Eq. (1) as a function of temperature:

$$N_2O_5 \neq NO_2 + NO_3. \tag{1}$$

The equilibrium constant  $K_1$  is defined as follows:

$$K_{1} = \frac{[\text{NO}_{2}][\text{NO}_{3}]}{[\text{N}_{2}\text{O}_{5}]} = \frac{k_{1}}{k_{-1}}.$$
 (a)

The square brackets represent concentrations in units of molecules cm<sup>-3</sup> for  $K_{1C}$  and units of atmospheres for  $K_{1P}$ .

Several direct and indirect studies designed to determine the value of  $K_1$  have been reported and are summarized in Table I. The accuracy of each study has been estimated based on reported error limits. In the absence of reported errors the accuracy was calculated from the reported temperature dependent expression assuming the error quoted on the slope of the logarithm  $K_1$  vs the inverse of temperature was representative of all the error of the study. The uncertainty at the 95% confidence level for the equilibrium constant at 298 K is also shown. Schott and Davidson<sup>2</sup> measured the concentrations of NO<sub>2</sub>, NO<sub>3</sub>, and N<sub>2</sub>O<sub>5</sub> in high temperature shock tube experiments (450-550 K) which resulted in the first direct determination of  $K_1$ . Graham and Johnston<sup>3</sup> reported a value for  $K_1$  from results of kinetics studies involving N2O5 catalyzed decomposition of O3, the reaction of NO<sub>2</sub> with ozone, and steady state measurements of NO<sub>3</sub>. This was the first report of measurements of the equilibrium constant near room temperature and the  $K_1$  data

are probably accepted as the best available at the present time.

More recently, direct measurements have been reported near room temperature,<sup>4,5</sup> as well as measurements over a range of temperatures.<sup>6</sup> These measurements have all used absorption spectroscopy to measure concentrations. NO<sub>3</sub> was detected near 627 or 662 nm, NO<sub>2</sub> in the visible<sup>4,6</sup> near 400 nm or in the infrared<sup>5</sup> near 1600 cm<sup>-1</sup>, and N<sub>2</sub>O<sub>5</sub> in the ultraviolet<sup>6</sup> at 220 and 250 nm or in the infrared<sup>4,5</sup> near 750 and 1250 cm<sup>-1</sup>. Near 298 K the equilibrium constants reported in these studies are either in essential agreement with Graham and Johnston<sup>4,6</sup> or are substantially lower.<sup>5</sup> The temperature dependence in Burrows et al.<sup>6</sup> is also reported to confirm the results of Graham and Johnston. Perner et al.<sup>4</sup> as well as Platt et al.7 reported results of indirect low temperature estimates of  $K_1$  from atmospheric measurements of NO2 and NO3 alone. These values which are subject to great uncertainty are systematically higher than the results of Graham and Johnston, and thus result in an apparent dependence of  $K_1$  on temperature which is significantly different.

As indicated in Eq. (a), the equilibrium constant must be consistent with the rate constants of the forward and reverse reactions in reaction (1). Thus knowledge of any two of  $K_1$ ,  $k_1$ , and  $k_{-1}$  allows calculation of the third value. Malko and Troe<sup>8</sup> used Graham and Johnston's equilibrium constant and the unimolecular decomposition of N<sub>2</sub>O<sub>5</sub> data of Connell and Johnston<sup>9</sup> and Viggiano *et al.*<sup>10</sup> to calculate fall-off curves for NO<sub>2</sub> + NO<sub>3</sub>. Kircher *et al.*<sup>11</sup> directly measured  $k_{-1}$  as a function of temperature and pressure and used the N<sub>2</sub>O<sub>5</sub> decomposition rate data ( $k_1$ ) to calculate  $K_1$ . Smith *et al.*<sup>12</sup> performed a similar study at room temperature only. These last two studies yield significantly lower values for  $K_1$  than those of most previous studies.

We have carried out direct determinations of the equi-

J. Chem. Phys. 88 (8), 15 April 1988

0021-9606/88/084997-10\$02.10

<sup>&</sup>lt;sup>a)</sup> The National Center for Atmospheric Research is funded by the National Science Foundation.

| TABLE I. Summary of previous measurements of the equil | ibrium constant for reaction (1). |
|--|-----------------------------------|
|--|-----------------------------------|

| Temperature<br>range<br>(K) | Preexponential factor $(molecule cm^{-3})$ | Internal <sup>a</sup><br>energy change<br>(cal mol <sup>-1</sup> ) | $K_1^{298}$<br>(molecule cm <sup>-3</sup> ) | Uncertainty<br>factor<br>95% confidence | Reference       |
|-----------------------------|--|--|---|---|-----------------|
| 450-550                     | 5.62×10 <sup>25</sup>                      | 20 100   | 1.02×10 <sup>11</sup>                       | 6.0                                     | 2               |
| 298-329                     | 8.4×10 <sup>26</sup>                       | 22 210   | 4.28×10 <sup>10</sup>                       | 1.4                                     | 3               |
| 298.4-300.4                 |  |  | 4.7×10 <sup>10</sup>                        | 1.3°                                    | 4               |
| 269.281                     |  |  |   |   | 4 <sup>6</sup>  |
| 297-299                     |  |  | 2.91×10 <sup>10</sup>                       | 1.3°                                    | 5               |
| 275-315                     | 1.23×10 <sup>28</sup>                      | 23 800   | 4.0×10 <sup>10</sup>                        | 1.5°                                    | 6               |
| 283                         |  |  | $2.0 \times 10^{10}$ (283 K)                |   | 7 <sup>6</sup>  |
| 262384                      | $3.18 \times 10^{29}/T$                    | 22 550*  | $3.08 \times 10^{10}$                       | 7.6                                     | 11              |
| 262-384                     | 3.66×10 <sup>26</sup>                      | 21 920   | 3.08×10 <sup>10</sup>                       | 7.6                                     | 11 <sup>d</sup> |
| 298                         |  |  | 2.50×10 <sup>10</sup>                       | 3.0                                     | 12 and 10       |
| 298                         |  |  | 4.85×10 <sup>10</sup>                       | 3.1                                     | 12 and 9        |
| 243-397                     | 1.30×10 <sup>26</sup>                      | 21 490   | 2.25×10 <sup>10</sup>                       | 1.3                                     | This work       |

<sup>a</sup> In all cases except the entry marked \*, these values are  $\Delta E$  of the reaction beacuse the standard state in each case is units of molecules cm<sup>-3</sup>. To obtain  $\Delta H_{rxn}$  over the temperature range studied, add RT to the entries in this column. The entry marked \* uses units of atmospheres as the standard state and thus is already  $\Delta H_{rxn}$ .

<sup>b</sup> These values are the result of low temperature estimates from atmospheric measurements of NO<sub>2</sub> and NO<sub>3</sub>.

<sup>c</sup>These error estimates the result of precision only and do not include possible systematic errors.

<sup>d</sup> These values were obtained by performing a linear regression on values calculated from the expression in the line above reported in Kircher *et al.* over the temperature range indicated in order to directly compare the fitting parameters with the results of the other studies. These two expressions yield values for the equilibrium constant within 1% of each other.

librium constant for Eq. (1), by measuring  $NO_2$ ,  $NO_3$ , and  $N_2O_5$  using long path visible and infrared absorption spectroscopy, as a function of temperature from 243 to 397 K. Additional experiments were performed to measure the first-order decay rate constant of  $N_2O_5$  as a function of temperature. In combination with our new equilibrium constant results, this can be used to derive a value of the rate coefficient for the NO forming channel in the reaction of  $NO_3$  with  $NO_2$ . The implications of the results of this study for atmospheric chemistry, the thermodynamics of  $NO_3$ , as well as laboratory kinetics studies are discussed.

### **II. EXPERIMENTAL**

All experiments described here were performed in a long path, temperature regulated stainless steel cell described previously.<sup>13</sup> The cell is constructed of three concentric tubes the innermost (15.8 cm internal diameter) of which houses multiple reflection optics. The optical path length is adjustable in increments of 8 m from 8.6 to 96.6 m (the input and output optical path which is not part of the multireflection path is 0.6 m). All studies reported here were performed with a 48.6 m optical path. The space between the inner two tubes contains temperature regulating fluid which is circulated from a temperature controlled bath. The space between the outer two tubes serves as an evacuable Dewar. The cell is interfaced to a BOMEM DA3.01 Fourier transform interferometer by use of evacuable transfer optics. Spectra were collected with the interferometer in the infrared spectral region at a resolution of  $5 \text{ cm}^{-1}$ . Alternatively, a component which was part of the transfer optics could be removed to allow interfacing to an photodiode array detector. The interface consists of an imaging telescope and a fiber optic mount. All spectra in the visible region were acquired with this spectrometer system. It consists of an Instruments SA 0.3 m Czerny–Turner monochromator with a 147.5 groove/mm grating blazed at 300 nm. The detector is an EG&G Princeton Applied Research model 1420 photodiode array with an intensifier designed for optimum blue spectral response. The monochromator-diode array combination yields a spectral interval of 0.51 nm and an effective spectral resolution of 1.5 nm. The detector exposure time and operating temperature is controlled with a model 1461 interface and a PC's Limited 286 microcomputer. The diode array spectrometer was selected because of its ability to measure very small absorbances ( < 0.001). A spectrum typically consisted of 1000 scans of the photodiode with exposure times of 0.015 s, ratioed to a reference spectrum collected with the cell evacuated.

The concentration of NO<sub>2</sub> was determined in three ways: (1) through the use of differential cross sections at eight selected wavelengths near 400 nm; (2) using peak heights at 150 wavelengths near 400 nm; (3) using band integration of the infrared band near  $1600 \text{ cm}^{-1}$ . The visible cross sections for (1) and (2) were measured in this laboratory as a function of temperature and NO<sub>2</sub> concentration, and the details of those experiments will be discussed in another report.<sup>14</sup> The integrated infrared band intensities were determined at each temperature of the study and found to be relatively insensitive to temperature. However, at the low pressure and low instrumental resolution used here (5  $cm^{-1}$ ), the integrated areas showed large deviations from linearity in NO<sub>2</sub> concentration. Thus, the areas were fitted to an exponential function of the form, area = A $+ B \exp(-D[NO_2]).$ 

The three  $NO_2$  measurement techniques yielded somewhat different results, but on the average differed less than 15% between the lowest and highest values and never showed systematic variation. This apparently large difference in methods is primarily due to quite low concentrations which were measured at the low temperature end of this study. Equilibrium constants were calculated using  $NO_2$ concentrations based on these three methods, and these *K* values were averaged for the results reported here.

The NO<sub>3</sub> concentration was determined by integration  $(14\ 910-15\ 290\ cm^{-1})$  of the visible band near 662 nm using an integrated band intensity of  $1.95 \times 10^{-15}$  cm<sup>2</sup> molecule<sup>-1</sup> cm<sup>-1</sup>. The temperature and concentration dependence of this cross section was also measured in this laboratory and those details are discussed in a previous report.<sup>15</sup> ln short, no statistically significant dependence on temperature was evident over the range of that study (215-347 K).

The concentration of  $N_2O_5$  was determined in most cases by the integration of the infrared band near  $1250 \text{ cm}^{-1}$ using a temperature independent integrated band intensity  $(1200-1275 \text{ cm}^{-1})$  of  $4.12 \times 10^{-17} \text{ cm}^2$  molecule<sup>-1</sup> cm<sup>-1</sup>. This was also measured in this laboratory. These data agree reasonably well with previous determinations. The band near  $1700 \text{ cm}^{-1}$  was also used as long as interference from the nearby NO<sub>2</sub> band was not a problem. The temperature independent integrated band strength (1655–1850 cm<sup>-1</sup>) used was  $1.08 \times 10^{-16} \text{ cm}^2 \text{ molecule}^{-1} \text{ cm}^{-1}$ .

The experimental approach to the equilibrium constant measurement depended on the temperature under study. In some cases a slow flow technique was used. At other temperatures, static decay was found to be the best approach. Each method will be described separately.

### A. Slow flow method of equilibrium constant determination

At cell temperatures from about 303 to 398 K, experiments were performed with a slow flow of  $N_2O_5$ ,  $NO_2$ , and NO<sub>3</sub> in a nitrogen carrier down the length of the long path cell. At the highest temperatures this was the only technique which could be used given the instrumentation available, because of the rapid rate of conversion of  $N_2O_5$  to  $NO_2$ . The source of the odd nitrogen species consisted of a glass vessel containing N<sub>2</sub>O<sub>5</sub> placed in a vacuum jacketed Dewar along with a copper coil through which temperature regulating fluid could be circulated. The N2O5 vessel had a tube entering the bottom through which  $N_2$  (UHP Linde) could be flowed. A fritted glass disk (4-8  $\mu$ ) was used in the exit tube, which was also in the low temperature bath, to trap any particulate  $N_2O_5$  which might escape and be carried along with the  $N_2$  flow. The temperature of the bath was typically kept at 243 K. One of six different flows through the  $N_2O_5$  was used in the range of 100-600 cm<sup>3</sup> min<sup>-1</sup> which was diluted with a main flow of 10  $\ell$  min<sup>-1</sup> before addition to the cell. An odd nitrogen balance  $([NO_2] + [NO_3])$  $+ 2[N_2O_5]$ ) over the range of conditions studied indicated the nitrogen flow through the N2O5 containing vessel was saturated with  $N_2O_5$ . Although saturation is not a requirement for this source to be successful, it implies stability in the concentration of odd nitrogen compounds in the inlet and in the cell. No systematic variation with flow rate was seen in measured equilibrium constants at any of the temperatures of this study. The inlet pressure was typically maintained slightly above ambient, near 700 Torr. These conditions were sufficient to keep the concentrations of the species of interest in a measurable range for temperatures from 303 to 398 K. The pressure in the cell was typically 30 Torr, with a residence time of the gaseous mixture of 12 s.

The reactions which describe the partitioning of odd nitrogen for our experimental conditions are reactions (1) and (-1) along with the following:

$$NO_2 + NO_3 \rightarrow NO + NO_2 + O_2, \qquad (2)$$

$$NO_3 + NO \rightarrow 2NO_2, \tag{3}$$

$$2NO_3 \rightarrow 2NO_2 + O_2. \tag{4}$$

At temperatures from 303 to 398 K the equilibrium is quickly reestablished by decomposition of  $N_2O_5$  to replace some of the reacted NO<sub>3</sub> lost in reactions (2), (3), and to a lesser extent (4). Computer simulations of the reaction system revealed that the concentration of all three species are not always expected to be constant down the length of the cell. It is important to note that this does not affect the equilibrium constant determination; the key requirement is that the average cell concentrations measured must yield the true value of the equilibrium constant. It can easily be shown that the concentration determined from an absorbance measurement is the average concentration over the optical path length.

At the low temperature end of the 303 to 398 K range, the equilibrium concentrations of NO<sub>2</sub> and NO<sub>3</sub> are fairly low, while most of the odd nitrogen is in the form of  $N_2 O_5$ . To a first approximation over the time scale of the measurement,  $[N_2O_5]$  is constant. Thus for each NO<sub>3</sub> lost, one NO<sub>2</sub> is formed. When the mixture enters the cell,  $[NO_3]$  is approximately equal to [NO<sub>2</sub>]. Based on computer simulations of the important reactions in this system we observed that the product [NO<sub>2</sub>][NO<sub>3</sub>] is constant within 10% until  $[NO_3]$  is less than about 50% of its initial value. The results of those simulations are summarized in Table II. Shown for two extreme temperatures and one intermediate temperature are the concentrations of NO<sub>2</sub>, NO<sub>3</sub>, and N<sub>2</sub>O<sub>5</sub> at three times corresponding to the beginning of the optical path near cell inlet, the center of the cell, and the end of the optical path near the cell exhaust. The maximum time shown is not equal to the total cell residence time (12 s) because the optics only measure over the central 80% of the cell. Also shown are the product of the concentrations of NO<sub>2</sub> and NO<sub>3</sub>, the ratio of the concentrations of NO<sub>3</sub> and  $N_2O_5$ , the recovered equilibrium constant based on average concentrations of each species, and the difference in percent relative to the equilibrium constant which was input into the simulation.

For the conditions of our experiments at the lower temperatures, the product of the NO<sub>2</sub> and the NO<sub>3</sub> concentration is nearly constant at each point down the cell; see column 6, Table II. The concentrations of these species determined from the visible spectra are the cell integrated average concentrations. Since the rate of formation of NO<sub>2</sub> is nearly the same as the rate of loss of NO<sub>3</sub>, then these average concentrations yield the correct value for the [NO<sub>2</sub>][NO<sub>3</sub>] product.

At temperatures from about 303 to 248 K, NO was added in an amount approximately 15% to 100% of the initial

TABLE II. Results of computer simulations of the decay profiles of odd nitrogen species in a slow flow experiment such as that used in the present study. The simulations indicate that at high temperatures the ratio of the  $NO_3$  and  $N_2O_5$  concentrations is very nearly constant, in spite of the fact that these species are decaying. At the lower temperatures the product of the  $NO_2$  and  $NO_3$  concentrations is approximately constant. These facts allow the equilibrium constant to be extracted using the technique described in the text.

| Temperature<br>(K) | Time<br>(s) | [NO <sub>2</sub> ]ª   | [NO <sub>3</sub> ]    | [N <sub>2</sub> O <sub>5</sub> ] | [NO <sub>2</sub> ]×[NO <sub>3</sub> ] | [NO <sub>3</sub> ]/[N <sub>2</sub> O <sub>5</sub> ] | $K_1$ , apparent <sup>b</sup><br>(molecules cm <sup>-3</sup> ) | Difference <sup>c</sup><br>(%) |
|--------------------|-------------|-----------------------|-----------------------|----------------------------------|---------------------------------------|---|--|--------------------------------|
| 398                | 1           | 1.88×1014             | 1.99×10 <sup>13</sup> | 1.82×10 <sup>13</sup>            | 3.74×10 <sup>27</sup>                 | 1.09  |  |                                |
|                    | 5           | 2.40×10 <sup>14</sup> | 1.62×10 <sup>12</sup> | 1.62×10 <sup>12</sup>            | 3.89×10 <sup>26</sup>                 | 1.00  | 2.34×10 <sup>14</sup>  | 13.3                           |
|                    | 10          | 2.44×10 <sup>14</sup> | 6.37×10 <sup>10</sup> | 6.37×10 <sup>10</sup>            | $1.55 \times 10^{25}$                 | 1.00  |  |                                |
| 398                | 1           | 1.25×10 <sup>15</sup> | 4.44×10 <sup>12</sup> | $2.71 \times 10^{13}$            | 1.53×10 <sup>28</sup>                 | 0.164   |  |                                |
|                    | 5           | 1.31×10 <sup>15</sup> | 7.04×10 <sup>10</sup> | 4.49×10 <sup>11</sup>            | 9.22×10 <sup>25</sup>                 | 0.157   | $2.11 \times 10^{14}$  | 1.9                            |
|                    | 10          | 1.31×10 <sup>15</sup> | $4.04 \times 10^{8}$  | 2.58×10 <sup>9</sup>             | 5.29×10 <sup>23</sup>                 | 0.156   |  |                                |
| 348                | 1           | 2.17×10 <sup>13</sup> | 1.82×10 <sup>13</sup> | 1.02×10 <sup>14</sup>            | 3.95×10 <sup>26</sup>                 | 0.178   |  |                                |
|                    | 5           | 2.97×10 <sup>13</sup> | $1.31 \times 10^{13}$ | $1.01 \times 10^{14}$            | 3.89×10 <sup>26</sup>                 | 0.130   | 4.02×10 <sup>12</sup>  | - 4.1                          |
|                    | 10          | 4.03×10 <sup>13</sup> | 9.32×10 <sup>12</sup> | 9.74×10 <sup>13</sup>            | 3.76×10 <sup>26</sup>                 | 0.096   |  |                                |
| 348                | 1           | 5.97×10 <sup>13</sup> | 3.23×10 <sup>13</sup> | 6.06×10 <sup>14</sup>            | 2.33×10 <sup>27</sup>                 | 0.064   |  |                                |
|                    | 5           | 1.11×10 <sup>14</sup> | $2.04 \times 10^{13}$ | 5.89×10 <sup>14</sup>            | 2.26×10 <sup>27</sup>                 | 0.035   | 4.27×10 <sup>12</sup>  | 1.9                            |
|                    | 10          | 1.79×10 <sup>14</sup> | 1.20×10 <sup>13</sup> | 5.60×10 <sup>14</sup>            | 2.15×10 <sup>27</sup>                 | 0.021   |  |                                |
| 303                | 1           | 2.26×10 <sup>12</sup> | 2.22×10 <sup>12</sup> | 1.20×10 <sup>14</sup>            | 5.02×10 <sup>24</sup>                 | 0.018   |  |                                |
|                    | 5           | 2.30×10 <sup>12</sup> | 2.17×10 <sup>12</sup> | 1.20×10 <sup>14</sup>            | 4.99×10 <sup>24</sup>                 | 0.018   | 4.16×10 <sup>10</sup>  | 0.1                            |
|                    | 10          | 2.36×10 <sup>12</sup> | $2.12 \times 10^{12}$ | 1.20×10 <sup>14</sup>            | 5.00×10 <sup>24</sup>                 | 0.018   |  |                                |
| 303                | 1           | 5.33×10 <sup>12</sup> | 5.09×10 <sup>12</sup> | 6.50×10 <sup>14</sup>            | $2.71 \times 10^{25}$                 | 0.0078  |  |                                |
|                    | 5           | 5.57×10 <sup>12</sup> | 4.87×10 <sup>12</sup> | 6.50×10 <sup>14</sup>            | $2.71 \times 10^{25}$                 | 0.0075  | 4.18×10 <sup>10</sup>  | 0.1                            |
|                    | 10          | 5.88×10 <sup>12</sup> | 4.61×10 <sup>12</sup> | 6.50×10 <sup>14</sup>            | $2.71 \times 10^{25}$                 | 0.0071  |  |                                |

<sup>a</sup>Brackets represent concentrations in units of molecules cm.<sup>-3</sup>

<sup>b</sup>Apparent equilibrium constant calculated from portion of the cell which is optically averaged by multipass mirror system from computer simulations. <sup>c</sup>Difference between equilibrium constant input to the computer simulation and the apparent equilibrium constant described above.

 $N_2O_5$  concentration in order to increase the ratio of  $[NO_2]$  to  $[NO_3]$ . The cross section for  $NO_3$  is much larger than that for  $NO_2$ , and thus it was desirable to keep the  $NO_2$  concentration somewhat higher than the  $NO_3$  concentration. For the experiments at 303 K the temperature of the  $N_2O_5$  source was raised to 248 K in order to increase the amount of odd nitrogen in the cell.

At the higher temperatures, more of the odd nitrogen is in the form of NO<sub>2</sub>, and NO<sub>3</sub> is fairly low because of the rapid decomposition reactions. The concentration of  $N_2O_5$ is also low because of reaction (1). Under these conditions, a reasonably accurate value of the equilibrium constant can be obtained because the ratio  $[NO_3]/[N_2O_5]$  is nearly constant down the length of the cell, for reasons similar to those discussed above; see column 7, Table II. In summary, one expects a slight systematic overestimate (15% in the worst case, more typically 2%-5%) of the equilibrium constant using the slow flow technique described here; the largest errors are expected for the highest temperatures and the lowest NO<sub>2</sub> concentrations. However the degree of overestimation is in most cases much smaller than the other sources of uncertainty associated with this experiment (primarily cross section determinations). Indeed, a propagation of errors calculation leads to an expected accuracy in the equilibrium constants recovered from direct absorbance measurements of  $\pm$  30% at the 95% confidence interval, approximately twice the difference for the worst case shown in Table II. In addition, the static decay experiments described below yield excellent agreement with this technique for the temperature range which they overlap.

### B. Static decay method of equilibrium constant determination

Experiments in a static mode were performed by adding known amounts of  $N_2O_5$  to the cell and monitoring all three species as a function of time. The ideal experiment of this sort would be to make visible and infrared measurements during the same decay period. However, this involves changing beamsplitters and light sources potentially yielding base line offset due to nonreproducibility in assembling the various components required. For this reason parallel experiments were performed by making a decay measurement in the infrared and then repeating the decay, using an identical amount of  $N_2O_5$ , while making visible measurements. This approach was tested by performing repeat experiments in the infrared and visible with essentially identical decay rates in each case. The measurements made in the infrared were then fitted to an exponential decay function and the concentration of N<sub>2</sub>O<sub>5</sub> was calculated at times corresponding to the times when the visible measurements were made and the equilibrium constant corresponding to each time was then determined.

For experiments from about 303 to 325 K,  $N_2O_5$  was introduced by adding a known pressure to a calibrated volume which was then flushed into the cell with  $N_2$  to a final cell pressure of about 100 Torr. As the temperature was decreased, more of the odd nitrogen was in the form of  $N_2O_5$ , and  $NO_2$  and  $NO_3$  became increasingly difficult to measure. The requirements of large concentrations of  $N_2O_5$  in order to maintain the concentrations of  $NO_2$  and  $NO_3$  above their detection limits from about 243 to 286 K required a change in the method of  $N_2O_5$  addition. Here  $N_2O_5$  was added directly to the cell, with the amount determined by pressure measurement. The initial amount of N2O5 was typically in the range of 1 to 5 Torr. Under these conditions it was only necessary to make measurements in the visible region because the N2O5 concentration was large and essentially constant over the time scale of the measurement. The low temperature to which these experiments could be extended was limited by the vapor pressure of  $N_2O_5$  and the detection limits of NO<sub>2</sub> and NO<sub>3</sub>. Also at these lowest temperatures, a small amount of O<sub>3</sub> was added to the cell in order to convert some of the NO<sub>2</sub> into NO<sub>3</sub>. The initial O<sub>3</sub> typically corresponded to about 0.02% of the  $N_2O_5$ . This was necessary because with these large amounts of N<sub>2</sub>O<sub>5</sub> a small percentage decay during the addition to the cell resulted in fairly high NO<sub>2</sub> concentrations. Thus the ozone served to convert some of this  $NO_2$  back to  $NO_3$ . For all of these static decay experiments, the total time of data collection was typically 20 min or less. This time was governed by the amount of time required to collect visible spectra and the amount of time the NO<sub>3</sub> concentration remained well above the detection limit. Often 20 useful spectra were obtained. Thus 20 determinations of the equilibrium constant were available, and were averaged for the results reported here. The time for data collection was also limited in these experiments because of the possibility of heterogeneous conversion of  $N_2O_5$  to HNO<sub>3</sub>. At the temperatures of the infrared measurements (near room temperature), no HNO<sub>3</sub> was seen on the short time scale discussed above. However, if the decay was allowed to proceed for several hours, some HNO<sub>3</sub> formation was noted; its concentration was typically less than 5% of the initial  $N_2O_5$ .

### C. N<sub>2</sub>O<sub>5</sub> decay studies

Experiments were also performed to measure the rate of decay of N<sub>2</sub>O<sub>5</sub> in order to determine the product of the equilibrium constant and the rate constant for reaction (2). As pointed out years ago, <sup>16</sup> in a clean dry cell the decay of  $N_2O_5$ is first order in the  $N_2O_5$  concentration:

$$-\frac{1}{2}\frac{d[N_2O_5]}{dt} = k'[N_2O_5],$$
 (b)

where it can be shown that  $k' = K_1 k_2$ . The rate coefficient is one-half the total rate of N<sub>2</sub>O<sub>5</sub> decay because one of the products of reaction (2) is NO, which rapidly reacts with NO<sub>3</sub> [reaction (3)] to, in effect, destroy a second  $N_2O_5$ molecule. Reaction (2) has often been designated in the literature as reaction (e) and typically the lower case k is left out, thus k' is often called Ke. At temperatures from about 313 to 363 K, the decay of  $N_2O_5$  was measured until its concentration was typically less than 5% of its initial value. The slope of the natural logarithm of the  $N_2O_5$  concentration over 2 vs time at each temperature is equal to k'. A weighted linear regression was then performed on these k'values vs the inverse of the absolute temperature, yielding an Arrhenius expression for the temperature dependence of k'. The weighting factors used in this regression procedure were the reciprocals of the squares of the standard deviations of

FIG. 1. Summary of previous studies of the equilibrium constant for N<sub>2</sub>O<sub>5</sub>  $\neq$  NO<sub>2</sub> + NO<sub>3</sub>. Error bars are shown for the studies of Graham and Johnston, and Kircher et al. The reported error bars on the other studies are the size of the data point shown or smaller. The region of a high density of data near room temperature is shown in more detail in Fig. 3.

the slopes from the concentration vs time fits.

### **III. RESULTS AND DISCUSSION**

The previous extensive work on the measurement of  $K_1$ is summarized in Table I and Fig. 1. There are significant discrepancies among the results of the various workers; see Fig. 1. The room temperature values vary by more than a factor of 2, and no study reports measurements over the range from room temperature to near the results of Schott and Davidson. There also have been few direct measurements applicable to lower temperatures representative of the atmosphere.

The results of this study are summarized in Table III and Fig. 2. They are also compared with previous results at temperatures near room temperature in Fig. 3. The  $N_2O_5$ decay profiles are shown in Fig. 4. As can be seen the direct equilibrium constants obtained in this study are very close to those of Kircher et al. derived from the ratio  $k_1 / k_{-1}$ . However, these results are systematically lower than the results of Schott and Davidson and those of Graham and Johnston. The results of Kircher et al. are expected to be reliable because the kinetic experiments on which this calculation is based do not rely on absolute cross sections for any of the species involved. For  $k_{-1}$ , the loss rate of NO<sub>3</sub> is followed in pseudo-first-order conditions, which only requires a signal proportional to the NO<sub>3</sub> concentration. Experiments to measure  $k_1$  only require a signal proportional to the concentration of  $N_2O_5$ , which was the case for the experiments reported by Viggiano et al. and Connell and Johnston.

Reasons for the difference between the present study and the high temperature study of Schott and Davidson cannot be resolved unequivocally. It is possible the NO<sub>3</sub> cross



TABLE III. Summary of individual measurements of the equilibrium constant from this study. "Flowing or static" refers to the mode of data collection which is described in the text.

| Temperature<br>(K) | Flowing (F)<br>or static (S) | $\frac{K_1}{(\text{molecules cm}^{-3})}$ | Standard<br>deviation (%) | Number of measurements |
|--------------------|------------------------------|--|---------------------------|------------------------|
| 397.0              | F                            | 1.85×10 <sup>14</sup>                    | 7.8                       | 17                     |
| 379.2              | F                            | 6.68×10 <sup>13</sup>                    | 25.4                      | 18                     |
| 363.2              | F                            | 1.36×10 <sup>13</sup>                    | 12.7                      | 16                     |
| 350.4ª             | F                            | 4.94×10 <sup>12</sup>                    | 8.3                       | 17                     |
| 349.4ª             | F                            | 4.65×10 <sup>12</sup>                    | 3.9                       | 18                     |
| 331.4ª             | F                            | 1.11×10 <sup>12</sup>                    | 15.5                      | 18                     |
| 325.6ª             | F                            | 5.46×10 <sup>11</sup>                    | 10.2                      | 18                     |
| 325.6              | S                            | 4.97×10 <sup>11</sup>                    | 14.1                      | 30                     |
| 317.6ª             | F                            | 2.19×10 <sup>11</sup>                    | 6.5                       | 12                     |
| 313.8ª             | F                            | 1.35×10 <sup>11</sup>                    | 20.4                      | 18                     |
| 313.8              | S                            | 1.19×10 <sup>11</sup>                    | 16.8                      | 20                     |
| 307.8ª             | F                            | 9.11×10 <sup>10</sup>                    | 15.0                      | 10                     |
| 303.0ª             | F                            | 5.01×10 <sup>10</sup>                    | 8.5                       | 18                     |
| 303.0              | S                            | 4.62×10 <sup>10</sup>                    | 16.2                      | 57                     |
| 286.4 <sup>ь</sup> | S                            | 4.26×10 <sup>9</sup>                     | 19.5                      | 27                     |
| 273.0 <sup>6</sup> | S                            | 5.68×10 <sup>8</sup>                     | 9.9                       | 20                     |
| 263.2 <sup>b</sup> | S                            | $2.24 \times 10^{8}$                     | 16.8                      | 40                     |
| 253.4              | S                            | $5.90 \times 10^{7}$                     | 7.7 <sup>b</sup>          | 35                     |
| 242.8 <sup>b</sup> | S                            | 4.69×10 <sup>6</sup>                     | 16.4                      | 40                     |

<sup>a</sup> For these experiments pure nitric oxide was added at a mixing ratio of 1 part per thousand.

<sup>b</sup> For these experiments ozonized oxygen was added to yield an ozone concentration in the cell of approximate-

ly  $2 \times 10^{13}$  molecules cm.<sup>-3</sup>

section which was measured by Schott and Davidson was systematically low. The wavelength used was a 3.6 nm region centered on 652 nm, between the two strong bands at 627 and 662 nm. Using their measured 652 nm cross section and photographic spectra of NO<sub>3</sub>, they estimated a 662 nm cross section of  $3000 \pm 1000 \ \ell \text{mol}^{-1} \text{ cm}$  (base 10)  $[1.15(\pm 0.38) \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}]$ . The peak cross



FIG. 2. Summary of the measurement of the equilibrium constant from this study. The temperature range of the measurement is extrapolated to the high temperature study of Schott and Davidson in order to allow a more direct comparison with their data, which has been corrected to be in accord with recent results on the NO<sub>3</sub> visible absorption cross section. The error bars shown for this study are 95% confidence intervals and are about  $\pm$  30%. The lines represent the results of Graham and Johnston, and Kircher *et al.* which are also shown in Fig. 1.

section which was measured in this laboratory is approximately a factor of 2.3 larger. Additionally, a reexamination of our NO<sub>3</sub> spectra yielded a temperature independent cross section of  $5.39(\pm 1.8) \times 10^{-19}$  cm<sup>2</sup> molecule<sup>-1</sup> at 652 nm, about a factor of 1.9 larger than that used by Schott and Davidson. This is also consistent with the results of Graham and Johnston who reported that their cross section at 652 nm was about a factor of 2.2 larger than that of Schott and Davidson extrapolated to room temperature. Dividing the individual data points of Schott and Davidson by a factor of 2.1 brings their results very close to the extrapolated fit of this



FIG. 3. Summary of equilibrium constant results of this study and the previous studies for a temperature region near room temperature. The error bar gives the estimated accuracy at the 95% confidence interval for this study.



FIG. 4. First-order decay plots for the decay of  $N_2O_5$  from this study. The slopes of fits to these data are shown in Fig. 6.

study, as shown in Fig. 2. Their measurements of NO<sub>2</sub> concentration were linked to the results of Verhoek and Daniels,<sup>17</sup> Bodenstein and Boës,<sup>18</sup> and Wourtzel<sup>19</sup> which are in reasonable agreement with our measurements of the NO<sub>2</sub> cross section and the N<sub>2</sub>O<sub>4</sub>  $\rightleftharpoons$  2NO<sub>2</sub> equilibrium constant. Measurement of N<sub>2</sub>O<sub>5</sub> in these experiments was accomplished by pressure measurement before the sample was shock heated, corrected for the formation of NO<sub>2</sub> and NO<sub>3</sub> ( < 10% conversion), and should be reasonably accurate.

Comparison with the results of Graham and Johnston is more difficult, because the value of the equilibrium constant is extracted from the results of three different experiments. They indicate that the cross section measurements of  $N_2O_5$ and NO<sub>3</sub> are proportional to each other and any errors which result in these determinations would cancel. As discussed earlier, we expect systematic errors associated with the slow flow technique used here to result in equilibrium constants somewhat higher than the true value at the higher temperatures, but the results of this study are systematically lower than the results of Graham and Johnston. In addition, there is no apparent systematic difference between the slow flow and the static decay experiments. Within the uncertainty of Graham and Johnston's result (using their quoted errors in the fitting parameters and assuming all the error is in the intercept) their value is systematically larger than the present result at all temperatures, and approximately a factor of 2 at room temperature.

Because the results of Burrows *et al.* show essential agreement with Graham and Johnston's result, they too are systematically higher than the results of the present study. It is also apparent from the stated uncertainty of the slope of their fit (1.2 kcal) that their data are considerably more scattered than the Graham and Johnston data (standard deviation of slope reported as 0.11 kcal). Agreement is good within the error limits, with the room temperature study of Tuazon *et al.* 

Reasons for the difference between the present study and the previous room temperature study in this laboratory<sup>4</sup> are not clear. The fact that alternating infrared and visible absorption measurements were made in the same decay may have caused an undetected base line offset in one or both spectral regions. The visible measurements were done at a higher spectral resolution than the present study so the effect of resolution on cross sections used, particularly for  $NO_2$ , cannot easily be checked. The fact that in this study multiple methods were used for the  $NO_2$  determination, with redundancy in each method, favors the present result.

The logarithms of the equilibrium constants from this study were fitted to a linear function vs 1/T(K). These values were weighted by the inverse of the square of the standard deviation of the mean of the several determinations at a given temperature. This yields the following expression for equilibrium constant:

$$K_{1C} = 1.30 \times 10^{26} \exp(-21.490/RT)$$
 molecules cm<sup>-3</sup>.  
(c)

The estimated accuracy of this result at the 95% confidence interval is  $\pm$  30% based on a propagation of errors calculation including uncertainties in cross sections, optical path length, and absorbance measurements. The precision of the slope and intercept (in base *e* logarithm units) are 1.1% and 2.0%, respectively, at the 95% confidence interval.

If the logarithm of the individual equilibrium constants in units of atmospheres are plotted vs 1/T(K), the slope is equal to  $\Delta H_1^0/R$  and the intercept is  $\Delta S_1^0/R$  under the assumptions that  $\Delta H_1^0$  and  $\Delta S_1^0$  are independent of temperature over the range under study. The data were treated as described above with a weighted least squares approach yielding the following expression for the equilibrium constant:

$$K_{1P} = 1.51 \times 10^7 \exp(-22\ 110/RT)$$
 atm. (d)

The precision of the slope and intercept for this expression are 4.1% and 2.0%, respectively, at the 95% confidence interval.

Due to the fact that data are now available for  $K_1$ ,  $k_1$ , and  $k_{-1}$ , the consistency of the reported values can be checked. While a complete analysis such as that done by Malko and Troe will not be done here, several general statements can be made about the kinetic vs equilibrium data for reactions (1) and (-1). Let us define the equilibrium constant from kinetic data such as that done by Kircher et al. as  $K_k$ , while direct measurements of the equilibrium constant equal  $K_d$ . The ratio  $K_d/K_k$  should equal 1 within the combined error limits of all the studies at all temperatures and pressures, with no systematic variation in either variable.  $K_d/K_k$  ratios were calculated using data from five sources:  $K_d$  data from this study and Graham and Johnston;  $K_k$  data using  $k_1$  from Viggiano et al. and Connell and Johnston and using  $k_{-1}$  data from Kircher et al. A summary of those calculations is shown in Fig. 5. The most consistent combination near room temperature was using the equilibrium constant of this study and  $k_1$  from Viggiano et al. The ratios calculated showed no systematic variation with pressure and yielded and average value for  $K_d/K_k$  of 0.86, well within the error limits of this study alone. In contrast, using the equilibrium constant of Graham and Johnston and  $k_1$  from Connell and Johnston calculated ratios near room temperature showed a marked pressure dependence changing from 1.3 at low pressures  $(5 \times 10^{17} \text{ molecules cm}^{-3})$  to 1.0 at higher pressures (about 2 atm). While this variation is within the combined error limits of all the studies, it does indicate inconsistency in the pressure dependence of the forward and reverse rate coefficients in the  $k_1$  data of Connell and Johnson and possibly Kircher *et al.* as well. Ratios calculated for the other two combinations yielded for  $K_d$  from this study and  $k_1$  from Connell and Johnston values of 0.48 to 0.42. For Graham and Johnston's  $K_d$  and  $k_1$  from Viggiano *et al.* the values are from 2.31 to 2.24.

The point is made clearer at higher temperatures. At the highest temperature of each of the  $k_1$  studies ratios were also calculated. For the data of Viggiano et al. this is about 360 K. Here  $K_d/K_k$  decreases with increasing pressure, changing from 0.54 at the lowest pressure to 0.28 at the highest pressure. Similarly, at Connell and Johnston's highest temperature (about 320 K), the ratio changes from 0.41 to 0.26 using the equilibrium constant from this study in both cases. This large variation in this ratio with pressure indicates definite inconsistency between  $k_1$  and  $k_{-1}$  for the data now available, both in the dependence on the concentration of the third body and in the temperature dependence of the low pressure limits or high pressure limits or both. The same calculations using Graham and Johnston's equilibrium constant yields ratios of 1.66 to 0.86 with the data of Viggiano et al. and ratios of 1.17 to 0.73 with Connell and Johnston's  $k_1$ . This all suggests further work is necessary on the tempera-



FIG. 5. Plot of  $K_d/K_k$  ratios (described in the text) vs temperature for various combinations of  $K_d$ ,  $k_1$ , and  $k_{-1}$  data available from this study and previous calculations at the following third-body concentrations:  $5 \times 10^{17}$ ,  $1 \times 10^{18}$ ,  $1 \times 10^{19}$ , and  $5 \times 10^{19}$  molecules cm.<sup>-3</sup> The upper two groups of curves were calculated using the  $K_d$  value of Graham and Johnston (Ref. 3) and the lower two groups used the  $K_d$  from this study. The curves which extend to the highest temperature (360 K) rely on  $k_f$  values from Viggiano *et al.* (Ref. 10) and the curves extending to the lowest temperatures (260 K) used  $k_f$  values of Connell and Johnston (Ref. 9). The horizontal line at a  $K_d/K_k$  ratio of 1 shows the ideal situation of perfect agreement between the direct and kinetic measurements of this system.

ture and pressure dependence of  $k_1$  and probably  $k_{-1}$ .

The enthalpy of reaction from the present study  $[\Delta_f H_1^0$ (298) =  $-22.1 \pm 0.4$  kcal mol<sup>-1</sup>] is in excellent agreement with the results of Kircher *et al.* ( $-22.5 \pm 0.5$  kcal mol<sup>-1</sup>) in good agreement with Graham and Johnston ( $-22.8 \pm 0.2$  kcal mol<sup>-1</sup>) and is within the error limits of most of the other temperature dependent studies which have been reported. The entropy of reaction of the above treatment ( $-32.8 \pm 0.7$  cal mol<sup>-1</sup> deg<sup>-1</sup>) overlaps the error bars of an entropy of reaction calculated using statistical mechanics and frequencies for each species as described in Burrows *et al.* ( $-36.2 \pm 3.0$  cal mol<sup>-1</sup> deg<sup>-1</sup>), and the JANAF<sup>20</sup> compilation (-34.9 + 1.4 cal mol<sup>-1</sup> deg<sup>-1</sup>).

The enthalpy of reaction obtained here can be used to calculate an enthalpy of formation for NO<sub>3</sub>. This calculation relies directly on accurate results for the enthalpies of formation of  $NO_2$  and  $N_2O_5$ . An investigation of the literature values for these parameters revealed that  $\Delta_f H^0(298)$  for NO<sub>2</sub> is known with reasonable accuracy. On the other hand, considerable uncertainty exists in the enthalpy of formation of  $N_2O_5(g)$ . Therefore, experiments were designed to redetermine accurately the value for  $\Delta_f H^0(298)$  of N<sub>2</sub>O<sub>5</sub>(g). The experimental details will be described in another report,<sup>21</sup> and thus only the results will be given here. The experiments involved measuring the enthalpy of hydrolysis of  $N_2O_5$  (cr), and the vapor pressure of  $N_2O_5$  over the solid phase as a function of temperature, identical to the treatment described in the JANAF compilation.<sup>20</sup> These two results were combined to yield a value for  $\Delta_f H^0(298)(N_2O_5,g)$  of 1.19 + 0.54 (95% confidence interval) kcal mol<sup>-1</sup>. This value is considerably less than the previously recommended value (2.70  $\pm$  0.31 kcal mol<sup>-1</sup>), and results in a lower value for the enthalpy of formation of NO<sub>3</sub> at 298 K. Using values of 7.90 kcal mol<sup>-1</sup> for the enthalpy of formation for NO<sub>2</sub> and 22.11 kcal  $mol^{-1}$  for the enthalpy of reaction (2.1), yields an enthalpy of formation for NO<sub>3</sub> at 298 K of  $15.39 \pm 0.72$  kcal mol<sup>-1</sup>. This result is within the error limits of the results given in the JANAF compilation, but is much lower than the average value previously accepted  $(17.0 \pm 4.8 \text{ kcal mol}^{-1})$ . This has considerable implications for our understanding of the thermodynamics and kinetics of reactions of NO3 with various species. For example, using 15.39 kcal mol<sup>-1</sup> for the enthalpy of formation of NO<sub>3</sub> results in calculated equilibrium constants for hydrogen abstraction reactions (such as  $NO_3 + HC1 \approx HNO_3 + Cl$ ) about 2.4% of that calculated using 17.6 kcal mol<sup>-1</sup> for the enthalpy of formation of NO<sub>3</sub>.

The results of the  $N_2O_5$  decay studies are summarized in Table IV and in Fig. 6. The logarithms of the apparent first-order rate constants (k') were fitted to the inverse of the absolute temperature using the same weighted least squares approach described above. The data of Johnston and Tao,<sup>15</sup> and Daniels and Johnston<sup>22</sup> appear in excellent agreement with the present study over the temperature range which they overlap and thus the entire data set was used to derive a best estimate for k'. The fit yielded the following result:

$$k' = 1.23 \times 10^{13} \exp(-24\ 300/RT) \ \mathrm{s}^{-1}.$$
 (e)

The estimated error limits are  $\pm 15\%$  at the 95% confi-

TABLE IV. Summary of first-order rate constants for  $N_2O_5$  decay from this study, that of Johnston and Tao, and Daniels and Johnston. These data are also shown in Fig. 6.

| Temperature<br>(K) | Rate constant<br>(s <sup>-1</sup> ) | Reference |
|--------------------|-------------------------------------|-----------|
| 396.2              | 5.25×10 <sup>-1</sup>               | 15        |
| 388.2              | 2.58×10 <sup>-1</sup>               | 15        |
| 378.0              | $1.22 \times 10^{-1}$               | 15        |
| 367.6              | 4.58×10 <sup>-2</sup>               | 15        |
| 363.4              | $2.84 \times 10^{-2}$               | This work |
| 363.4              | $2.86 \times 10^{-2}$               | This work |
| 357.6              | $1.61 \times 10^{-2}$               | 15        |
| 350.8              | 9.35×10 <sup>-3</sup>               | This work |
| 350.8              | 9.20×10 <sup>-3</sup>               | This work |
| 348.6              | 6.83×10 <sup>-3</sup>               | 15        |
| 338.2              | $2.43 \times 10^{-3}$               | 21        |
| 337.6              | $2.56 \times 10^{-3}$               | 15        |
| 331.4              | $1.12 \times 10^{-3}$               | This work |
| 328.2              | 7.50×10 <sup>-4</sup>               | 21        |
| 325.6              | 6.18×10 <sup>-4</sup>               | This work |
| 318.2              | 2.49×10 <sup>-4</sup>               | 21        |
| 313.8              | 1.49×10 <sup>-4</sup>               | This work |
| 308.2              | 6.73×10 <sup>-5</sup>               | 21        |
| 298.2              | 1.69×10 <sup>-5</sup>               | 21        |

dence interval, and the equation is plotted as the line in Fig. 6. This result is very close to the previously accepted value derived from the Johnston and Tao, and the Daniels and Johnston data  $[k'_{JT} = 2.05 \times 10^{13} \exp(-24.650/RT) \text{ s}^{-1}]$ , yielding agreement within 6% over the range where they overlap and to within 10% when extrapolated to 298 K. The result of this experiment can be combined with the equilibrium constant result to yield an expression for  $k_2$ :

$$k_2 = 9.5 \times 10^{-14} \exp(-2810/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$
 (f)

The estimated accuracy of the above expression is  $\pm 35\%$  at



FIG. 6. Arrhenius plot for the first-order decay of  $N_2O_5$  from this study as well as Johnston and Tao, and Daniels and Johnston. The data from all studies were used to derive a temperature dependent expression for the first-order decay rate constant.

$$k_2 = 2.5 \pm 0.5 \times 10^{-14} \exp[-(2440 \pm 200)/RT]$$
  
  $\times \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$  (g)

Expression (f) yields a value a factor 2 larger than expression (g) at 298 K and a factor of 1.8 larger at 220 K; however, we believe the combined data, including the present results, yield the most reliable estimate.

#### **IV. SUMMARY**

The value for equilibrium constant for reaction (1) has been measured directly over a wide range of temperatures and yields values significantly lower than previously accepted. The implications of this result to atmospheric chemistry are the increased importance in the storage of NO<sub>2</sub> and NO<sub>3</sub> in the  $N_2O_5$  reservoir, and (for a given  $[N_2O_5]$  and  $[NO_2]$  the reduced concentration of the NO<sub>3</sub> radical in the atmosphere. Laboratory kinetics studies which use the value of the equilibrium constant to calculate concentrations of  $NO_3$  based on concentrations of  $N_2O_5$  and  $NO_2$  may require correction in light of the present result. Caution should be exercised here because several groups which perform experiments of this sort have also made direct equilibrium constant measurements.<sup>4,5</sup> While these results are markedly different, it can be shown that any errors in their equilibrium constant measurement would cancel in the determination of the concentration of NO3 as long as the same analytical techniques were used for the equilibrium constant measurement and the NO<sub>3</sub> reaction rate study. Thus, at least in the case of results from this laboratory, we recommend that the NO<sub>3</sub> rate constant studies previously performed remain as reported in the literature 15,23,24

A value for the NO forming channel in the reaction of  $NO_3$  with  $NO_2$  was also verified, and when combined with the equilibrium constant of the present study, results in a value approximately twice as large as previously accepted.

### ACKNOWLEDGMENTS

This work was supported in large part through project W16042 of the Upper Atmosphere Research Program, Earth Science and Applications Division, The National Aeronautics and Space Administration. Support for one of the authors (C.A.C.) was provided under Contract No. AP-13 from the Coordinating Research Council. The authors are grateful to Professor Harold Johnston for many useful discussions related to this work.

<sup>1</sup>H. S. Johnston, C. A. Cantrell, and J. G. Calvert, J. Geophys. Res. 91, 5159 (1985).

- <sup>2</sup>G. Schott and N. Davidson, J. Am. Chem. Soc. **80**, 1841 (1958).
- <sup>3</sup>R. A. Graham and H. S. Johnston, J. Phys. Chem. 82, 254 (1978).
- <sup>4</sup>D. Perner, A. Schmeltekopf, R. H. Winkler, H. S. Johnston, J. G. Calvert, C. A. Cantrell, and W. R. Stockwell, J. Geophys. Res. **90**, 3807 (1985).
- <sup>5</sup>E. C. Tuazon, E. Sanhueza, R. Atkinson, W. P. L. Carter, A. M. Winer,
- E. C. Fullon, E. Sannacza, R. Atkinson, W. F. E. Carter, A. M. Winer

- and J. N. Pitts, Jr., J. Phys. Chem. 88, 3095 (1984).
- <sup>6</sup>J. P. Burrows, G. S. Tyndall, and G. K. Moortgat, Chem. Phys. Lett. **119**, 193 (1985).
- <sup>7</sup>U. Platt, D. Perner, J. Schröder, C. Kessler, and A. Toennissen, J. Geophys. Res. 86, 11965 (1981).
- <sup>8</sup>M. W. Malko and J. Troe, Int. J. Chem. Kinet. 14, 399 (1982).
- <sup>9</sup>P. Connell and H. S. Johnston, Geophys. Res. Lett. 6, 553 (1979).
- <sup>10</sup>A. A. Viggiano, J. A. Davidson, F. C. Fehsenfeld, and E. E. Ferguson, J. Chem. Phys. 74, 6113 (1981).
- <sup>11</sup>C. C. Kircher, J. J. Margitan, and S. P. Sander, J. Phys. Chem. 88, 4370 (1984).
- <sup>12</sup>C. A. Smith, A. R. Ravishankara, and P. H. Wine, J. Phys. Chem. 89, 1423 (1985).
- <sup>13</sup>R. E. Shetter, J. A. Davidson, C. A. Cantrell, and J. G. Calvert, Rev. Sci. Instrum. 58, 1428 (1987).
- <sup>14</sup>J. A. Davidson, C. A. Cantrell, A. H. McDaniel, R. E. Shetter, S. Madronich, and J. G. Calvert, J. Geophys. Res. (in press).

- <sup>15</sup>C. A. Cantrell, J. A. Davidson, R. E. Shetter, B. A. Anderson, and J. G. Calvert, J. Phys. Chem. **91**, 5858 (1987).
- <sup>16</sup>H. S. Johnston and Y.-S. Tao, J. Am. Chem. Soc. 73, 2948 (1951).
  - <sup>17</sup>F. H. Verhoek and F. Daniels, J. Am. Chem. Soc. 53, 1250 (1931).
  - <sup>18</sup>M. Bodenstein and F. Boës, Z. Phys. Chem. A **100**, 75 (1922).
- <sup>19</sup>E. Wourtzel, Comp. Rend. **169**, 1937 (1919).
- <sup>20</sup>M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, and A. N. Syverud, *JANAF Thermochemical Tables*, 3rd ed. (American Institute of Physics, New York, 1985).
- <sup>21</sup>A. H. McDaniel, J. A. Davidson, C. A. Cantrell, R. E. Shetter, and J. G. Calvert, J. Phys. Chem. (in press).
- <sup>22</sup>F. Daniels and E. H. Johnston, J. Am. Chem Soc. 43, 53 (1921).
- <sup>23</sup>C. A. Cantrell, W. R. Stockwell, L. G. Anderson, K. L. Busarow, D. Perner, A. Schmeltekopf, J. G. Calvert, and H. S. Johnston, J. Phys. Chem. 89, 139 (1985).
- <sup>24</sup>C. A. Cantrell, J. A. Davidson, K. L. Busarow, and J. G. Calvert, J. Geophys. Res. 91, 5347 (1986).