

# Temperature Dependent Rate Coefficient for the Reaction $\text{O}(^3\text{P}) + \text{NO}_2 \rightarrow \text{NO} + \text{O}_2$

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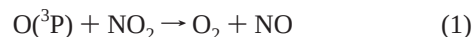
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The rate coefficient ( $k_1$ ) for the reaction  $\text{O}(^3\text{P}) + \text{NO}_2 \rightarrow \text{O}_2 + \text{NO}$  was measured under pseudo-first-order conditions in  $\text{O}(^3\text{P})$  atom concentration over the temperature range 220–412 K. Measurements were made using pulsed laser photolysis of  $\text{NO}_2$  to produce oxygen atoms and time-resolved vacuum UV resonance fluorescence detection of O atoms. The  $\text{NO}_2$  concentration was measured using three techniques: flow rate, UV absorption, and chemical titration ( $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$ ). The  $\text{NO}_2$  UV absorption cross section at 413.4 nm was determined as a function of temperature using the chemical titration and flow methods. Including the low-temperature data of Harder et al.<sup>1</sup>, the temperature-dependent  $\text{NO}_2$  cross section is given by  $\sigma_{413.4}(T) = (9.49 - 0.00549 T) \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1}$ . The measured rate coefficients for reaction 1 can be expressed as  $k_1(T) = (5.26 \pm 0.60) \times 10^{-12} \exp[(209 \pm 35)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , where the quoted uncertainties are  $2\sigma$  and include estimated systematic errors. This result is compared with previously reported measurements of  $k_1$ .

## Introduction

Nitrogen oxides, NO and  $\text{NO}_2$  (collectively called  $\text{NO}_x$ ), play a crucial role in atmospheric ozone chemistry: they lead to photochemical ozone production in the troposphere and catalytic ozone destruction in the stratosphere. In the stratosphere,  $\text{NO}_x$  chemistry affects both the ozone abundance and its vertical profile. Of the many possible catalytic ozone destruction cycles involving  $\text{NO}_x$ , the following is the most important:



net:



Atmospheric model calculations of ozone abundances and vertical profiles rely on the temperature-dependent rate coefficients for reactions 1 and 2. Reaction 1 is the rate-limiting step in this catalytic cycle and has been studied many times over the past few decades. However, a careful examination of the available data shows that there are significant discrepancies and that a more accurate rate coefficient would be beneficial.

Current recommendations<sup>2,3</sup> for reaction 1 give  $k_1(T) = 6.5 \times 10^{-12} \exp(120/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and are based on the studies of Davis et al.,<sup>4</sup> Slinger et al.,<sup>5</sup> Bemand et al.,<sup>6</sup> Ongstad and Birks,<sup>7</sup> and Geers-Muller and Stuhl.<sup>8</sup> Other earlier studies, which yielded lower values of  $k_1(298 \text{ K})$  and positive activation energies, have not been included in deriving the recommenda-

tions. The values of  $k_1(298 \text{ K})$  reported in the above five studies agree within 10%. However, the temperature dependence of  $k_1$  from these studies disagree significantly; the activation energies reported from various groups fall in the range 0 to  $\sim -400 \text{ cal mol}^{-1}$ . The recommended value of the activation energy,  $240 \pm 240 \text{ cal mol}^{-1}$ , has been derived from the studies of Davis et al., Ongstad and Birks, and Geers-Muller and Stuhl. The current recommendations suggest an uncertainty of  $\sim 60\%$  in the value of  $k_1(200 \text{ K})$ ; this large range for  $k_1(200 \text{ K})$  is mostly due to the uncertainty in the activation energy. This level of uncertainty has significant implications in the interpretation of atmospheric measurements of trace species and model calculated abundances and trends of ozone. The rate coefficient has been identified as a major source of uncertainty in stratospheric models (see, for example, ref 9)

Here, we report the temperature dependence of  $k_1$  measured using the technique of pulsed laser photolysis with resonance fluorescence detection of  $\text{O}(^3\text{P})$  atoms (PP–RF). During these experiments, special emphasis was placed on the determination of  $\text{NO}_2$  concentration and measurements of  $k_1$  at stratospheric temperatures. Our results are compared with previous measurements and a new value for stratospheric modeling is suggested.

## Experimental Section

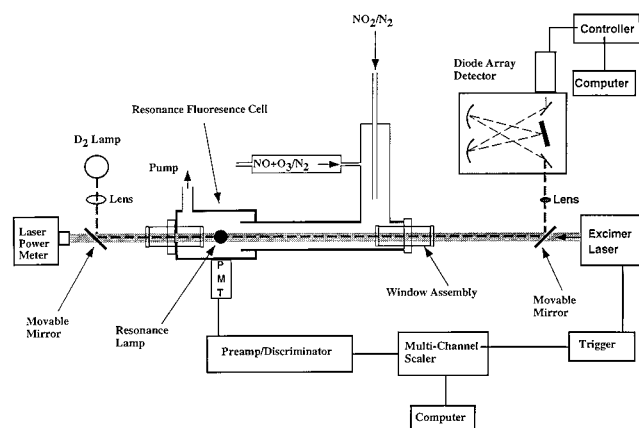
The accuracy of the value of  $k_1$ , determined in a system where the temporal profile of  $\text{O}(^3\text{P})$  atoms are measured under pseudo-first-order conditions, depends on how well the concentration of  $\text{NO}_2$  is known. Even though  $\text{NO}_2$  is a stable gas, there are a few difficulties associated with its handling and knowing its concentration accurately. First,  $\text{NO}_2$  can react on the walls of the reactor, thermally decompose (e.g., in electronic flow meters), and be photolyzed by room light. Second, it can undergo self-association



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**Figure 1.** Experimental apparatus used to measure the rate coefficient for reaction 1,  $\text{O}(^3\text{P}) + \text{NO}_2 \rightarrow \text{NO} + \text{O}_2$ , utilizing atomic resonance fluorescence detection of O atoms. O atoms were produced by photolysis of  $\text{NO}_2$  via an excimer laser. The  $\text{NO}_2$  concentration in the reaction cell was determined by UV absorption, flow rate measurements, or chemical titration ( $\text{NO} + \text{O}_3 \rightarrow \text{NO} + \text{O}_2$ ) as discussed in the text.

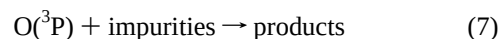
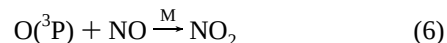
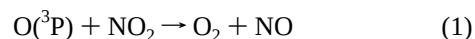
to make significant amounts of  $\text{N}_2\text{O}_4$  if the  $\text{NO}_2$  concentrations are large and/or the temperatures are low ( $K_{\text{eq}}(T) = 5.2 \times 10^{-29} \exp(6643/T) \text{ cm}^3 \text{ molecule}^{-1}$  from ref 3). The large temperature dependence of the equilibrium constant can make even small changes in temperature result in significant changes in the  $\text{NO}_2$  concentration at low temperatures. This factor alone has limited previous kinetic studies to measurements above 230 K. Third, because  $k_1$  is large, only small concentrations of  $\text{NO}_2$  which are difficult to accurately determine, have to be used; otherwise, the loss rate coefficients for  $\text{O}(^3\text{P})$  atoms exceeds the measurable range ( $< 10^4 \text{ s}^{-1}$ ). In this work, several methods were employed to determine the concentration of  $\text{NO}_2$  in the reactor. Use of a combination of these methods reduced the possible systematic errors in  $\text{NO}_2$  concentration and, therefore, yielded a more accurate value of  $k_1$ . The details of these methods are outlined in a separate section below.

The pulsed photolysis resonance fluorescence (PP-RF) apparatus and the methodology used to measure rate coefficients for  $\text{O}(^3\text{P})$  atom reactions have been described in detail previously.<sup>10,11</sup> The apparatus was slightly modified for the present study, as shown in Figure 1, to directly measure  $\text{NO}_2$  via UV-visible absorption in the reactor. The photolysis laser beam was propagated along the same path as the light beam for absorption measurements. The beams were interchanged by moving two mirrors mounted on repositioning mounts. The metal reaction cell was designed to reduce scattered light and increase the efficiency for detecting fluorescence.<sup>12</sup> A solar blind photomultiplier tube (PMT) detector was mounted orthogonal to both the photolysis laser and resonance lamp to detect the fluorescence. A 1 mm thick  $\text{CaF}_2$  window mounted in front of the PMT blocked short wavelength radiation ( $\lambda < 130 \text{ nm}$ ) from reaching the PMT. The volume between the cell window and the PMT was flushed with  $\text{N}_2$  to eliminate absorption of the oxygen atom fluorescence by air. The sensitivity for detection of  $\text{O}(^3\text{P})$  was nominally  $\sim 5 \times 10^8 \text{ atom cm}^{-3}$  for a 1 s integration; this was measured by generating a known concentration of  $\text{O}(^3\text{P})$  via photolysis of a known concentration of ozone in  $\text{N}_2$  at 248 nm using pulsed KrF excimer laser of known fluence. ( $\text{N}_2$  quickly quenched  $\text{O}(^1\text{D})$ , formed in ozone photolysis, to  $\text{O}(^3\text{P})$ .)

$\text{O}(^3\text{P})$  for measuring  $k_1$  was generated by photolyzing  $\text{NO}_2$  at 308 nm (XeCl excimer laser) in the presence of  $\text{N}_2$ .



The yield of  $\text{O}(^3\text{P})$  in reaction 5 is unity.<sup>3</sup> The  $\text{O}(^3\text{P})$  atom temporal profile (loss) in the presence of  $\text{NO}_2$  was governed by the following processes:



Reaction 6 needs only to be considered in experiments in which NO was added to the reaction mixture, as described below. Process 7 represents possible loss of  $\text{O}(^3\text{P})$  via reactions with any impurities in the carrier gas, while reaction 8 represents a pseudo-first-order loss of  $\text{O}(^3\text{P})$  due to diffusion and flow out of the reaction volume. In our experiments, reactions 7 and 8 were indistinguishable and together accounted for a first-order loss rate constant of  $\sim 20 \text{ s}^{-1}$ . Note that the first-order rate constant for loss of  $\text{O}(^3\text{P})$  due to reaction 1 was at least five times, and on the average a few hundred times, larger than that due to processes 7 and 8. Oxygen atom temporal profiles were measured under pseudo-first-order conditions, i.e.,  $[\text{NO}_2] \gg [\text{O}(^3\text{P})]_0$ , with a ratio  $[\text{NO}_2]/[\text{O}(^3\text{P})]_0$  typically  $> 2.5 \times 10^3$  (for photolyzing with a 308 nm pulse of  $\sim 1 \text{ mJ cm}^{-2}$ ). The exact ratio of  $[\text{NO}_2]/[\text{O}(^3\text{P})]_0$  was controlled by the photolysis laser fluence and was varied over a wide range ( $\sim 0.5$  to  $7.5 \text{ mJ cm}^{-2}$ ). The  $\text{O}(^3\text{P})$  decays were represented by a simple exponential:

$$\ln(S_t) = \ln(S_0) - k't \quad (9)$$

where  $S_t$  and  $S_0$  are the  $\text{O}(^3\text{P})$  resonance fluorescence signals at time  $t$  and time zero (i.e., right after the photolysis) and

$$k' = k_1[\text{NO}_2] + k_6[\text{NO}] + k_7[\text{impurity}] + k_8 \quad (10)$$

Approximately 1000–5000 temporal profiles were coadded to improve the signal-to-noise ratio. Measured  $\text{O}(^3\text{P})$  atom temporal profiles were fit to eq 9 using linear least squares routines to obtain  $k'$ . Such temporal profiles were measured at various  $\text{NO}_2$  concentrations over the range  $(0.04\text{--}4) \times 10^{15} \text{ molecule cm}^{-3}$ . The slope of the plots of  $k'$  vs  $[\text{NO}_2]$  yielded the bimolecular rate coefficient for reaction 1,  $k_1$ . The bimolecular rate constants were measured at 15 different temperatures between 220 and 412 K.

All experiments were performed under flow conditions (i.e., flow velocity  $\approx 100 \text{ cm s}^{-1}$ ). The photolysis laser (XeCl excimer laser, 308 nm) beam passed along the length of the absorption cell (parallel to the gas flow). The laser was operated at a repetition rate of 5 Hz. Therefore, the flowing gas sample was exposed to no more than three photolysis laser pulses before reaching the detection zone. At the highest laser fluence, about 0.3% of  $\text{NO}_2$  was lost due to photolysis. The kinetic data was not corrected for this small loss.

The temperature of the Pyrex extension (see below) and metal cell, which together formed the absorption cell for measuring the  $\text{NO}_2$  concentration, were regulated by flowing either cooled methanol or heated ethylene glycol through their jackets. The temperature was varied over the range 220–412 K. The

temperature of the gas flowing through the cell and the Pyrex extension were measured with a chromel–alumel thermocouple under flow conditions identical to those used in measuring  $k_1$ . The temperature was measured at various locations using a retractable thermocouple. The thermocouple was retracted during kinetic measurements. The measured gas temperature was estimated to be accurate to 1 K. A temperature gradient from one end to the other was less than 8 K even at 220 K, the lowest temperature of the experiments. This temperature gradient was sufficiently small as not to affect the NO<sub>2</sub> concentration via N<sub>2</sub>O<sub>4</sub> formation or change the effective path length. The temperature in the region where O atoms temporal profiles were measured was constant to better than 0.5 K and was known to better than 0.5 K.

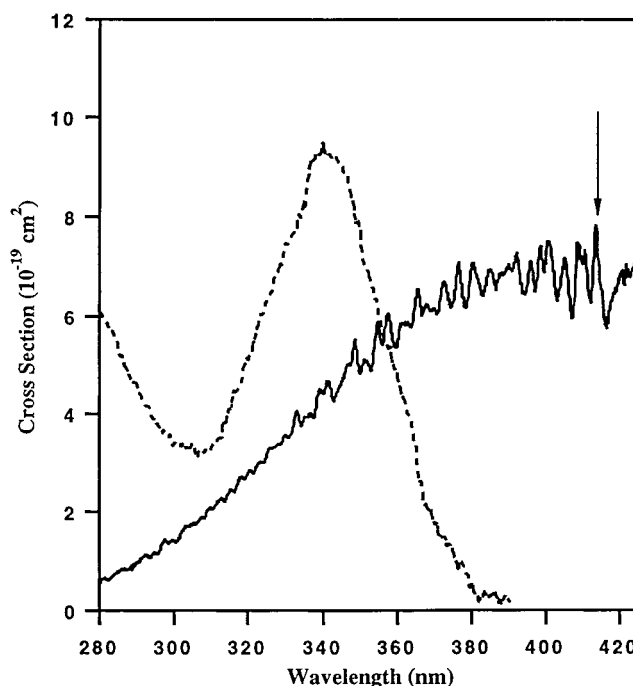
**[NO<sub>2</sub>] Determination Methods.** Three methods were used to determine the NO<sub>2</sub> concentration for measuring  $k_1$ : (1) UV absorption, (2) flow, and (3) chemical titration. The UV–vis absorption cross sections of NO<sub>2</sub> were determined using flow, chemical titration, and absolute pressure measurements; hence, using the UV absorption to determine NO<sub>2</sub> concentration was not truly independent of the other two methods. The combination of these methods was used to reduce possible systematic errors associated with the NO<sub>2</sub> concentration determination. Each of these methods is described separately below.

**Flow.** The rate of change of pressure,  $dp/dt$ , in a calibrated volume was measured using a flow of pure NO<sub>2</sub>. This flow was added to the measured flows of the other gases, mostly N<sub>2</sub>. The pressure in the reactor and the flow tube were measured with 100 Torr electronic capacitance manometers. The concentration of NO<sub>2</sub> was calculated using the measured flow rate of NO<sub>2</sub> and other gases, and pressure in the reactor. The N<sub>2</sub> flow rates were measured using calibrated electronic mass flow meters. This method provided an accurate measurement of NO<sub>2</sub> concentrations for levels below those measurable accurately using UV absorption,  $<1 \times 10^{14}$  molecule cm<sup>-3</sup>. This method was most advantageous for low temperature ( $T < 230$  K) measurements where low concentrations of NO<sub>2</sub>,  $<1 \times 10^{14}$  molecule cm<sup>-3</sup>, were required to avoid interference from N<sub>2</sub>O<sub>4</sub> formation, reaction 4. The overall accuracy of this method was controlled by the accuracy in measuring  $dp/dt$ ,  $\pm 3\%$ , N<sub>2</sub> flow rate,  $\pm 3\%$ , and pressure,  $\pm 1\%$ , as well as the purity of the NO<sub>2</sub> sample,  $>99.9\%$ . Thus the absolute accuracy of NO<sub>2</sub> concentrations determined from this method is estimated to be  $\sim 5\%$  by assuming the above uncertainties to be uncorrelated.

**Chemical Titration.** This method was used to produce NO<sub>2</sub> directly upstream of the absorption cell via the reaction



where  $k_2(298 \text{ K}) = 1.8 \times 10^{-14}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.<sup>3</sup> Note that the measured NO<sub>2</sub> concentration is not dependent on the exact value of this rate constant because all O<sub>3</sub> was converted to NO<sub>2</sub>. NO was used in excess over O<sub>3</sub>, and the reaction was run to completion (i.e., more than five lifetimes with respect to reaction 2) in a sidearm reactor (Pyrex, 3 cm i.d. and 20 cm long). The residence time of the gas in the reactor was about 2 s. The loss of O<sub>3</sub> and formation of NO<sub>2</sub> were monitored simultaneously by UV absorption with the diode array spectrometer. Concentrations of NO were determined by the  $dp/dt$  method, which was described above for the case of NO<sub>2</sub>. The concentration of NO was in the range  $(1 \text{ to } 8) \times 10^{14}$  molecule cm<sup>-3</sup>. The initial ozone concentration was calculated using its absorption spectrum measured using the diode array spectrometer and the known absorption cross section at 253.7 nm. In some experiments, the concentration of NO was held constant while varying the



**Figure 2.** UV absorption spectra of NO<sub>2</sub> (solid line) and N<sub>2</sub>O<sub>4</sub> (dashed line) over the range used by the diode array spectrometer. The arrow indicates the location of the NO<sub>2</sub> feature used in the cross section determinations (see text for details).

concentration of O<sub>3</sub> that was added to change the NO<sub>2</sub> concentration. In most experiments, the concentration of NO was varied along with that of O<sub>3</sub> to ensure that all the ozone reacted and, yet, had the minimum amount of NO left over. At low O<sub>3</sub> concentrations, NO<sub>2</sub> formed upon addition of NO could not be measured by absorption because its absorption cross section is low, approximately a factor of 20 lower than that of ozone. In these cases, total conversion of O<sub>3</sub> to NO<sub>2</sub> was assumed. The concentration of N<sub>2</sub>O<sub>3</sub> was calculated, on the basis of the known equilibrium constants,<sup>3</sup> to be always less than 0.6% of the NO<sub>2</sub> concentration. Only for the measurements at 220 K were the corrections for N<sub>2</sub>O<sub>4</sub> significant, i.e., 4% at the highest NO<sub>2</sub> concentration used.

The accuracy of this [NO<sub>2</sub>] determination method is estimated to be  $\sim 5\%$ . This estimate is determined from the uncertainty in the O<sub>3</sub> absorption cross sections,  $\pm 2\%$ , and the precision of the absorption measurements,  $\pm 3\%$ .

**NO<sub>2</sub> UV Absorption.** In this method the concentration of NO<sub>2</sub> was measured by UV–visible absorption. The collimated output of a 30 W D<sub>2</sub> lamp was passed through the cell (see Figure 1) and was focused onto the entrance slit of a spectrograph with a 1024 element diode array detector. The combined path through the metal reactor and the Pyrex extension was 42.1 cm. A 100  $\mu\text{m}$  entrance slit, resolution of  $\sim 1$  nm, was used for all absorption measurements. The wavelength of the spectrometer was calibrated using a Hg pen ray lamp and a 10  $\mu\text{m}$  entrance slit. The NO<sub>2</sub> spectrum was recorded between 280 and 420 nm. A spectrum of NO<sub>2</sub> in this wavelength region is shown in Figure 2. The prominent absorption feature at 413.4 nm was chosen for NO<sub>2</sub> concentration quantification. At this wavelength, the contribution of N<sub>2</sub>O<sub>4</sub>, if present, would be minimal (see Figure 2) and the NO<sub>2</sub> cross section is near its maximum value. The NO<sub>2</sub> spectrum contains diffuse structure at this resolution and the cross sections depend on both temperature and resolution.

NO<sub>2</sub> absorption cross sections have been previously measured<sup>3</sup> and recently remeasured in several laboratories<sup>1,13,14</sup> using

spectrometers with different resolutions. Harder et al.<sup>1</sup> have provided high-resolution measurements at 216, 230, 238, and 293 K. Cross sections at lower resolution were calculated from these measurements. However, there is limited cross section data available at temperatures above 298 K. Therefore, we measured NO<sub>2</sub> cross sections over the temperature range 259–385 K using the same spectrograph used in the kinetic measurements, i.e., the same resolution. The measurements of Harder et al. were used to confirm our low-temperature measurement and help establish an empirical relationship between the cross section and temperature.

The NO<sub>2</sub> cross sections were determined using known concentrations of NO<sub>2</sub> generated by the titration reaction 11 as described above. The absorption cross section for NO<sub>2</sub> at 308 nm is  $\sim 2 \times 10^{-19}$  cm<sup>2</sup> molecule<sup>-1</sup> (see Figure 1).

**Material.** NO<sub>2</sub> was prepared by reacting purified NO with excess O<sub>2</sub> which had been passed through a molecular sieve trap at dry ice temperature. NO<sub>2</sub> was collected in a dry ice cooled trap and purified by trap-to-trap distillation in an excess O<sub>2</sub> flow until a pure white solid remained. The major impurities (<0.1%) in our sample of NO<sub>2</sub> are NO and O<sub>2</sub>, whose reactions with O atoms are slow compared to reaction 1. Because  $k_1$  is so large, impurities do not contribute significantly to its measured value, unless the impurity levels reach a few percent. NO (C. P. Grade) was purified by passage through the silica gel trap at dry ice temperature. N<sub>2</sub> (UHP, 99.9995%) was used as the carrier gas in all experiments and was used as supplied.

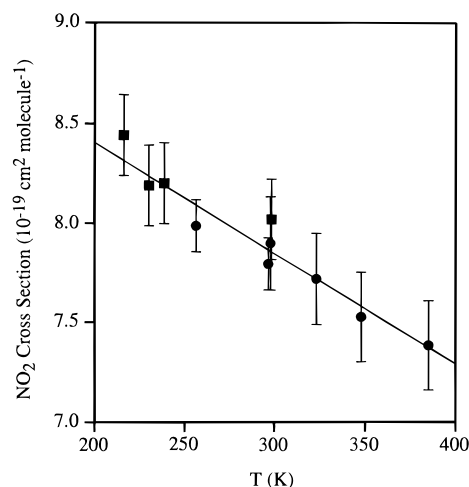
## Results and Discussion

**NO<sub>2</sub> Cross-Section Measurements.** UV–visible absorption cross sections of NO<sub>2</sub> were determined at five temperatures: 385, 348, 323, 298, and 259 K. Absorbances at 4–6 different NO<sub>2</sub> concentrations were measured at each temperature. Beer's law was obeyed at all temperatures. The cross-section values at 413.4 nm, in units of 10<sup>-19</sup> cm<sup>2</sup>, determined are  $7.39 \pm 0.07$  (385 K),  $7.53 \pm 0.04$  (348 K),  $7.72 \pm 0.04$  (323 K),  $7.90 \pm 0.06$  (298 K), and  $7.79 \pm 0.11$  (259 K). The quoted errors are two standard deviations of the slopes of the absorbance vs concentration plots as determined by linear least-squares analyses. The absolute uncertainty in the cross-section values is estimated to be 3% from the measurements in which both O<sub>3</sub> and NO<sub>2</sub> were measured simultaneously. Our room temperature cross section at 413.4 nm is  $\sim 2\%$  lower than that obtained from Harder et al.<sup>1</sup> and  $\sim 4\%$  lower than that reported by Vandaele et al.<sup>14</sup> The cross sections measured here and those of Harder et al. at 413.4 nm are shown in Figure 3. The agreement between the two sets of measurements is exceptionally good. Our NO<sub>2</sub> cross sections are tied to the cross sections of ozone, which is known to very high accuracy (within 2%)<sup>3</sup>. Thus, normalizing other NO<sub>2</sub> spectra to our cross sections, after properly accounting for differences in resolution, would be reasonable. For a critical evaluation of previous NO<sub>2</sub> cross-section determinations readers are referred to Harder et al.<sup>1</sup>

A weighted linear least-squares fit to the cross sections at 413.4 nm measured by Harder et al. and us yields

$$\sigma_{413.4}(T) = (9.49 - 0.00549T) \times 10^{-19} \text{ cm}^2 \quad (11)$$

This relationship was used to calculate the NO<sub>2</sub> cross sections at the temperatures used in the kinetic measurements. The cross section at 413.4 nm was also used to normalize the diode array spectra. On the basis of our measurements and comparison with previous reports, we believe that the absorption cross section of NO<sub>2</sub> at 413.4 nm is known to better than 5% and, hence, our



**Figure 3.** NO<sub>2</sub> UV absorption cross section at 413.4 nm as a function of temperature as determined using methods described in the text. This work (solid circles). Harder et al.<sup>1</sup> (solid squares, after resolution correction). The solid line is the weighted (according to the precision of the measured values) least-squares fit to all the data yielding  $\sigma_{413.4}(T) = (9.49 - 0.00549T) \times 10^{-19}$  cm<sup>2</sup> molecule<sup>-1</sup>.

measured concentration of NO<sub>2</sub> in the reactor could have no more than a 5% uncertainty due to its cross section.

**Kinetic Measurements.** Rate coefficients for reaction 1 were measured at 15 temperatures over the range 220 to 412 K. The results of these measurements are listed in Table 1 and are plotted in Figure 4. A least-squares fit of the data ( $\ln k_1$  vs  $1/T$ ) yielded  $k_1(T) = (5.26 \pm 0.27) \times 10^{-12} \exp[(209 \pm 15)/T]$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, where the quoted errors represent  $2\sigma$  precision of the fit and  $\sigma_A = A\sigma_{\ln A}$ . The 298 K rate coefficient derived from this fit is  $10.6 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, and it agrees with that measured at this temperature; therefore, we quote our 298 K value to be  $k_1(298 \text{ K}) = (10.6 \pm 0.8) \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (Table 2).

Several experimental checks were conducted to ensure that the measured rate coefficients did not depend systematically on the experimental conditions. In three room temperature experiments, the initial (photolytically produced) oxygen atom concentration was varied by a factor of 20. The rate coefficients determined in these measurements agreed to within 8%, well within the estimated accuracy of our measurements.

The pressure was varied between 15 and 105 Torr in two room temperature experiments. This tested for possible interference from the third body reaction



where  $k_{12}(15 \text{ Torr}, 298 \text{ K}) \sim 4 \times 10^{-14}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and  $k_{12}(105 \text{ Torr}, 298 \text{ K}) = 2.7 \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.<sup>3</sup> Higher pressures were used only at 298 K and above to test for secondary reactions. Under the low-pressure conditions used here ( $\sim 15$  Torr), reaction 12 makes a negligible contribution (<1%) to the O(<sup>3</sup>P) decay even at 220 K, where  $k_{12}(15 \text{ Torr}, 220 \text{ K}) \sim 1 \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. Our measured values of  $k_1$  at 15 and 105 Torr total pressure at 298 K agree within the measurement uncertainties (see Table 1). A single elevated pressure measurement, 103 Torr, was also performed at 393 K. The value of  $k_1$  determined under these conditions agreed very well with the value calculated from our Arrhenius fit. These results confirm that reaction 13 was not significant under our conditions.

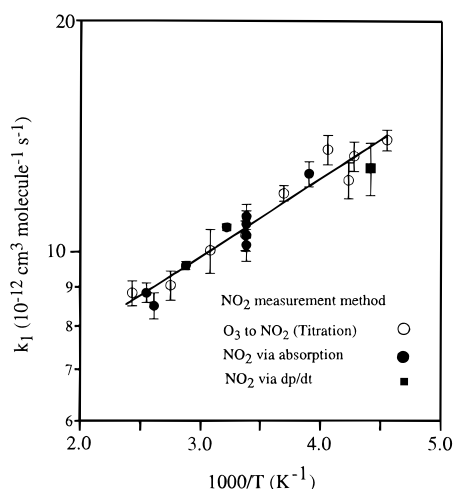
The methods used for the determination of NO<sub>2</sub> concentration are given in Table 1. In most experiments where the chemical



**TABLE 1: Experimental Conditions and Measured Rate Coefficients for O(<sup>3</sup>P) + NO<sub>2</sub> → NO + O<sub>2</sub> (*k*<sub>1</sub>)**

| <i>T</i> (K) | [NO <sub>2</sub> ] method <sup>a</sup> | [O] × 10 <sup>-11</sup> atom cm <sup>-3</sup> | [NO <sub>2</sub> ] × 10 <sup>-14</sup> molecule cm <sup>-3</sup> | <i>P</i> (Torr) | <i>k</i> × 10 <sup>12</sup> cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> |
|--------------|----------------------------------------|-----------------------------------------------|------------------------------------------------------------------|-----------------|------------------------------------------------------------------------------------|
| 412          | O <sub>3</sub> + NO                    | 0.4–2.9                                       | 0.15–1.0                                                         | 15              | 9.09 ± 0.2                                                                         |
| 393          | abs                                    | 1.3–12.7                                      | 3.9–37.7                                                         | 103             | 9.24 ± 0.3                                                                         |
| 383          | abs                                    | 4.4–37.2                                      | 2.0–16.7                                                         | 15              | 8.57 ± 0.15                                                                        |
| 364          | O <sub>3</sub> + NO                    | 0.3–3.5                                       | 0.1–1.2                                                          | 15              | 8.96 ± 0.2                                                                         |
| 348          | abs                                    | 4.5–35.9                                      | 2.0–16.2                                                         | 15              | 9.39 ± 0.12                                                                        |
| 325          | O <sub>3</sub> + NO                    | 0.2–1.8                                       | 0.08–0.6                                                         | 15              | 9.60 ± 0.32                                                                        |
| 311          | abs                                    | 0.8–12.5                                      | 2.4–36.9                                                         | 15              | 10.8 ± 0.5                                                                         |
| 297          | O <sub>3</sub> + NO                    | 10–32.2                                       | 4.6–12.3                                                         | 101             | 10.3 ± 0.2                                                                         |
| 296          | abs                                    | 0.4–3.7                                       | 3.1–32.6                                                         | 15              | 11.0 ± 0.2                                                                         |
| 296          | abs                                    | 1.7–28.7                                      | 1.9–32.5                                                         | 105             | 11.0 ± 0.3                                                                         |
| 296          | abs                                    | 7.6–74.3                                      | 4.0–39.2                                                         | 15              | 10.2 ± 0.3                                                                         |
| 296          | dp/dt                                  | 0.4–4.6                                       | 0.1–1.1                                                          | 15              | 10.5 ± 0.5                                                                         |
| 298          |                                        | average                                       |                                                                  |                 | 10.7 ± 0.8 <sup>b</sup>                                                            |
| 271          | O <sub>3</sub> + NO/abs                | 1.9–18.9                                      | 2.2–21.7                                                         | 15              | 11.6 ± 0.2                                                                         |
| 256.5        | abs                                    | 1.0–7.6                                       | 4.4–33.9                                                         | 15              | 12.6 ± 0.2                                                                         |
| 247          | O <sub>3</sub> + NO                    | 0.6–2.2                                       | 0.2–0.8                                                          | 15              | 12.4 ± 0.8                                                                         |
| 236.5        | O <sub>3</sub> + NO                    | 0.3–3.0                                       | 0.1–1.0                                                          | 15              | 12.6 ± 0.3                                                                         |
| 234          | O <sub>3</sub> + NO                    | 0.2–2.1                                       | 0.06–0.8                                                         | 15              | 12.7 ± 0.5                                                                         |
| 227          | dp/dt                                  | 0.6–2.2                                       | 0.2–0.8                                                          | 15              | 12.4 ± 0.05                                                                        |
| 220          | O <sub>3</sub> + NO                    | 0.1–2.0                                       | 0.04–0.6                                                         | 15              | 13.7 ± 0.52                                                                        |

<sup>a</sup> O<sub>3</sub> + NO indicates that the NO<sub>2</sub> concentration was measured by converting a measured amount of ozone to NO<sub>2</sub> via reaction with NO. abs indicates that NO<sub>2</sub> was measured via UV absorption at 413.4 nm. dp/dt indicates the NO<sub>2</sub> concentration was measured by determining the time rate of change of pressure in a known volume as NO<sub>2</sub> was flowed into it. (See text for details.) <sup>b</sup> The value was obtained by correcting the values measured close to 298 K for the difference in temperature using the *E*/*R* measured here and averaging them. The quoted uncertainty is 2σ of the average.



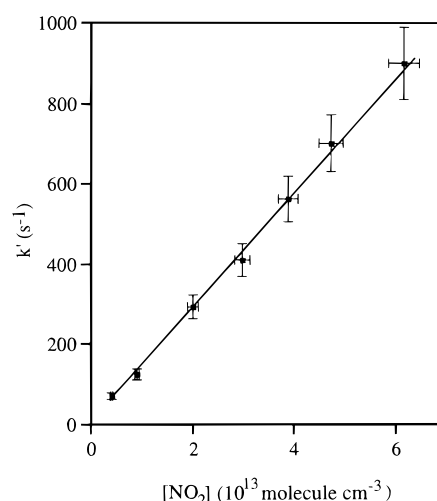
**Figure 4.** The temperature dependence of the rate coefficient for O(<sup>3</sup>P) + NO<sub>2</sub> → NO + O<sub>2</sub> (*k*<sub>1</sub>) measured in this work. The solid line is the weighted (according to the precision of the measured rate constants) least-squares fit.

titration method was used, the NO concentration was only in slight excess to limit contributions to the O(<sup>3</sup>P) atom decay from the reaction



where *k*<sub>6</sub> ~ 4 × 10<sup>-14</sup> at 298 K and 15 Torr.<sup>3</sup> The measured pseudo-first-order rates were corrected for reaction 6 using the measured NO concentration. The corrections ranged from 50 to 130 s<sup>-1</sup>, which are small (less than 3%) compared to the first-order loss rate constants due to reaction 1. When a constant concentration of NO was used, the contribution to measured *k'* was an intercept in the *k'* vs [NO<sub>2</sub>] concentration plots.

Geers-Muller and Stuhl<sup>8</sup> have estimated upper limits for the rate coefficients for the reactions



**Figure 5.** Plot of *k'* versus [NO<sub>2</sub>] at 220 K. The NO<sub>2</sub> concentration has been corrected for the formation of N<sub>2</sub>O<sub>4</sub> and contributions to the O atom loss due to the O + NO reaction. The solid line is a weighted (according to the precision of the measured *k'*) least-squares fit to the data yielding a rate coefficient for reaction 1 of 13.7 × 10<sup>-12</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

and



at 199 K to be *k*<sub>13</sub> < 2 × 10<sup>-12</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and *k*<sub>14</sub> < 4.5 × 10<sup>-13</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, respectively. Hence, the contributions to the measured O atoms decay rate constants of reactions 13 and 14 are at least 7 and 30 times smaller than the contribution from reaction 1 at 199 K. At warmer temperatures, they are negligibly small. Therefore, reaction 13 and 14 should not significantly influence the measurement of *k*<sub>1</sub>. However, in experiments at temperatures below 230 K where the NO<sub>2</sub> concentration was deduced from flows and chemical titration rather than measured by UV absorption, we corrected the NO<sub>2</sub> concentration for the formation of N<sub>2</sub>O<sub>4</sub>. Figure 5 shows a plot of *k'* vs [NO<sub>2</sub>] at 220 K, where the deduced [NO<sub>2</sub>] was corrected

**TABLE 2: Summary of Rate Coefficient Measurements for  $O(^3P) + NO_2 \rightarrow NO + O_2$  ( $k_1$ )**

| $k(298\text{ K})^a$ | $A^a$           | $-E/R$ (K)    | $T$ Range (K) | experimental technique <sup>b</sup> | ref               |
|---------------------|-----------------|---------------|---------------|-------------------------------------|-------------------|
| $9.12 \pm 0.46$     | $8.70 \pm 0.65$ | $13 \pm 21$   | 230–339       | FP–RF                               | 4                 |
| $9.5 \pm 1.1$       | $3.72 \pm 0.30$ | $267 \pm 30$  | 298–1055      | DF–RF/MS                            | 6                 |
| $9.3 \pm 1.4^c$     | 5.53            | 154           | 240–296       | FP–CL                               | 5                 |
| $10.3 \pm 0.9$      | $6.58 \pm 0.52$ | $142 \pm 23$  | 224–354       | DF–CL                               | 7                 |
| $10.3 \pm 0.2^d$    | $5.21 \pm 0.50$ | $202 \pm 27$  | 233–357       | FP–CL                               | 8                 |
| $9.7^e$             | 6.5             | $120 \pm 120$ |               |                                     | 2,3               |
| $10.6 \pm 0.8$      | $5.26 \pm 0.6$  | $209 \pm 35$  | 220–412       | PP–RF                               | this work         |
| $10.6^e$            | 5.22            | $210 \pm 30$  |               |                                     | rec. <sup>f</sup> |

<sup>a</sup> Units are  $10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. <sup>b</sup> FP: flash photolysis. DF: discharge flow. RF: resonance fluorescence. MS: mass spectrometry. CL: chemical luminescence. PP: pulse photolysis. <sup>c</sup>  $k(296\text{ K})$ . <sup>d</sup> Calculated from value measured at 301 K using  $E/R = -202\text{ K}^{-1}$ . <sup>e</sup> Uncertainty of  $f(298) = 1.1$ . Uncertainties at other temperatures are calculated using  $f(T) = f(298) \exp[\Delta E/R\{(1/T) - (1/298)\}]$ . <sup>f</sup> Recommended based on results of this study and refs 7 and 8.

for the formation of  $N_2O_4$  using the equilibrium constant.<sup>3</sup> These corrections were small and amounted to a change in rate constant of  $\sim 7\%$ . Therefore, even if the equilibrium constant were somewhat uncertain, the rate coefficients would not change much.

The fits of  $k'$  vs  $[NO_2]$ , and hence the obtained values of  $k_1$ , were precise. However, this is not a true representation of the reproducibility between measurements. The expression for  $k_1$  given above does include, to a first approximation, the systematic errors in the  $NO_2$  concentration measurements because multiple methods were used. Yet, we include other estimated systematic errors, derived for each  $NO_2$  concentration method, and suggest the following expression for  $k_1$  as a function of temperature:

$$k_1(T) = (5.26 \pm 0.60) \times 10^{-12} \times \exp[(209 \pm 35)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

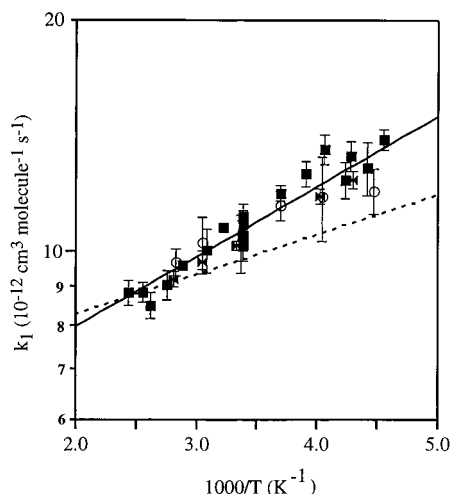
There are a number of relatively recent kinetic studies<sup>4–8</sup> of reaction 1 with which to compare and contrast our results. An overview of our results and those from previous works is given in Table 2. The recent report of  $k_1(298\text{ K}) = (9.3 \pm 1.0) \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> reported by Paulson et al.<sup>15</sup> is not included in the table. Davis et al.<sup>4</sup> studied reaction 1 using broadband flash photolysis of  $NO_2$  to produce O atoms and vacuum UV resonance fluorescence to detect them. They measured  $k_1$  over the temperature range 230 to 339 K. The range of  $NO_2$  concentrations used was sufficiently low that corrections for  $N_2O_4$  were small even at the lowest temperatures used. They determined the  $NO_2$  concentrations using manometrically prepared gas mixtures in Ar,  $N_2$ ,  $O_2$ , and  $CO_2$  used as the buffer gas. (Their stock mixtures necessarily had much higher concentrations of  $NO_2$  than those present in the reactor.) The details of the mixture preparation methods was not provided (i.e., the corrections for  $N_2O_4$  in the stock mixture are not known and could have led to small overestimation of  $NO_2$  and, hence, the lower values of  $k_1$ ). They report  $k_1 = (9.12 \pm 0.44) \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> independent of temperature. The quoted error limit is  $1\sigma$  of the measurement precision and does not include possible systematic errors. This value is about 10% smaller than our room temperature value but within the combined  $2\sigma$  uncertainty limits. The experimental technique used by Davis et al. was similar to that used in our work, but with a few significant differences. In our experiments the gas mixture was flowed through the reactor, a laser was used to photolyze  $NO_2$  at a single wavelength, the mixture was exposed to at most two photolysis pulses, and  $NO_2$  was directly measured in the reactor in most cases. Davis et al. used a static mixture, broadband photolysis, and exposure of the mixture to multiple photolysis pulses, and deduced the concentration of  $NO_2$  using

manometrically prepared stock mixtures. Considering these differences the agreement with our results is surprisingly good. Due to the limitations in the precision of their measurements the weak temperature dependence of  $k_1$  eluded their detection. It is very important to note that Davis et al.'s experiments were excellent for that period, and we have learned much since then as to how to handle gases such as  $NO_2$ .

Bemand et al.<sup>6</sup> studied reaction 1 under pseudo-first-order conditions using a discharge flow tube and detected O atoms via resonance fluorescence (in an excess of  $NO_2$ ) and  $NO_2$  via mass spectrometry (in excess of O atoms) to determine  $k_1$  at sixteen temperatures between 298 and 1055 K. In experiments with  $NO_2$  in excess, the  $NO_2$  concentration was varied over the range  $(0.4\text{--}4) \times 10^{13}$  molecule cm<sup>-3</sup>.  $NO_2$  concentrations were determined using flow measurements. Under these conditions,  $N_2O_4$  formation was negligible. In experiments with O(<sup>3</sup>P) atoms in excess, the O(<sup>3</sup>P) atom concentration was varied over the range  $(4\text{ to }26) \times 10^{12}$  atom cm<sup>-3</sup>. The rate coefficient data measured at each temperature shows considerable scatter with values differing by as much as 50%. Fitting the data given in their Table 1 (weighting the 298 K value by a factor of 20, the number of 298 K values measured by them) yields  $k_1(T) = (3.68 \pm 1.0) \times 10^{-12} \exp[(274 \pm 80)/T]$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>,  $k_1(298) = 9.3 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, where the error limits are  $1\sigma$  precision of the fit. This fit yields values of  $k_1$  which are systematically lower than our measurements,  $\sim 6\%$ , over our temperature range. However, these differences are small compared to the accuracy of the measurements reported by Bemand et al. Also, the possibility of thermal decomposition of  $NO_2$  in their system at high temperatures could have led to the higher negative temperature dependence that they reported.

Slinger et al.<sup>5</sup> measured  $k_1$  using pulsed photolysis of  $O_2$  at 147 nm to generate O(<sup>3</sup>P) atoms in the presence of excess  $NO_2$ . O(<sup>3</sup>P) atoms were detected by reacting it with NO and measuring the chemiluminescence from the  $NO_2$  product.  $NO_2$  concentrations in the range  $(0.6\text{--}6) \times 10^{13}$  molecule cm<sup>-3</sup> were used.  $NO_2$  concentrations were determined by UV absorption of a  $NO_2/N_2$  mixture prior to being diluted in the reaction gas mixture. Small corrections were applied to account for  $N_2O_4$  formation. Measurements were made at 296 and 240 K yielding  $k_1$  values of  $(9.3 \pm 1.4) \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and  $(10.5 \pm 1.6) \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, respectively. These results indicate a small negative temperature dependence and are systematically less than our results but are within the combined uncertainties of the two data sets.

Ongstad and Birks<sup>7</sup> used a discharge flow tube reactor and also detected O atoms by the chemiluminescence method. They measured  $k_1$  at six temperatures in the range 224 to 354 K at 2.5 Torr total pressure. Their  $NO_2$  concentrations were calculated from measured flow rates of manometrically prepared gas



**Figure 6.** Comparison of recent reaction 1 rate coefficient measurements and current value recommended for stratospheric model calculations (dashed line). The heavy solid line is a weighted least-squares fit to the data from this work (solid squares) and that of Ongstad and Birks<sup>7</sup> (open circles) and Geers-Muller and Stuhl<sup>8</sup> (solid bow tie) yielding a value of  $k_1(T) = (5.22 \pm 0.50) \times 10^{-12} \exp[(210 \pm 30)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

mixtures. NO<sub>2</sub> concentrations were varied over the range  $(1-10) \times 10^{12} \text{ molecule cm}^{-3}$ . These low NO<sub>2</sub> concentrations made corrections for N<sub>2</sub>O<sub>4</sub> formation negligible at all temperatures. They report  $k_1(T) = (6.58 \pm 0.52) \times 10^{-12} \exp[(142 \pm 23)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,  $k_1(298) = 1.06 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , where the error limits are  $1\sigma$  and represent the precision of the measurements only. Their room temperature value is in excellent agreement with the present results while the temperature dependence,  $E/R$ , is smaller but lies within the combined  $2\sigma$  uncertainty limits.

Geers-Muller and Stuhl<sup>8</sup> used pulsed H<sub>2</sub> laser ( $\sim 160 \text{ nm}$ ) photolysis of NO to produce O(<sup>3</sup>P) atoms in the presence of NO<sub>2</sub>. They measured the temporal profile of O(<sup>3</sup>P) using the chemiluminescence method noted above and obtained  $k_1$  at five temperatures over the range 233–357 K using NO<sub>2</sub> concentrations in the range  $(0.5-4) \times 10^{14} \text{ molecule cm}^{-3}$ . NO<sub>2</sub> concentrations were calculated using mass flow rates measured with calibrated flow controllers. Corrections to the NO<sub>2</sub> concentration due to N<sub>2</sub>O<sub>4</sub> formation were less than 4% under these conditions. The addition of NO,  $8 \times 10^{15} \text{ molecule cm}^{-3}$ , in the detection region led to the formation of N<sub>2</sub>O<sub>3</sub> via



However, corrections to the NO<sub>2</sub> concentration were less than 1.4% under these conditions. They report  $k_1(T) = (5.21 \pm 0.50) \times 10^{-12} \exp[(202 \pm 27)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,  $k_1(298) = 1.03 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , where the quoted error limits are  $3\sigma$  and include estimated systematic errors. This value is in excellent agreement with our results with  $k_1$  at 233 K only 5% less than the value derived from the present results.

From the above description, it is clear that there are reasons to suspect that the data of Davis et al. may not be highly accurate, especially at low temperatures. The data of Ongstad and Birks and of Geers-Muller and Stuhl are quite accurate. Figure 6 shows a plot of the data obtained by these two groups, along with those from our study. The data from these three studies were fit to the Arrhenius expression using an unweighted linear least squares routine ( $\ln k_1$  vs  $1/T$ ) to obtain:

$$k_1(T) = (5.22 \pm 0.50) \times 10^{-12} \times \exp[(210 \pm 26)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

where the errors are  $2\sigma$  of the fit and  $\sigma_A = A \sigma_{\ln A}$ . The fit is also shown in the figure. This expression may be used for modeling studies. It should be noted that this lies beyond the  $1\sigma$  error bounds indicated by 1997-NASA/JPL evaluation. The numbers that can be used for modeling studies are listed in the last row of Table 2.

**Atmospheric implications.** The rate coefficient obtained in this study is approximately 20–30% higher than that derived in the current kinetic evaluations at stratospheric temperatures.<sup>3</sup> Given that reaction 1 is the rate-limiting step in the major NO<sub>x</sub> catalyzed ozone destruction cycle (see Introduction), this change in the rate coefficient will have a significant impact on the calculated stratospheric ozone abundance. Further, increases in  $k_1$  will alter the calculated ozone depletion due to chlorine and the impact of aircraft emissions on ozone levels. We have discussed some these consequences in a separate paper<sup>16</sup> which reexamines the role of NO<sub>x</sub> in the stratosphere in light of the changes in the rate coefficients for the reactions of OH with HNO<sub>3</sub> ref 17 and NO<sub>2</sub> (ref 18) as well as  $k_1$ .

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