

# Measurements of the 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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## Abstract

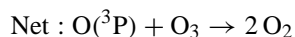
Measurements of the absolute rate coefficient for the reaction  $\text{O}(^3\text{P}) + \text{NO}_2 \rightarrow \text{NO} + \text{O}_2$  were made by the discharge-flow resonance fluorescence technique over the temperature range 216–413 K at pressures between 1 and 2.5 Torr. The measured rate coefficients for atmospherically relevant temperatures can be expressed in Arrhenius form as  $k(T) = (5.64 \pm 0.12) \times 10^{-12} \exp[(165 \pm 10)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , where the quoted uncertainties are  $2\sigma$  precision. This result is compared with previous measurements of the rate coefficient and implications for the importance of this reaction in the middle atmosphere are discussed.

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## 1. Introduction

Nitrogen oxides ( $\text{NO}_x$ ), including nitric oxide (NO) and nitrogen dioxide ( $\text{NO}_2$ ), play key roles in the chemistry of both tropospheric and stratospheric ozone. Nitrogen oxides are ingredients in the production of ozone in the troposphere, but contribute to the destruction of ozone in the stratosphere. When Johnston [1] proposed that direct injection of nitrogen oxides into the stratospheric ozone layer by supersonic transport aircraft (SSTs) could have disastrous consequences, the study of the kinetics of nitrogen oxide reactions was propelled to the forefront. In particular, calculating the rate of catalytic ozone destruction by the reaction sequence



has been of considerable interest for more than three decades. Because ozone destruction by nitrogen oxides is the dominant ozone loss mechanism throughout the middle stratosphere (about 25–40 km in the middle latitudes) [2], an accurate knowledge of the rates of reactions 1 and 2 is essential to understanding ozone balance.

The earliest kinetic studies of the rate coefficient for the reaction of oxygen atoms with nitrogen dioxide focussed on

measurements at or above room temperatures. There was considerable scatter in these observations, so that the positive temperature dependence deduced from them was given a large uncertainty. Measurements of the rate coefficient of reaction 1,  $k_1$ , made at the height of the supersonic aircraft controversy [3,4] encompassed temperatures characteristic of the stratosphere and found either no apparent temperature dependence [3] or a weak negative dependence [4]. These results were, however, in excellent agreement with one another at room temperature.

Although the supersonic aircraft controversy faded, it, and the discovery of the antarctic “ozone hole”, promoted continued study of reactions of importance to stratospheric ozone balance. Four subsequent laboratory measurements [5–8] of  $k_1$  have better defined both the room-temperature rate and the temperature-dependence, now known to display a negative activation energy of about  $1.5\text{--}2 \text{ kJ mol}^{-1}$ . Assessments of these studies suggest that the rate is uncertain by 25–35% over the temperature range characteristic of the middle stratosphere (220–250 K) [9].

Given that the uncertainties in any individual determination of a rate coefficient are rarely less than 15%, why should we continue to try to improve our understanding of a process such as reaction 1? This reaction, in particular, is of critical importance to calculations of ozone abundances in the middle stratosphere. Sensitivity studies have shown that uncertainties in reaction 1 are among the top 10 most significant sources of uncertainty in calculations of ozone loss rates in the background atmosphere [10] and under

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perturbed conditions resulting from a fleet of high-speed civilian transports (HSCTs, the SSTs of the 1990s) [11]. Although it seems unlikely that a fleet of HSCTs will be developed in the near future, the aircraft industry is pursuing the so-called “sonic cruiser” concept—an aircraft that flies just under the speed of sound (Mach 0.98) at altitudes in excess of 13 km. Over much of the globe, these altitudes will be in the lowermost stratosphere, so the nitrogen oxides deposited there could directly impact the ozone layer.

The two most recent studies of the  $O + NO_2$  reaction [7,8] both employed laser-photolysis techniques for generation of oxygen atoms, followed by resonance fluorescence detection. The use of a different experimental technique, especially one that employs significantly lower concentrations of reactants (as much as 10–100 times lower in this case) to limit the impact of secondary chemistry, provides an important constraint on how well the rate coefficient  $k_1$  is known. Here, I report measurements of the temperature-dependence of the rate coefficient of reaction 1 over the temperature range 216 to 413 K using the discharge-flow method with resonance fluorescence detection of  $O(^3P)$  atoms. As in the two most recent studies, special emphasis was placed on obtaining precise and accurate measurements of  $k_1$  at stratospheric temperatures, where there is still a large uncertainty and significant disagreement among the various published results. The results of this work are compared with previously published measurements and with current recommendations for atmospheric modeling.

## 2. Experimental methods

The measurements of the rate coefficient for the reaction between oxygen atoms and nitrogen dioxide reported here were obtained using the discharge-flow method with resonance fluorescence detection of oxygen atoms. The discharge-flow system has been described in detail elsewhere [12,13], so only a brief summary is given here. The reactor is composed of two sections of Pyrex separated by a laser magnetic resonance (LMR) detection axis not used for this study. Circulating heated or cooled fluids through an outer jacket thermally regulates the upstream section of this reactor, which is 70 cm long and 2.5 cm in diameter (i.d.). The downstream section, which is 30 cm long and 2.5 cm in diameter (i.d.), passes through the resonance fluorescence detection block, which houses three separate detection axes. All reactor surfaces are coated with Teflon.

Oxygen atoms were generated by microwave discharge of trace  $O_2$  (HP, 99.994%) in helium (UHP, 99.999%) in an uncoated quartz side-arm located 35 cm upstream of the detection region. The resonance fluorescence detection system for O has been described previously [13]. The light source for this experiment was a sealed low-pressure helium-discharge lamp with a  $MgF_2$  window that contained  $KMnO_4$  as an oxygen atom source and barium as a getter for gas-phase

impurities. The resonance fluorescence emission from oxygen atoms (a triplet at 130.4 nm) was collected by a photomultiplier with CsI photocathode set at a right angle to the lamp. A photodiode positioned across the detection volume from the lamp was used to monitor changes in lamp intensity, which were always less than 0.5% over the course of a kinetics run.

The oxygen atom detection system was calibrated using the titration reaction  $N + NO \rightarrow N_2 + O$ , in excess N. Nitrogen atoms were produced by microwave discharge of nitrogen (UHP, 99.999%) and the concentration of the limiting reagent, NO, was determined from the flow rate of a mixture of 2.5% NO in UHP helium. This detection axis had a sensitivity of  $5.5 \times 10^{-8} \text{ cm}^3 \text{ atom}^{-1} \text{ s}^{-1}$ ; with a typical background of 3–5  $\text{cts s}^{-1}$ , the O atom detection limit was about  $1.8 \times 10^7 \text{ cm}^{-3}$  for a 10 s integration. Oxygen atom signals reported here are typically averages of at least 30 s, so the corresponding detection limit is even lower than given above. The detection limit in this experiment is smaller by at least a factor of 10 than that of other recent studies [7].

Known flows of the excess reagent  $NO_2$  were obtained by measuring the pressure drop ( $dp/dt$ ) out of a reservoir of known volume. The  $NO_2$  mixtures were made either by combining NO (Matheson, CP, 99.0%), purified with a molecular sieve trap, with  $O_2$ , (UHP, 99.999%) to make  $NO_2$  via the reaction  $NO + NO + O_2 \rightarrow 2NO_2$ , or by diluting  $NO_2$  (Matheson, 99.5%) with helium (UHP, 99.999%). The pressure of the mixture was measured with a calibrated MKS Baratron capacitance manometer. The accuracy to which the mixture fraction is known is estimated to be better than  $\pm 3\%$ . The  $NO_2$  mixture was introduced to the flow system through a movable injector and O atom decays were monitored as a function of the  $NO_2$  injector distance from the fixed detection axis.

All kinetics experiments were conducted under pseudo-first-order conditions with  $NO_2$  in large excess over oxygen atoms. The conditions employed are summarized in Table 1. Temperatures were measured with iron-constantan thermocouples placed within both the circulating fluid and the flow reactor. These thermocouples were calibrated against a mercury thermometer and were accurate to  $\pm 1^\circ\text{C}$ . Temperature gradients along the flow system were not monitored in this experiment, but have been shown in previous work to be small. Pressure was measured with an MKS Baratron capacitance manometer calibrated against a mercury manometer and was accurate to  $\pm 0.1$  Torr.

Table 1  
Summary of conditions

Pressure range (Torr)	1.0–2.2
Flow velocity ( $\text{cm s}^{-1}$ )	800–1350
Excess reactant ( $\text{molecules cm}^{-3}$ )	$[NO_2] = (0.06\text{--}3.5) \times 10^{13}$
Initial O concentrations ( $\text{atoms cm}^{-3}$ )	$< 8 \times 10^{10}$
Stoichiometric ratio	7.5–600
Observed wall removal rates ( $\text{s}^{-1}$ )	$< 5$
O diffusion coefficient ( $\text{cm}^2 \text{ s}^{-1}$ )	0.135

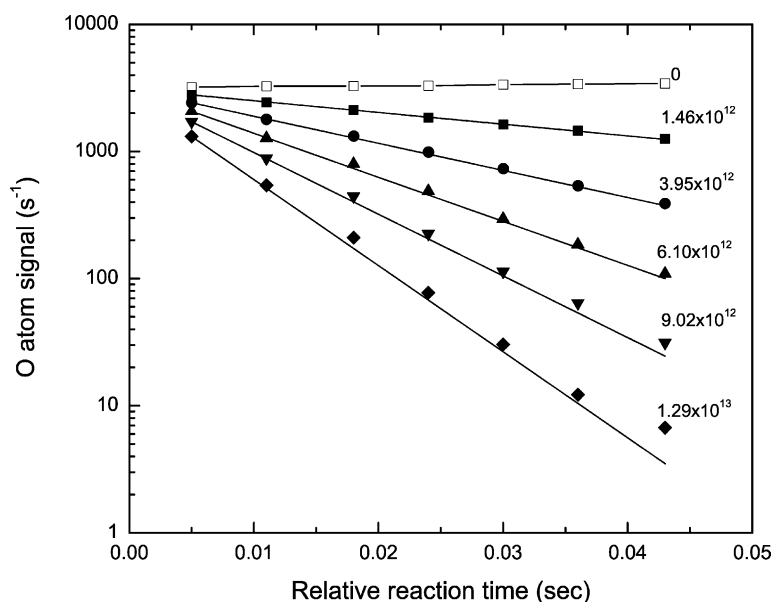


Fig. 1. Series of oxygen atom decays for kinetics measurements obtained at 239 K. Values listed at the end of each decay indicate the concentration of the excess reagent,  $\text{NO}_2$ , in molecules  $\text{cm}^{-3}$ . “Reaction time” denotes the amount of time elapsed between the addition of  $\text{NO}_2$  and detection of oxygen atoms at the resonance fluorescence axis.

### 3. Results

Fig. 1 shows a series of oxygen atom decays from experiments performed at 239 K. A small loss of oxygen atoms on the exterior surface of the movable injector used to add the excess reagent was observed with no  $\text{NO}_2$  present. This so-called “probe loss” is evident in the positive slope of the first decay (open squares, labeled “0”). The probe loss was always less than  $5 \text{ s}^{-1}$ . Because these experiments were performed at low pressures and relatively low concentrations of reactant gases, there is no significant interference in the oxygen atom decays due to the three-body reaction  $\text{O}(^3\text{P}) + \text{NO}_2 + \text{M} \rightarrow \text{NO}_3 + \text{M}$ . Based on recent measurements of the rate constant for this process [14,15], which disagree by a factor of two over the temperature range of this experiment, the maximum effect in this study would be less than  $1 \text{ s}^{-1}$  at 216 K and  $[\text{NO}_2] = 2 \times 10^{13} \text{ molecule cm}^{-3}$ .

A semilogarithmic weighted-least-squares fit was calculated for each observed oxygen atom decay to obtain the first-order rate constant ( $k^1$ ). Small corrections were applied to all first-order rate constants to account for the probe loss and for axial diffusion of O, as listed in Table 1. A plot of  $k^1$  versus  $\text{NO}_2$  concentration for all experiments performed at 297 K is shown in Fig. 2. The slope of the least-squares fit to these data gives the rate coefficient of reaction 1 ( $k_1$ ) at room temperature,  $k^{297} = (9.93 \pm 0.19) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , where the uncertainty is the  $2\sigma$  precision of the weighted least-squares fit. Weights were determined based on the precision of the semilogarithmic fits to the decay plots. Note that the fit to the  $k^1$  versus concentration plot in Fig. 2 passes through zero. This is an important test of the lack of secondary

chemistry. Compare, for example, similar plots given in the studies of Gierczak et al. [7] (Fig. 5) and Estupiñán et al. [8] (Fig. 3), both of which show positive offsets from zero.

It is necessary to account for the effects of  $\text{NO}_2$  dimerization ( $\text{NO}_2 + \text{NO}_2 \leftrightarrow \text{N}_2\text{O}_4$ ) both in making mixtures of  $\text{NO}_2$  and in the actual kinetics experiments. All mixtures were made in a blackened glass bulb and stored at room temperature; the equilibrium constant recommended by the JPL panel [16] was used to estimate the fraction of total  $\text{NO}_2$  present as  $\text{N}_2\text{O}_4$  in the mixture. Since the change in pressure with time ( $dp/dt$ ) in the mixture bulb is employed to determine the concentration of  $\text{NO}_2$  added to the flow tube, one must account for the fact that some of the  $\text{NO}_2$  is present as  $\text{N}_2\text{O}_4$ . In addition, as the mixture is expanded into the flow tube, where the pressure is low, the  $\text{N}_2\text{O}_4$  dissociates, producing more  $\text{NO}_2$  than one would anticipate from the change in bulb pressure alone. This latter effect is greatest for large mixing ratios of  $\text{NO}_2$ , but less than about 1% for the mixtures used in this study. Most mixtures in this experiment were made by converting NO to  $\text{NO}_2$  with  $\text{O}_2$ , so there is an accurate measure of  $\text{NO}_x$  ( $\text{NO}_2 + 2 \times \text{N}_2\text{O}_4$ ), based on the initial pressure of NO added to the mixture bulb. Thus, the flow rate of  $\text{NO}_x$  is the measured quantity; this accurately represents the amount of  $\text{NO}_2$  added to the flow system, assuming all  $\text{N}_2\text{O}_4$  dissociates in the low-pressure flow-tube environment. For the mixtures employed in this experiment, the  $\text{NO}_x$  fraction was less than 5% at all times.

The formation of  $\text{N}_2\text{O}_4$  during the kinetics experiments is also important, because it is both a reservoir of  $\text{NO}_2$  and can react with oxygen atoms. Using the low-temperature values for the equilibrium expression reported by Harwood and Jones [17],  $\text{N}_2\text{O}_4$  could account for, at most, 4% of

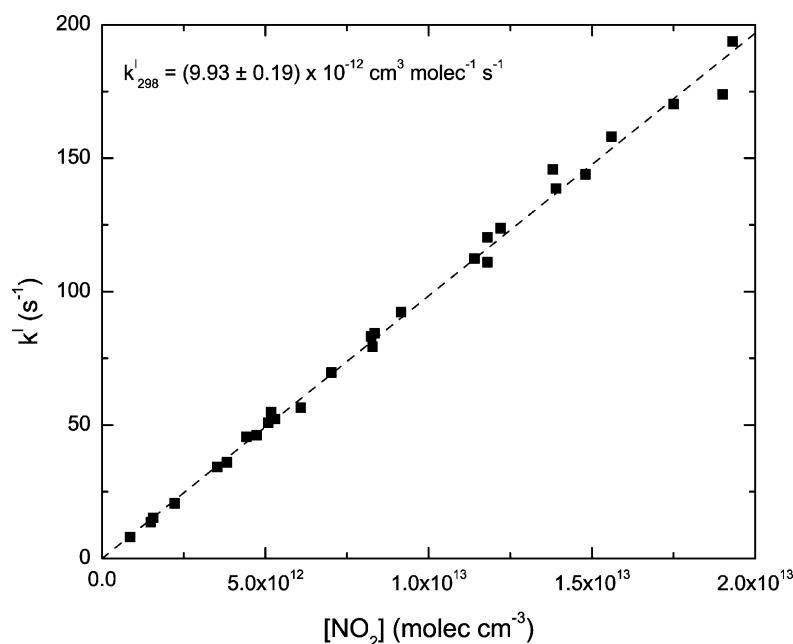


Fig. 2. Plot of first-order rate constant ( $k^I$ ) vs.  $\text{NO}_2$  concentration for all experiments performed at 297 K. A value of  $k_1 = (9.93 \pm 0.19) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  was obtained for this temperature. The quoted uncertainty is the  $2\sigma$  precision of a weighted least-squares fit to the measurements.

the  $\text{NO}_2$  added (at the highest  $\text{NO}_2$  concentration and lowest temperature). The JPL recommended value for  $K_{\text{eq}}$  [16] gives essentially the same result. Geers-Müller and Stuhl [6] determined that the rate constant for the reaction between oxygen atoms and  $\text{N}_2\text{O}_4$  at 199 K was less than  $2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . At the maximum  $\text{N}_2\text{O}_4$  concentration in the 216 K experiment, this reaction would contribute less than  $2 \text{ s}^{-1}$  loss of oxygen atoms, less than corrections applied for wall loss.

Table 2 summarizes the values and uncertainties of  $k_1$  for the eight temperatures at which measurements were obtained in this study. Uncertainties are the  $2\sigma$  precision of the weighted-least-squares fits of the  $k^I$  versus  $\text{NO}_2$  concentration plots. A weighted least-squares fit to these data for atmospherically relevant temperatures ( $T \leq 298 \text{ K}$ ) in the traditional Arrhenius form ( $\ln k^I$  versus  $T^{-1}$ ) gives:

$$k_1(T) (\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) = (5.64 \pm 0.12) \times 10^{-12} \exp \left[ \frac{165 \pm 10}{T} \right]$$

Table 2  
Summary of measurements of  $k_1$

Temperature	$k_1 \pm 2\sigma$ ( $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	Number of experiments
216	$12.3 \pm 0.6$	7
239	$11.4 \pm 0.6$	6
254	$10.9 \pm 0.4$	7
273	$10.4 \pm 0.4$	6
297	$9.93 \pm 0.2$	28
336	$8.76 \pm 0.2$	8
373	$7.88 \pm 0.2$	8
412	$7.26 \pm 0.2$	8

where the uncertainty is the  $2\sigma$  precision of the fit. Alternatively, the rate coefficients can be parameterized in the form  $k = A(T/300)^{-n}$ . The results presented in Table 2 give rise to the expression:

$$k_1(T) (\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) = (9.85 \pm 0.10) \times 10^{-12} \left( \frac{T}{300} \right)^{-(0.65 \pm 0.06)}$$

where the uncertainty is the  $2\sigma$  precision of the fit.

The overall accuracy of the rate coefficients reported here is estimated from errors associated with the measurement of pressure ( $\pm 5\%$ ), temperature ( $\pm 1\%$ ), and flow rates ( $\pm 2\%$ ), as well as how well the mixture fraction is known ( $\pm 3\%$ ). Adding these quantities in quadrature gives a total uncertainty of about  $\pm 6\%$ . There could be additional systematic errors resulting from the value of the equilibrium constant used to correct for the effects of  $\text{N}_2\text{O}_4$  on the kinetics runs. As the magnitude of these errors is unknown, they are not included in the estimated accuracy of the value of  $k_1$ .

#### 4. Discussion

Fig. 3 shows a comparison of results obtained in this work with the Arrhenius expression recommended by the JPL panel [9] and a weighted-least-squares fit to the rate coefficients for  $T \leq 298 \text{ K}$ . Results from all previous studies [4–8] and this work are shown in Fig. 4. The errorbars in this figure are those given by each author and generally represent the  $2\sigma$  accuracy of the measurements;  $2\sigma$  precision is shown when accuracy estimates are unavailable. A

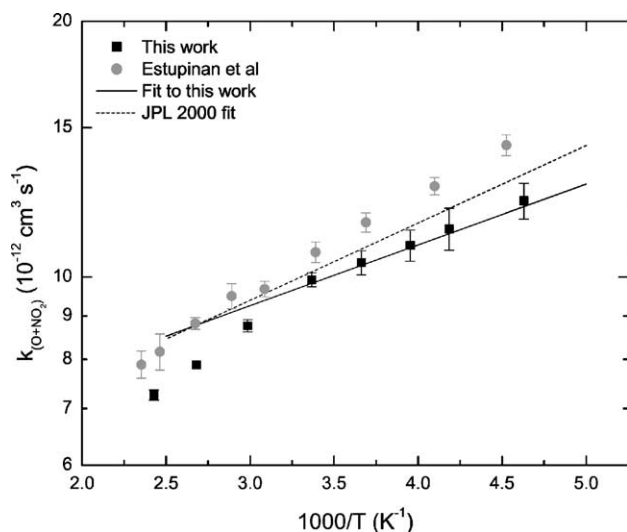


Fig. 3. Arrhenius plot of  $k_1$  vs.  $T^{-1}$  for this study and that of Estupiñán et al. [8]. The short-dashed line is the current recommendation of the JPL panel [9] and the solid line is a weighted least-squares fit to the results from this work at temperatures less than or equal to 298 K.

least-squares fit to all of these data, with each point weighted by  $(1/\sigma)^2$ , results in the Arrhenius expression  $(5.0 \pm 0.4) \times 10^{-12} \exp[(210 \pm 22)/T]$ , where the uncertainties are the  $2\sigma$  precision of the fit. This expression gives values within 3% of those derived from the JPL recommendation, well within the uncertainties of either fit. The IUPAC expression [18], which was determined prior to the newest results for this reaction [7,8], gives rate coefficients considerably slower at stratospheric temperatures than those calculated from either the JPL recommendation or from the expression derived above; for example, at 220 K, the IUPAC rate is 14% slower than the JPL value.

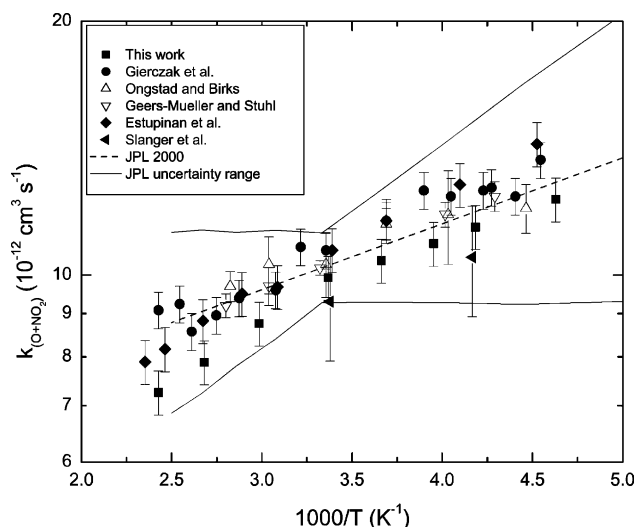


Fig. 4. Arrhenius plot of  $k_1$  vs.  $T^{-1}$  for this study and five previous reports of the temperature dependence. The dashed line is the recommendation of the JPL panel [9] and the solid lines are the uncertainty bounds. See text for further discussion.

The results from this study are 5–10% smaller at all temperatures than most other experiments, with the exception of Slanger et al. [4], although those are consistent within the combined uncertainties of the two experiments. Because low concentrations of reactants are used and flow rates are fast, the low-pressure discharge-flow method tends to suffer less from secondary reactions and wall-loss than other techniques, such as flash photolysis [7,8], so a smaller rate coefficient may simply be closer to the true rate coefficient for this reaction. I can not, however, entirely rule out interference from the regeneration of atomic oxygen by the reaction of nitrogen atoms with  $\text{NO}_2$ . There is some impurity nitrogen in the oxygen discharged to create O, so some N atoms can also be created. In order to explain a 5% slower rate coefficient, about  $3 \times 10^6$  N atoms  $\text{cm}^{-3}$  would be required. Even if the microwave discharge were 100% efficient, all of the impurity in the oxygen would have to be molecular nitrogen to produce the required nitrogen atom concentration. While this is possible, it seems unlikely, given the generally low efficiency of microwave discharge of nitrogen.

As can be seen in Fig. 3, the Arrhenius plot from this study begins to exhibit downward curvature at temperatures above 298 K. This behavior is also apparent in data from other studies; see, for example, the Estupiñán et al. data [8] that are also plotted in Fig. 3. While systematic errors at high temperatures related to temperature gradients within the flow system cannot be ruled out, it seems possible that this curvature is the true behavior of this reaction, given that it is seen in more than one study. Such curvature may provide insight into the mechanism for the O +  $\text{NO}_2$  reaction and deserves further study by a technique better suited to operation at high temperatures.

The new results obtained in this study do not alter the conclusions reached by others about the importance of the O +  $\text{NO}_2$  reaction in the middle stratosphere. They do, however, add weight to the rather small ensemble of laboratory measurements made at stratospherically relevant temperatures. Significant changes were made to the recommended reaction rate by the JPL panel [9,16] as a result of the studies of Gierczak et al. [7]. Portmann et al. [19] show that the 20% larger rate coefficient measured by Gierczak et al. for stratospheric conditions leads to as much as 15% faster odd-oxygen (O +  $\text{O}_3$ ) loss in the middle stratosphere. Further, Smith et al. [10] have shown that ozone loss rates calculated with chemical models of the stratosphere are extremely sensitive to uncertainties (or changes) in the rate for O +  $\text{NO}_2$ , particularly at low temperatures.

In Fig. 4, the JPL 2000 recommended rate coefficient is plotted as a dashed line and the solid lines represent the uncertainty bounds calculated from the JPL “uncertainty parameter” and the temperature dependence of the reaction. The uncertainty at any given temperature may be estimated from the expression:

$$f(T) = f(298) \exp \left[ \frac{\Delta E}{R} \left( \frac{1}{T} - \frac{1}{298} \right) \right]$$



where  $f(298)$  is the uncertainty at room temperature and  $\Delta E$  is the uncertainty in the activation energy.  $f(298)$  for this reaction is given as 1.1. It is clear from the data shown in Fig. 4 that the current uncertainty bounds on reaction 1 given by the JPL recommendation are reasonable at room temperature and too large at low, stratospheric temperatures. I argue that there is sufficient evidence to permit a reduction of the uncertainty in  $k_1$  at stratospheric temperatures.

The uncertainty in atmospheric model calculations of  $O_3$  can be estimated from the expression  $S(O_3) \times (\sigma k/k)$ , where  $S(O_3)$  describes the relative change in  $O_3$  for a given change in a rate parameter. The uncertainty in  $k_1$  suggested by JPL 2000 is 36% at 220 K and 24% at 250 K. Given the sensitivity coefficient of Smith et al.,  $S(O_3) = -0.327$ , these uncertainties in  $k_1$  lead to an ozone uncertainty of 11.7% at 220 K and 7.8% at 250 K. If smaller error bounds, consistent with the data shown in Fig. 4, were adopted, the uncertainty in ozone at 220 K could be reduced to about 5.5%, while that at 250 K could be as small as 4.5%.

## 5. Summary

The reaction of oxygen atoms with nitrogen dioxide is an example of a rate coefficient that has been studied carefully using a number of different experimental approaches and widely varying conditions of temperature, pressure, and reactant concentrations. Both reactants are relatively easy to detect and quantify at low concentrations with well-understood techniques. Although differences among the various determinations of the rate coefficient  $k_1$  have been pointed out here and by other authors, the degree of agreement—better than  $\pm 15\%$  at nearly all atmospherically relevant temperatures—is really quite remarkable. This is, arguably, as well as one might expect to know a rate coefficient with current laboratory technology.

## Acknowledgements

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