Kinetics and Products of the Reaction $O_2(^1\Sigma_g^+)$ with N_2O

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Dedicated to Prof. Dr. Reinhard Zellner on the occasion of his 65th birthday

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Previous studies have suggested that the reaction of $O_2({}^{1}\Sigma_g^+) + N_2O \rightarrow NO + NO_2$ may be a significant source of NO_x in the atmosphere if the branching ratio of this channel is greater than ~1%. We have measured the overall rate coefficient (k₁) for the reaction of $O_2({}^{1}\Sigma_g^+)$ with N₂O to be k₁(295 K) = $(1.06\pm0.14)\times10^{-13}$ cm³ molecule⁻¹ s⁻¹ at 295 K and k₁(T) = $(7.48\pm1.66)\times10^{-14} \exp[(87\pm40)/T]$ cm³ molecule⁻¹ s⁻¹ as a function of temperature over the range 210–370 K. The yields of NO, NO₂ or O₃ that are possible reaction products from the title reaction were undetectably small. Also, the net loss of N₂O from the title reaction was negligibly small. We report upper limits for the yields for the production of NO_x, the production of O₃ and the loss of N₂O (all at 298 K) to be $< 2\times10^{-4}$, $< 1\times10^{-3}$, and $< 3\times10^{-3}$, respectively. We conclude that the reaction of $O_2({}^{1}\Sigma_g^+) + N_2O$ is neither a significant source of NO_x in the atmosphere nor a significant sink for N₂O.

1. Introduction

The reaction of $O_2(^{1}\Sigma_g^{+})$ with N_2O has several potential exothermic channels at room temperature (heats of formation used to derive the heats of reaction are from Sander et al., 2006 [1]):

$$O_2({}^{1}\Sigma_{g}^{+}) + N_2O \rightarrow NO + NO_2; \quad \Delta_{rxn}H^{o}_{298} = -27.6 \text{ kcal/mol}$$
 (1a)

$$\rightarrow N_2 + O_3; \quad \Delta_{rxn} H^o_{298} = -23.0 \text{ kcal/mol}$$
 (1b)

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$$\stackrel{\text{M}}{\to}$$
 N₂O₃; $\Delta_{\text{rxn}} H^{o}_{298} = -37.3 \text{ kcal/mol}$ (1c)

$$\rightarrow O_2(^{3}\Sigma_g^{-}) + N_2O; \quad \Delta_{rxn}H^{o}_{298} = -37.5 \text{ kcal/mol}$$
 (1d)

$$\rightarrow O_2(^1\Delta_g) + N_2O; \quad \Delta_{rxn}H^o{}_{298} = -15.0 \text{ kcal/mol}$$
(1e)

Several researchers have speculated that reaction (1) may be a significant source of odd-nitrogen to the stratosphere [2–4]. Toumi [3] postulated that a 1% yield for channel (1a) would lead to a NO_x production rate from reaction (1) that would be approximately as large as that from the main NO_x source in the stratosphere, the reaction of $O(^{1}D)$ with N₂O:

$$O(^{1}D) + N_{2}O \rightarrow 2 NO$$
(2a)

Siskind et al. [2] revised the conclusions of Toumi by using a more accurate solar flux to better calculate the production of $O_2({}^{1}\Sigma_{g}^{+})$ and concluded that a yield of 2% for channel (1a) would be necessary for the NO_x production rate noted above. Additionally, Prasad [4] has suggested that reaction (1c), with subsequent photolysis of N₂O₃, is another potential production method for NO_x in the stratosphere. Despite these speculations, there has not yet been an experimental study to attempt to observe the production of NO_x from this reaction directly.

In addition to acting as a source of NO_x , there is also the possibility that reaction (1) may act as a sink for N_2O – if any of the channels (1a), (1b) or (1c) has a significant yield. If this reaction does occur, the atmospheric lifetime of N_2O , a potent greenhouse gas, may need to be revised, since the currently assumed N_2O destruction pathways are primarily from stratospheric photolysis of N_2O or reaction of $O(^1D)$ with N_2O , and do not include the reaction of N_2O with $O_2(^{1}\Sigma_{g}^{+})$.

In this study, we examine the reaction of $O_2({}^{1}\Sigma_{g}^{+})$ with N_2O by measuring the following: (a) the overall rate coefficient for the total loss of $O_2({}^{1}\Sigma_{g}^{+})$ due to interaction with N_2O , k_1 ; (b) the yield of NO from channel (1a); (c) the yield of NO_2 from channel (1a); (d) the yield of O_3 from channel (1b); (e) the loss of N_2O from the sum of channels (1a), (1b) and (1c). The overall rate coefficient, k_1 , has been measured several times in the past. Our results serve to compare our measurement technique with those used in previous studies and our experiments more thoroughly explore the temperature dependence over the range of atmospherically relevant temperatures. Finally, we employed a simple atmospheric box model to assess the atmospheric implications of the measured upper limits for the yields of the products and the overall reaction rate coefficient.

2. Experiment

2.1 Rate coefficient measurement

This study consisted of measurements of the rate coefficient for reaction (1) and products from this reaction. The rate coefficients were measured by pulsed

excitation of molecular oxygen, $O_2({}^{3}\Sigma_{g}^{-})$, to $O_2({}^{1}\Sigma_{g}^{+})$ followed by resonance fluorescence detection of $O({}^{3}P)$ produced by the reaction of $O_2({}^{1}\Sigma_{g}^{+})$ with O_3 . The product studies employed several different instruments: a chemiluminescence instrument for the detection of NO, a diode array spectrometer for the detection of NO₂ and O₃, and a FTIR spectrometer for the detection of N₂O. These experiments are described in the next section.

2.1.1 Detection of $O(^{3}P)$ via resonance fluorescence

The overall rate coefficient, k_1 , was measured using a standard pulsed photolysis – resonance fluorescence instrument for the detection of O(³P). A complete description of this technique can be found elsewhere [5, 6], and only the important details are described here. In these experiments, we generated $O_2({}^{1}\Sigma_{g}^{+})$ by directly exciting ground state O_2 with a Nd:YAG pumped tunable dye laser in the wavelength range (760–762) nm:

$$O_2(^{3}\Sigma_g^{-}) + h\nu(\sim 762 \text{ nm}) \rightarrow O_2(^{1}\Sigma_g^{+})$$
 (3)

A small portion of the excitation laser beam was diverted through a separate absorption cell filled with O₂ (1000 Torr) where photoacoustic spectroscopy was employed to ensure that the laser was tuned to the peak of an O₂(${}^{1}\Sigma_{g}^{+}$) \leftarrow O₂(${}^{3}\Sigma_{g}^{-}$) transition [7]. In the main reaction cell, where the O₂(${}^{1}\Sigma_{g}^{+}$) reaction was studied, O₂(${}^{1}\Sigma_{g}^{+}$) was reacted with O₃ to produce O(${}^{3}P$):

$$O_2({}^{1}\Sigma_{g}^{+}) + O_3 \rightarrow 2 O_2 + O({}^{3}P)$$
 (4)

 $O(^{3}P)$ was detected via VUV atomic resonance fluorescence near 131 nm employing a microwave discharge lamp as a continuous VUV excitation light source. The dye laser was operated at a repetition rate of (1–10) Hz and resonance fluorescence signal was counted using VUV photon detection by a solar blind photomultiplier and photon counting methods. An entire temporal profile of $O(^{3}P)$ was obtained subsequent to each laser shot. Thousands of such $O(^{3}P)$ temporal profiles were added together to produce $O(^{3}P)$ temporal profiles with sufficient signal to fit well to an analytical expression. The $O(^{3}P)$ temporal profiles with different concentrations of N₂O but fixed concentrations of O₃ and O₂. The O₃ concentration in the gas stream flowing through the reactor was determined by measuring the absorption of 253.7 nm light ($\sigma = 1.15 \times 10^{-17}$ cm²) [1] in a 100 cm long cell. The overall rate coefficient for $O_2(^{1}\Sigma_{g}^{+})$ removal by N₂O, k₁, which is the sum of all quenching and reaction channels, was obtained from these data. See Table 1 for the experimental conditions employed.

Temp (K)	Press (Torr)	$[O_3]$ (10 ¹³ mole- cule cm ⁻³)	$[O_2]$ (10 ¹⁷ mole- cule cm ⁻³)	762 nm Fluence (mJ/ cm ² pulse)	$\begin{array}{c} [O_2(^1\Sigma_g^+)] \\ (10^{11} \mbox{ mole-} cule \mbox{ cm}^{-3}) \end{array}$	N_2O Concentration Range (10 ¹⁵ mole- cule cm ⁻³)	Rate Coefficient $(10^{-13} \text{ cm}^3 \text{ mole-} \text{cule}^{-1} \text{ s}^{-1})$
210	23.2	1.6	1.9	11-22	11-22	0.79-4.87	1.15±0.11
228	24.6	1.6	2.0	8-20	8.5-21	0.66-4.94	1.13±0.06
256	24.7	2.0	1.9	2.5-19	2.5-19	0.44-4.53	1.07±0.09
295	25.5	1.7–9.8	1.9	4-20	3.6-15	1.07-5.44	1.06±0.14
331	26.0	1.5	1.8	3-21	2.4-17	0.73-4.34	1.01±0.08
370	19.0	1.2-1.7	1.0	10	5–7	0.49-1.42	0.92±0.19

Table 1. Experimental conditions for rate coefficient measurements performed with pulsed photolysis – resonance fluorescence instrument for detection of $O(^{3}P)$.

Table 2. Rate coefficient measurements for the reaction $O_2({}^{1}\Sigma_{g}^{+}) + N_2O$.

Tempera- ture Range (K)	295 K Rate Coefficient $(10^{-14} \text{ cm}^{-3} \text{ mole-}$ $\text{cule}^{-1} \text{ s}^{-1})$	Arrhenius A Factor $(10^{-14} \text{ cm}^{-3} \text{ mole-cule}^{-1} \text{ s}^{-1})$	Arrhenius E _a /R (K)	Reference	Method
	7.0 ± 1.8			Filseth et al., 1970 [20]	Flash photolysis – $O_2(^{1}\Sigma_{g}^{+})$ emission
	4.6 ± 4.5*			Gauthier & Snel- ling, 1975 [18]	$\begin{array}{l} Flash \ photolysis - \\ O_2({}^l\Sigma_g^+) \ emission, \ relative \ rate \end{array}$
	7.7 ± 1.0			Thomas and Thrush, 1977 [19]	$\begin{array}{l} Microwave \ discharge - \\ O_2(^l\Sigma_g^+) \ emission \end{array}$
300-1300	9.78 ± 0.42		0	Borrell et al., 1983 [21]	Flowing discharge – shock tube
210-370	10.6 ± 1.4	7.48 ± 1.66	-87 ± 40	This work, 2010	Pulsed Photolysis – Res- onance Fluorescence (PP-RF) detection of O(³ P)

* Assumed to be 2σ .

2.2 Product studies

2.2.1 Detection of NO via chemiluminescence

The possible production of NO from channel (1a) was examined by producing $O_2({}^{1}\Sigma_g^{+})$ via pulsed laser excitation and detecting NO via chemiluminescence [8, 9]. The chemiluminescence detector consisted of a chamber with highly reflective inner walls where the gas flow potentially containing NO was mixed with a large flow of O₃, such that the reaction of NO with O₃ was complete in the chamber. The fluorescence at wavelengths greater than 630 nm from the electronically excited NO₂ produced from the reaction of NO with O₃ was detected. The photomultiplier tube (detection range of 300–900 nm) used to detect NO₂ fluorescence was cooled to ~200 K to minimize dark counts. A red filter (Schott glass) was placed in front of the PMT to block light at wavelengths shorter than

600 nm. Ozone from an ozone generator was directly flowed into the chamber to have a concentration of ~1×10¹⁶ molecule cm⁻³ in the chamber. A gas mixture of O₂ and N₂O was irradiated with pulsed lasers to excite $O_2(^{3}\Sigma_{g}^{-})$ to $O_2(^{1}\Sigma_{g}^{+})$, and the entire content of the photolysis cell was flowed into the chemiluminescence detector before the next laser pulse. Background signals (photon count rate) with just O₃ and He present (typically 1000–1800 Hz) were measured prior to and/or following each NO concentration determination. These background signals were subtracted from those measured subsequent to N₂O reaction with $O_2(^{1}\Sigma_{g}^{+})$. The response of the chemiluminescence detector for detection of NO was calibrated by introduction of a known quantity of NO; the chemiluminescence signal was linear over the range of NO concentrations used in this study, $(0-5) \times 10^{10}$ molecule cm⁻³.

2.2.2 Detection of NO_2 via absorption with diode array spectrometer

A diode array spectrometer was used to detect NO_2 from channel (1a) by taking advantage of its structured absorption feature in the 350-500 nm range. A 30 W Deuterium lamp was used as the light source. The resolution of the spectrometer was estimated to be ~1.7 nm from the measured full width at half-maximum (FWHM) of several Hg lines. This was sufficiently narrow to discern the structure in the NO₂ absorption feature and thus positively identify the presence of NO2. The NO2 concentration was determined using the known absorption cross section of NO₂ at 417.9 nm, $\sigma_{417.9 \text{ nm}} = 7.87 \times 10^{-19} \text{ cm}^2$ [10] and the measured absorption attributable to NO₂. The instrument was calibrated by using known NO₂ concentrations prepared from a dilute mixture of NO₂ (0.92 % in UHP He) in a 12 L glass bulb. For each calibration measurement, a spectrum of the evacuated cell, I₀, was recorded. Then, the NO₂ mixture was expanded into the absorption cell, several spectra, I, were recorded at a series of decreasing pressures (and thus decreasing concentrations of NO₂). Finally, another I₀ spectrum was recorded. Calibrations for NO2 detection were performed using known concentrations of NO₂ before and after each experiment where $O_2(^{1}\Sigma_g^{+})$ was reacted with N_2O ; they agreed to within 5%.

2.2.3 Detection of O_3 via absorption with diode array spectrometer

For measuring the yield of O_3 from channel (1b), we employed a diode array spectrometer similar to that used for the NO₂ yield determination described in the previous section. The diode array spectrometer was tuned to operate in the wavelength range of 210 to 460 nm to observe the strong absorption feature of O_3 in the Hartley bands centered at 254 nm. Mixtures of O_3 in O_2 were prepared at pressures up to 1000 Torr in a photolysis cell (100 cm long, ~300 cm³). To establish the precision of the O_3 measurements, O_3/O_2 mixtures were expanded into the diode array spectrometer, the O_3 concentration was measured via absorption, the absorption cell was evacuated, and the contents of the photolysis cell were again expanded into the absorption cell. O_3 concentrations measured repeat-

edly in this manner over the range $(1.5-17.9) \times 10^{13}$ molecule cm⁻³ agreed to within 5% with that calculated using manometrically measured mixtures of O₃ in the bath gas, thus defining the limit to which we could determine the O₃ concentration.

2.2.4 Detection of N_2O with FTIR spectrometer

In an attempt to observe the loss of N₂O via channels (1a), (1b) or (1c), we monitored its concentration with an FTIR spectrometer (Nicolet 560, resolution = 0.5 cm^{-1}) subsequent to repeated generation of $O_2({}^{1}\Sigma_{g}^{+})$ in a mixture of O_3 , O_2 and N₂O. The concentration of N₂O in the mixture was calculated using the known integrated line strength for the entire v_1 stretch centered at 2223 cm⁻¹ ($5.53 \times 10^{-17} \text{ cm}^2 \text{ cm}^{-1}$ in the wavelength range (2259–2167) cm⁻¹ [11]). Known concentrations of N₂O were used to calibrate its detection using IR absorption. The size of the 762 nm beam used to produce $O_2({}^{1}\Sigma_{g}^{+})$ was 0.2 cm² and the cross sectional area of the cylindrical absorption cell was 3.8 cm². The differences between the photolysis volume and the total absorption cell volume were accounted for in the analysis.

2.3 Materials

UHP O₂ (Scott Specialty Gases, >99.99 %), UHP He (US Welding, > 99.999 %) and N₂O (Matheson Gases, >99.99 %) were used without further purification. A dilute (<1%) mixture of NO in He was prepared by passing NO through a dry ice/ethanol bath at 195 K to remove NO₂ and other impurities. A dilute mixture of NO₂ in He (0.92%) was prepared manometrically, where we accounted for the presence of N₂O₄ in the stock of NO₂ used for preparing this mixture.

3. Results

3.1 Rate coefficient for the reaction of $O_2(^{1}\Sigma_g^{+})$ with N_2O

First order rate coefficients for the loss of $O_2({}^{1}\Sigma_{g}^{+})$ were determined from the temporal profiles of $O({}^{3}P)$ measured following $O_2({}^{1}\Sigma_{g}^{+})$ production in a mixture of O_3 , N_2O , O_2 and He that is described above via a well-established procedure [12, 13]. The temporal profiles of $O({}^{3}P)$ measured here were described by a biexponential function:

$$[O(^{3}P)]_{t} = Ae^{-Bt} + Ce^{-Dt}$$
(I)

For the title reaction of $O_2({}^1\Sigma_g^+) + N_2O$, the parameters A, B, C, and D are defined as follows:

$$A = [O_2({}^{1}\Sigma_g^{+})]_0 \frac{(k_4 [O_3] + k_1 [N_2O])}{(D-B)}$$
(II)



Fig. 1. Example of a temporal profile of $O({}^{3}P)$ measured following the generation of $O_{2}({}^{1}\Sigma_{g}^{+})$ in the presence of O_{3} and $N_{2}O$. Data points are shown in light gray points, biexponential fit (see text) is shown in solid black line. Inset shows same profile, but only first millisecond of profile to more closely examine the biexponential fit. Experimental conditions for this profile were: T = 298 K, $[O_{3}] = 1.81 \times 10^{13}$, $[O_{2}] = 1.91 \times 10^{17}$, $[N_{2}O] = 1.07 \times 10^{15}$ (all concentrations given in molecule cm⁻³). Results of the fit were: A = -3715, B = 588, C = 3736, D = 104 (again, see text for explanation).

$$B = k_4[O_3] + k_1[N_2O] + k_6$$
(III)

$$C = [O(^{3}P)]_{0} - A \tag{IV}$$

$$D = k_5 \tag{V}$$

 k_5 and k_6 are, respectively, the rate coefficient for the first order loss of O(³P) due to flow out of the reaction zone, and the rate coefficient for the first order loss of $O_2({}^{1}\Sigma_{g}^{+})$ due to both flow and quenching by the bath gas.

$$O(^{3}P) \rightarrow loss$$
 (5)

$$O_2(^{l}\Sigma_g^{+}) \rightarrow loss \tag{6}$$

The sum of the parameters A + C was equal to the initial concentration of O(³P), $[O(^{3}P)]_{0}$, produced via the photolysis of O₃ in the Chappuis band at 762 nm. It was very small compared to the total O(³P) signal from the O₂(¹ $\Sigma_{g}^{+})$ + O₃ reaction as mentioned above. Figure 1 shows an example temporal profile of O(³P) from these measurements.

Figure 2a shows a plot of the first order rate coefficients for the appearance of $O({}^{3}P)$ at various concentrations of N₂O at room temperature, determined from the fits of the observed individual $O({}^{3}P)$ temporal profiles [5]. In these experiments, the first order rate coefficient for the appearance of $O({}^{3}P)$ was equivalent



Fig. 2. Results for the measurement of the overall rate coefficient for loss of $O_2({}^1\Sigma_g^+)$ due to collision with N₂O. The top panel shows the first order appearance rate coefficients for the production of $O({}^3P)$, which is equivalent to the loss rate coefficients of $O_2({}^1\Sigma_g^+)$, at room temperature as a function of N₂O concentration. The slope of the fit is the bimolecular rate coefficient, k₁, for total removal of $O_2({}^1\Sigma_g^+)$ by N₂O via both reaction and quenching. The bottom panel shows our results for k₁ versus the inverse of the temperature in standard Arrhenius form.

to the first order loss rate coefficient for the removal of $O_2({}^{1}\Sigma_{g}^{+})$. The slope of this plot is the bimolecular rate coefficient for the overall interaction of $O_2({}^{1}\Sigma_{g}^{+}) + N_2O$, k_1 , and the intercept is the first order rate coefficient for loss of $O_2({}^{1}\Sigma_{g}^{+})$ via reaction (4) and other background losses. The first order rate coefficients for all of these losses together were typically < 500 s⁻¹. Our value for k_1 at 295 K is $(1.06 \pm 0.14) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹. The quoted uncertainties are at the 95% confidence level and include the 2σ precision in the fits of k' vs. [N₂O] and the estimated systematic errors primarily due to the uncertainty in [N₂O], which was $\pm 10\%$.

Large concentrations of N₂O (> 4×10¹⁴ molecule cm⁻³) were necessary to observe a change in the measured rate coefficient for loss of O₂(¹Σ⁺_g). However, N₂O absorbs the VUV radiation used for O(³P) detection ($\sigma_{131nm}(N_2O) \sim 7\times10^{-17}$ cm² [14]). Therefore, the range of first order rate coefficients measurable for loss of O₂(¹Σ⁺_g) was limited to less than an order of magnitude. The maximum usable N₂O concentration was 5×10¹⁵ molecule cm⁻³. This interference restricted the precision in our determination of k₁. We measured k₁ at six temperatures over the temperature range 210–370 K. Figure 2b presents these results in the Arrhenius form. Our value for k₁ as a function of temperature is k₁ = (7.48±1.66)×10⁻¹⁴ exp[(87±40)/T] cm³ molecule⁻¹ s⁻¹. The quoted errors are at the 95% level of confidence and include estimated systematic errors. The uncertainty in A was calculated from that in ln(A), determined a linear least squares fit of lnk vs. 1/T data to a straight line (Figure 2b), using the relation $\sigma A = A \sigma \ln(A)$) and adding our estimated uncertainty in measuring N₂O concentration estimated to be 10% in the reactor.

3.2 Product studies

3.2.1 Upper limit for NO production from $O_2({}^{l}\Sigma_{g}^{+}) + N_2O$

To measure the upper limit for the production of NO from reaction (1a), a series of three sequential experiments, designated A, B and C, were performed; these experiments were then repeated. For all three experiments in a series, the same gas mixture of O_2/N_2O was flowed through the photolysis cell and only the photolysis laser used was changed: experiment A employed a 193 nm excimer laser; experiment B used a 762 nm dye laser (described in the experimental section); experiment C employed measurements in the absence of photolysis. Both of the 193 nm and 762 nm lasers were run at a repetition rate of 1 Hz, allowing a complete replacement of the content of the reactor between pulses.

In experiment A, a known concentration of NO was produced using a 193 nm photolysis laser via the reaction sequence:

$$N_2O + h\nu(193 \text{ nm}) \rightarrow N_2 + O(^{1}\Delta)$$
(7)

$$O(^{1}D) + N_{2}O \rightarrow 2 NO$$
(2a)

$$\rightarrow N_2 + O_2 \tag{2b}$$

$$O(^{1}\Delta) + O_{2} \rightarrow O(^{3}P) + O_{2}(^{1}\Sigma_{g}^{+}) / O_{2}(^{1}\Delta_{g}) / O_{2}(^{3}\Sigma_{g}^{-})$$
(8)

where $k_{2a} = 6.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k_{2b} = 4.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [1], and $k_8 = 3.85 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [13]. The NO concentration produced in the photolysis cell was calculated via equation (VI):

$$[NO] = [N_2O] \times F_{193} \times \sigma_{193}(N_2O) \times \frac{V_{\text{photolysis}}}{V_{\text{cell}}} \times \frac{2 k_{2a}[N_2O]}{(k_{2a} + k_{2b}) [N_2O] + k_8 [O_2]}$$
(VI)



Fig. 3. Temporal profiles of various runs with NO chemiluminescence detector used to search for NO production from $O_2(^{1}\Sigma_g^{+}) + N_2O$. The medium gray crosses (experiment A) are the signal from the photolysis of an O_2/N_2O mixture with a 193 nm excimer laser to produce a known amount of NO. The temporal variation is due to flow parameters, and not chemical reactions, making the area under the curve proportional to the total amount of NO produced in the photolysis cell (see text). The black open circles (experiment B) are the signal from the photolysis of the same O_2/N_2O mixture with a 762 nm dye laser to produce $O_2(^{1}\Sigma_g^{+})$. No signal from NO was apparent. The light gray open squares (experiment C shown for I ms) are the background signal level of the chemiluminescence detector in the absence of laser photolysis.

where F_{193} was the 193 nm laser fluence, $\sigma_{193\uparrow}(N_2O)$ was the N₂O cross section at 193 nm ($\sigma_{193nm} = 8.95 \times 10^{-20}$ cm² [1]), V_{photolysis} was the volume of gas illuminated by the photolysis laser and V_{cell} was the volume of the entire photolysis cell. Any $O_2({}^{1}\Sigma_{g}^{+})$ produced in reaction (8) would not lead to a significant concentration of NO. Table 3 lists the experimental conditions and Figure 3 shows typical temporal profiles of NO for these experiments. The NO temporal profile was dictated by the time required for the gases to flow through the detector, rather than chemical loss of NO. The integrated signal under the curve, with the background signal removed, was proportional to the total NO concentration produced. Several thousand laser shots were added together to produce a well defined NO chemiluminescence signal profile. It is noted that the exothermicity of channel (1a) is not sufficient to produce electronically excited NO₂, which could have potentially fluoresced in the detection region and interfered with fluorescence from the NO + O₃ reaction used for NO detection. Additionally, direct photolysis of O2 at 193 nm within the photolysis cell was prevented by passing the 193 nm laser beam through approximately 4 m of room air in the laboratory before reaching the photolysis cell, effectively removing all photons in the 193 nm laser beam that could have photolyzed O₂.

	210 K	295 K	295 K	365 K
Average Pressure (Torr)	7.3	8.5	7.4	7.3
Total Flow Rate (sccm)	210	340	210	200
Flow of O ₂ (sccm)	200	330	200	190
$[O_2]$ (molecule cm ⁻³)	3.2×10^{17}	2.7×10^{17}	2.3×10^{17}	1.8×10^{17}
Flow of N ₂ O (sccm)	10	7	10	10
$[N_2O]$ (molecule cm ⁻³)	1.5×10^{16}	5.5×10^{15}	1.1×10^{16}	9.1×10^{15}
Flow from O ₃ generator	1800	1900	1900	1800
(sccm)				
193 nm fluence	0.14	0.5	0.14	0.12
(mJ pulse ⁻¹ cm ⁻²)				
762 nm fluence -2	32	25	28	32
(mJ pulse ² cm ²)				
[NO] produced in 193 nm photolysis (molecule cm^{-3})	3.2×10^{9}	2.9×10^{9}	2.3×10^{9}	1.7×10^{9}
Area under the curve from	190	570	220	170
NO (Hz)				
$O_2(^1\Sigma_g^+)$ in 760 nm	8.3×10^{11}	7.7×10^{11}	4.6×10^{11}	3.6×10^{11}
photolysis (molecule cm^{-3})				
Maximum possible signal	50	130	60	40
due to NO (Hz)				
Maximum possible [NO]	8.3×10^{8}	6.7×10^{8}	6.3×10^{8}	4.0×10^{8}
(molecule cm^{-3})				
Branching ratio for reaction (1a)	< 0.0010	< 0.0008	< 0.0014	< 0.0011

Table 3. Experimental conditions for NO chemiluminescence experiments.

In experiment B, the O_2/N_2O gas mixture was excited with the 762 nm laser to create $O_2({}^{1}\Sigma_{g}^{+})$. Sufficient $O_2({}^{1}\Sigma_{g}^{+})$ was generated such that if reaction (1a) produced NO in any appreciable amount, it would have been observed in this experiment; see Table 3. The concentrations of N_2O in the reactor were such that the first order rate coefficient for the reaction of $O_2({}^{1}\Sigma_{g}^{+})$ with N_2O was sufficient (~900 s⁻¹) to completely suppress the loss of $O_2({}^{1}\Sigma_{g}^{+})$ via reaction with O_2 [1] and He [15] and via loss on the reactor walls. In experiment (C), both lasers were blocked and the background signal in the absence of any NO was measured. As can be seen immediately in Figure 3 by comparing the profile from experiment B to that from experiment C, reaction (1) did not lead to any observable NO production.

In the absence of a measurable NO signal in experiment B, we calculated an upper limit for the yield of NO via channel (1a). The sum of twice the standard deviation of the mean from experiments B and C was taken as the upper limit on the amount of NO signal from reaction (1a). This maximum NO signal was converted to a maximum NO concentration using the ratio of the signal to a known amount of NO from experiment A. We calculated the concentration of $O_2({}^{1}\Sigma_{g}^{+})$ from the measured laser fluence at 762 nm and the absorption line

strength for the $O_2({}^{1}\Sigma_{g}^{+}) \leftarrow O_2({}^{3}\Sigma_{g}^{-})$ transition [7]. This was checked by measuring the signal of $O({}^{3}P)$ produced by reacting all $O_2({}^{1}\Sigma_{g}^{+})$ with O_3 and comparing it with that produced by ozone photolysis at 248 nm. The concentration of $O({}^{3}P)$ produced from O_3 photolysis was calculated from measured fluence and ozone concentrations and using the known absorption cross section. The upper limit on the yield of NO produced via channel (1a) is the ratio of the maximum possible NO concentration produced divided by the $O_2({}^{1}\Sigma_{g}^{+})$ concentration; this assumes that there are no other losses of $O_2({}^{1}\Sigma_{g}^{+})$. Table 3 lists the calculated upper limits for the yield of NO at three different temperatures. Our overall value for the upper limit of the yield was < 0.0015 over the range 210 to 365 K. The chemiluminescence detection of NO in these experiments was limited by small signal to noise levels and drift in the background signal. For this reason, we elected to additionally measure the yield of NO₂ from channel (1a); see the next section.

3.2.2 Upper limit of NO₂ production from $O_2({}^{l}\Sigma_{g}^{+}) + N_2O$

For experiments aimed at measuring the NO₂ yield from reaction (1) as well as those in the next two sections, a large total amount of $O_2({}^{1}\Sigma_{g}^{+})$ was produced by the repeated excitation of a static O_2/N_2O gas mixture with the 762 nm laser tuned to the peak of a $O_2({}^{1}\Sigma_{g}^{+}) \leftarrow O_2({}^{3}\Sigma_{g}^{-})$ transition. The mixture was then expanded into a second absorption cell for the detection of the product. In these experiments, the product gas mixture was expanded from the photolysis cell (~400 cm³) into a cell (65.72 cm long, ~750 cm³) used with the diode array spectrometer (described previously) to observe NO₂ production.

Any loss of NO₂ during in this transfer would lead to an error in the yield; therefore we examined various possible losses for NO₂ in the system. First, NO₂ loss via its ternary reactions with NO or itself (NO₂ + NO + M \rightarrow N₂O₃ + M or NO₂ + NO₂ + M \rightarrow N₂O₄ + M) were insignificant ($\ll 1\%$ of initial [NO₂] lost) for our experimental conditions and timescales (k(NO₂ + NO + M = 3.1×10^{-34} cm⁶ molecule⁻² s⁻¹; k(NO₂ + NO₂ + M = 1.4×10^{-33} cm⁶ molecule⁻² s⁻¹ [16]) and N₂O₃ or N₂O₄ would readily decompose back to NO₂. The reactions of NO₂ with either O₂($^{1}\Sigma_{g}^{+}$) or O₂($^{1}\Delta_{g}$) are sufficiently endothermic at our experimental temperatures as to be unimportant. Lastly, multi-photon photolysis of NO₂/O₂/N₂O were subjected to > 3×10^{4} pulses from the 762 nm laser to create a large amount of O₂($^{1}\Sigma_{g}^{+}$). We concluded that NO₂ loss was negligible; we assumed that the total loss of NO₂ < 5% in the calculations below.

To measure NO₂ production from reaction (1a), we repeatedly produced large concentrations of $O_2({}^{1}\Sigma_{g}^{+})$ by the repeated excitation of O_2 at 762 nm in a static mixture of O_2 and N_2O . No evidence of NO₂ production was seen in several experiments. Experimental conditions and results are reported in Table 4 for the experiments that produced the largest concentrations of $O_2({}^{1}\Sigma_{g}^{+})$. An upper limit for the NO₂ yield from channel (1a) was calculated. The maximum possible number of NO₂ molecules produced was calculated from the minimum detectable NO₂ concentration, determined from the calibration experiment (described in

Experi- ment (Temper- ature in K)	O ₂ (mole- cule cm ⁻³)	N_2O (mole- cule cm ⁻³)	$O_2(^{1}\Sigma_g^+)$ Made per Laser Shot (mole- cule cm ⁻³)	Num- ber of Laser Shots	$\begin{array}{c} Total \\ O_2(^{l}\Sigma_g^{+}) \\ Generated \\ (mole-cule \ cm^{-3}) \end{array}$	Quantity Measured	Yield
NO ₂ Diod	le Array					Maximum NO ₂ Produced (mole- cule cm ^{-3})	Yield of NO ₂ From Channel (1a)
210	3.0×10^{19}	2.1×10^{18}	2.6×10^{12}	180,125	4.7×10^{17}	9.3×10^{13}	2×10^{-4}
295	3.0×10^{19}	2.0×10^{18}	4.7×10^{12}	183,898	8.6×10^{17}	10.0×10^{13}	1.2×10^{-4}
						Upper Limit for NO ₂ Pro- duction	2×10 ⁻⁴
O ₃ Diode	Array					Maximum O_3 Produced (mole- cule cm ⁻³)	Yield of O ₃ From Channel (1c)
298	1.75×10^{19}	4.83×10^{17}	2.74×10^{13}	18,000	4.9×10^{17}	0.79×10^{13}	1.6×10^{-5}
298	1.81×10^{19}	6.44×10^{17}	1.13×10^{13}	24,000	2.7×10^{17}	1.20×10^{13}	4.4×10^{-5}
298	3.20×10 ¹⁹	9.88×10^{17}	1.24×10^{13}	30,200	3.7×10^{17}	1.70×10^{13}	4.5×10^{-5}
298	1.70×10^{19}	8.00×10^{17}	1.86×10^{13}	46,700	8.7×10^{17}	1.00×10^{13}	1.2×10^{-5}
298	3.24×10^{19}	3.47×10^{17}	1.26×10^{13}	21,400	2.7×10^{17}	1.75×10^{13}	6.5×10^{-5}
298	1.76×10^{19}	1.59×10^{19}	0.53×10^{13}	21,100	1.1×10^{17}	7.10×10^{13}	6.4×10^{-4}
						Upper Limit for O ₃ Pro- duction	1×10 ⁻³
N ₂ O FTI	R					$\begin{array}{l} Maximum \\ N_2O \ Lost \\ (mole- \\ cule \ cm^{-3}) \end{array}$	Yield of N_2O Lost From Channel (1a), (1b) and (1c)
298	2.01×10^{19}	11×10^{16}	8.46×10^{12}	27,540	2.3×10^{17}	2.73×10^{14}	1.2×10^{-3}
298	2.07×10^{19}	1.08×10^{17}	6.49×10^{12}	16,174	1.0×10^{17}	2.81×10^{14}	2.7×10^{-3}
						Upper Limit for N ₂ O De- struction	3×10 ⁻³

Table 4. Experimental conditions for product studies employing static cell experiments.

experiment section above) carried out either just before or just after the photolysis experiment, and accounting for the possible loss of NO_2 and potential conversion of NO produced by reaction (1a) to NO_2 via the slow reaction with O_2 :

 $NO + NO + O_2 \rightarrow 2 NO_2$

(9)

where $k_9 = 2.0 \times 10^{-38}$ cm⁻⁶ molecule⁻² s⁻¹ [17]. We emphasize that the estimated maximum concentration of NO₂ produced was not based on the detection limit of the diode array instrument, but by our conservative upper limit for the yield. The upper limit for the yield of NO₂ production from reaction (1a) was calculated to be $< 2 \times 10^{-4}$.

3.2.3 Upper limit for O_3 production from $O_2({}^{l}\Sigma_g^{+}) + N_2O$

Possible O₃ production from reaction (1b) was measured in experiments similar to those used to measure NO₂ from channel (1a), except that the diode array spectrometer was tuned to detect O₃. O₃ is destroyed by $O_2({}^{1}\Sigma_{g}^{+})$ via reaction (4). However, the product of this reaction, O(³P), combines with the excess O₂ in our experiments to reform O₃. Thus, 762 nm photolysis of a mixture of O₂ and O₃ should result in no net loss of O₃. This assertion was confirmed by photolyzing several O₃/O₂ mixtures with the 762 nm laser to produce large amounts of O₂(${}^{1}\Sigma_{g}^{+}$) and observing negligible (< 5%) loss of O₃. Varying the laser fluence by more than a factor of 3, using two different ro-vibrational transitions for O₂(${}^{1}\Sigma_{g}^{+}$), and tuning the 762 nm laser off of any O₂(${}^{1}\Sigma_{g}^{-}$) \leftarrow O₂(${}^{3}\Sigma_{g}^{-}$) transitions all yielded the same results. We concluded that the excitation process did not result in any O₃ loss within our ability to detect it.

To search for O₃ production from channel (1b), several N₂O/O₂ mixtures were excited with the 762 nm laser to produce $O_2({}^{1}\Sigma_{g}^{+})$. No evidence of O₃ production was observed in any of six different experiments. The pressure of N₂O in these mixtures was varied from 10 to 490 Torr and two different $O_2({}^{1}\Sigma_{g}^{+})$ $\leftarrow O_2({}^{3}\Sigma_{g}^{-})$ ro-vibrational transitions were used. The maximum O₃ concentration that was produced was calculated from the noise in the absorption spectrum recorded after the excitation (defined as twice the standard deviation of the mean signal). The ratio of this maximum possible O₃ concentration produced to the $O_2({}^{1}\Sigma_{g}^{+})$ concentration was taken to be the upper limit for the yield of O₃ from channel (1b). The experimental conditions and results are listed in Table 4. The measured upper limits ranged from 1.2×10^{-5} to 6.4×10^{-4} . We conservatively place an upper limit of 1×10^{-3} for reaction (1b) at 298 K. This yield was not measured at other temperatures.

3.2.4 Upper limit for N_2O destruction by $O_2({}^{l}\Sigma_g^{+}) + N_2O$

To measure the possible loss of N₂O from reaction (1), we excited static N₂O/O₂ mixtures with the 762 nm laser to produce large concentrations of $O_2({}^{1}\Sigma_{g}^{+})$ and measured the concentration of N₂O before and after excitation. Experiments were run with the 762 nm laser tuned to the R7Q8 transition in $O_2({}^{1}\Sigma_{g}^{+}) \leftarrow O_2({}^{3}\Sigma_{g}^{-})$, and, also with the laser tuned off the $O_2({}^{1}\Sigma_{g}^{+})$ transitions (Table 4). No significant destruction of N₂O was observed, and the difference of the peak area of the N₂O IR absorption feature when the laser was tuned on the $O_2({}^{1}\Sigma_{g}^{+})$ $O_2({}^{3}\Sigma_{g}^{-})$ transition was always less than or equal to that measured with the laser tuned off of the transition. The maximum difference in peak areas of the N₂O

absorption feature in these experiments was 0.02 cm⁻¹. We combined this maximum "signal" with the noise level in a background section of the baseline in the absorption spectrum (twice the standard deviation of the mean signal multiplied by the wavelength range) of 0.006 cm⁻¹ to estimate a conservative upper limit for the possible decrease in the integrated area of the N₂O feature of 0.05 cm⁻¹. The total concentration of $O_2({}^{1}\Sigma_{g}^{+})$ was calculated as before, by accounting for the ratio of the photolysis laser beam size to the total cross sectional area of the cylindrical absorption cell. Our overall value for the upper limit for the fraction of N₂O lost from reaction (1) was < 3×10^{-3} at 298 K. This yield was not measured at other temperatures.

4. Discussion

4.1 Rate coefficient for the reaction of $O_2(^1\Sigma_g^+)$ with N_2O

Our room temperature value of k_1 and previous measurements of k_1 are listed in Table 2. Our value is higher than three previously reported values [18–20], while it agrees well with that reported by Borrell et al. [21]. It should be noted that the results of Gauthier and Snelling [18] are very uncertain. The reasons for the differences between our measurement and those of Thomas and Thrush [19] and Filseth et al. [20] are not apparent; but, it is worth noting that they all overlap with our values given the combined uncertainties. In a recent study, we have shown that rate coefficients for other reactions of $O_2({}^{1}\Sigma_g^{+})$ determined with this same experimental apparatus compared well to other previous determinations [5]. For the room temperature value of k_1 , we therefore recommend a weighted average of the two most recent studies (Borrell's group and ours), $k_1(298 \text{ K}) = (1.02 \pm 0.14) \times 10^{-13} \text{ cm}^{3}$ molecule⁻¹ s⁻¹.

Only Borrell et al. [21, 22] measured k_1 at temperatures other than 298 K. They reported k_1 at room temperature and at temperatures greater than 500 K. Our results (E_a/R of (-87 ± 40) K) are completely consistent with that reported by Borrell et al. For atmospheric purposes however, our results should supersede those of Borrell et al. because our study incorporated measurements at more temperatures in the range applicable to the atmosphere, allowing for a more precise determination of $k_1(T)$ in this temperature range and the results of Borrell's group will be an extrapolation from a different temperature regime.

We suggest values of k_1 in the format used by the NASA/JPL data evaluation panel for atmospheric models [1] to be:

 $k_1 = 1.0 \times 10^{-13} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$; f(298 K) = 1.1 A = 7.5×10⁻¹⁴ cm³ molecule⁻¹ s⁻¹ E/R = 85 K and g = 40 K The parameters f and g are defined in the evaluation. The above values are slightly different from the values recommended by the NASA/JPL evaluation, [1] which also used the results from our study.

4.2 Product studies

Our results on the possible products of reaction (1) can be summarized as follows: (a) The yield of NO is less than 0.0015, independent of temperature between 210 and 365 K; (b) The yield of NO₂ is less than 2×10^{-4} , independent of temperature between 210 and 295 K; (c) Yield of O₃ is less than 1×10^{-3} at 298 K; and (d) The net loss of N₂O in the interactions with $O_2(^{1}\Sigma_g^{+})$ is less than 1×10^{-3} at 298 K. Based on these, we place the upper limits for the branching ratios of channels (1a) and (1b), respectively, to be 2×10^{-4} and 1×10^{-3} respectively. If N₂O₃ were formed in channel (1c), we would have observed production of either NO in the chemiluminescence experiments or of NO2 in the diode array experiments; N₂O₃ readily thermally decomposes into NO and NO₂ at room temperature (K_{eq}(295 K) = 2.1×10^{-20} cm⁻³ molecule⁻¹ [1] for NO + $NO_2 \leftrightarrow N_2O_3$ reaction). Therefore, the upper limit for the production of NO_2 of 2×10^{-4} is a measure of the yields of channels (1a) and (1c). Lastly, we did not observe any measurable destruction of N₂O, due to the sum of channels (1a), (1b) and (1c), with an upper limit of 3×10^{-3} for the total reactive loss. As discussed in a recent study from our lab, there exists a log-linear trend between $O_2({}^{1}\Sigma_{g}^{+})$ rate coefficients and the highest vibrational frequency of the quenching molecule [5]. N₂O falls in line with this trend ($k_1 = 1.06 \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹ and $v \sim 3490$ cm⁻¹ [23]). Therefore, we conclude that channel (1e) is the predominant channel, >99.6%, for this reaction.

5. Atmospheric implications

As noted in the introduction, there are two potential impacts of reaction (1) on the atmosphere: (1) production of NO_x in the atmosphere and (2) decreasing the lifetime of N₂O. Our upper limit for the branching ratio for NO production in reaction (1a) shows that it is approximately an order of magnitude lower than the values used by Toumi [3] and Siskind [2]; therefore, our results lead to the conclusion that reaction (1a) can be discounted as a source of NO_x production in the stratosphere. Toumi [3] calculated that a 1% yield for channel (1a) would equal the currently accepted scheme of O(¹D) + N₂O reaction as the source of NO_x in the stratosphere. Our upper limit for the NO₂ yield from reaction (1a) of 2×10^{-4} leads us to conclude that reaction (1a) contributes at most 2% to the NO_x production in the stratosphere. To examine other altitudes, we employed an atmospheric box model (described elsewhere [24]) and calculated the NO_x production rate from channel (1a) using our value for the upper limit of the NO_x yield. Figure 4 shows a comparison of NO_x production from reactions (1a) and



Fig. 4. Results from a simple atmospheric box model. In the top panel, the atmospheric NO_x production rate from $O_2(^{1}\Sigma_{g}^{+}) + N_2O$ and $O(^{1}D) + N_2O$ are shown as a function of altitude at two different solar zenith angles. In the bottom panel, the fraction of the total NO_x production rate contributed by the reaction of $O_2(^{1}\Sigma_{g}^{+}) + N_2O$, derived from the top panel, is also shown as a function of altitude. We conclude that the reaction $O_2(^{1}\Sigma_{g}^{+}) + N_2O$ is not a significant source of NO_x in the atmosphere.

(2a). The largest relative contribution of reaction (1a) to the NO_x production rate is below 10 km, where other NO_x production pathways dominate. (These pathways include anthropogenic emissions and lightning.) In the stratosphere, where Toumi [3] and Siskind [2] speculated that reaction (1a) could be influential, the largest contribution from reaction (1) was at most 10% of the total production of NO_x, but only at high sun zenith angles when the production rates are very low. Prasad [4] has speculated on the possibility of NO_x production via N₂O₃ formation in channel (1c) followed by N₂O₃ photolysis. Based on our results, we conclude that this pathway is a negligible contributor to NO_x production. These conclusions are based on our conservative upper limit for the yield of NO_x from



Fig. 5. The lifetime of N₂O due to photolysis and due to the reaction of $O_2({}^{1}\Sigma_{g}^{+}) + N_2O$, as determined from our upper limit for the destruction of N₂O, is shown as a function of altitude.

reaction (1a), and we generally conclude that the reaction of $O_2(^{1}\Sigma_g^{+})$ with N_2O is not an important source of NO_x anywhere in the atmosphere.

Lastly, we utilized our simple atmospheric box model to determine the relative influence of reaction (1) on the loss rate of N_2O from our upper limit for the destruction of N_2O . Figure 5 shows the lifetime of N_2O due to reaction (1) versus altitude, as well as the lifetime of N_2O due to photolytic loss [1] for comparison. The loss rate for N_2O due to reaction (1) is only comparable to the photolysis rate below 20 km where the lifetime of N_2O is greater than 1000 years, much greater than transport lifetimes. Thus, reaction (1) is concluded to be an insignificant sink of N_2O everywhere in the atmosphere.

In conclusion, this study has shown that the reaction of $O_2({}^{1}\Sigma_{g}^{+})$ with N₂O is not an important source of NO_x anywhere in the atmosphere. In addition reaction (1) is not a significant sink for N₂O anywhere in the atmosphere either.

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