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The Effect of Oxygen on Nonthermal-Plasma Reactions of Nitrogen Oxides in Nitrogen

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Abstract

NO is mainly converted to NO$_2$ by chemical oxidation in the presence of oxygen. Initial selectivity analysis shows that three electron collision reactions are important for NO$_x$ evolution in O$_2$/N$_2$. The rate constants of these reactions decrease with increasing oxygen concentration. This is because oxygen is electronegative and hence reduces electron concentration. The rate constant of O$_2$ dissociation by electron collision reaction is almost two orders of magnitude higher than that of N$_2$ dissociation. NO formation occurs predominantly through N($^2$D) + O$_2$ → NO + O. The critical oxygen concentration, defined as the concentration above which the NO$_x$ formation rate exceeds the NO$_x$ decomposition rate, increases with increasing the initial NO concentration.

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Introduction

The removal of nitrogen oxides (NO\textsubscript{x}) from combustion exhaust streams has become an important international technology issue because of the key role NO\textsubscript{x} play in many global environmental problems, such as acid rain, photochemical smog formation, and the greenhouse effect. There is considerable political pressure for the adoption of increasingly stringent emission standards. Among the emerging technologies for NO\textsubscript{x} decomposition, non-thermal plasma is one of the most promising. A pulsed corona discharge reactor (PCDR) is one of the non-thermal plasma technologies characterized by low gas temperature and high electron temperature achieved by producing high energy electrons in the gas while leaving the bulk temperature of the gas unchanged. A PCDR utilizes a high-voltage short-duration (<100 ns) electrical discharge between non-uniform electrodes to produce streamers through the growth of electron avalanches formed by electron collision ionization events in the gas.\textsuperscript{1} A streamer is a region of highly ionized gas in which a variety of active radicals and chemical species are formed through electron collision reactions with the background gas.\textsuperscript{2} These active species, in turn, initiate bulk phase reactions that lead to NO\textsubscript{x} conversion.

NO\textsubscript{x} removal is generally a problem of NO removal because NO accounts for about 95 mol\% of NO\textsubscript{x} emitted.\textsuperscript{3} There are two main pathways for NO conversion: chemical oxidation and chemical reduction. Conversion of NO to its molecular elements (N\textsubscript{2} and O\textsubscript{2}) through chemical reduction is one of the most attractive methods, especially for mobile source applications.

NO conversion in N\textsubscript{2} using non-thermal plasma has been extensively investigated.\textsuperscript{2,4-8} In such a system, NO is readily converted to benign gas (N\textsubscript{2} and O\textsubscript{2}) through a reduction mechanism involving N radicals, with formation of only small amounts of byproduct N\textsubscript{2}O (1-2\% of initial NO concentration).\textsuperscript{9} However, real combustion flue gas, for example, from furnaces
and fired heaters, contains 1-6% of oxygen depending on combustion conditions.\textsuperscript{10} Our recent measurements indicate the oxygen concentration in diesel engine exhaust is even higher (12~14%), which makes NO conversion more complex.

Oxygen can reduce the rate of NO reduction to \( \text{N}_2 \) and \( \text{O}_2 \) in two ways. First, as an electronegative gas (with an electron affinity of 0.45 eV for \( \text{O}_2 \) compared to about -1.5 eV for \( \text{N}_2 \)),\textsuperscript{11,12} oxygen decreases the discharge current due to the electron attachment process, as found by Kanazawa \textit{et al.}\textsuperscript{13} and Mok \textit{et al.}\textsuperscript{14} Sathiamoorthy \textit{et al.}\textsuperscript{2} investigated the NO\(_x\) reaction mechanism in nitrogen and dry air by both experiment and simulation. They found that the electron density in dry air decreases by several orders of magnitude compared to that in \( \text{N}_2 \) due to the effect of the electron attachment to \( \text{O}_2 \). A similar effect of oxygen on the electrical discharge was observed by Gallimberti.\textsuperscript{15} Therefore, the presence of oxygen decreases the formation rate of N radicals, which decreases the NO reduction rate to benign \( \text{N}_2 \) and \( \text{O}_2 \). Second, oxygen has a lower dissociation energy (5.2 eV/molecule) than nitrogen (9.8 eV/molecule\textsuperscript{16}), which causes electrons to preferentially interact with \( \text{O}_2 \) to produce strongly oxidizing species such as O and \( \text{O}_3 \). These oxidizing species promote the oxidation of NO to produce byproducts, such as NO\(_2\) and \( \text{N}_2\text{O} \), instead of the desired reduction products, \( \text{N}_2 \) and \( \text{O}_2 \). McLarnon and Penetrante\textsuperscript{17} investigated the effect of 0-6% oxygen concentrations on NO\(_x\) conversion and found that the amount of NO chemically reduced to \( \text{N}_2 \) decreases and the amount of NO oxidized to NO\(_2\) increases, as the \( \text{O}_2 \) content increases. Tas \textit{et al.}\textsuperscript{18} carried out detailed studies on the effect of \( \text{O}_2 \) on energy consumption and NO removal efficiency in \( \text{N}_2 \). They found that over 90% of NO conversion occurs through oxidation in the presence of \( \text{O}_2 \). Therefore, total NO\(_x\) (NO, NO\(_2\) and \( \text{N}_2\text{O} \)) conversion in the corona discharge remarkably declines in oxygen-rich gases, such as \( \text{N}_2/\text{O}_2/\text{NO} \) gas mixtures.\textsuperscript{2,8,19,20} As a result of the relative ease of dissociating \( \text{O}_2 \),
under certain conditions, NOx conversion becomes negative in the presence of O2 (i.e., NOx is produced). Yan et al.\textsuperscript{8} found that the rate of oxidation reactions exceeds the rate of reduction reactions, such as \( N + NO \rightarrow N_2 + O \), when the O2 concentration is higher than 3.6%. Penetrante \textit{et al.}\textsuperscript{21} found that the reduction of NO with ground state N atoms is almost completely counterbalanced by the production of NO at 10\% O2 concentration. Finally, Aritoshi \textit{et al.}\textsuperscript{20} found that the production of NOx becomes dominant when the concentration of O2 reaches 2\%.

These literature results show that there is a critical oxygen concentration above which the NOx formation rate exceeds the NOx decomposition rate.

However, some issues are still unclear. The first is the mechanism of NO formation during electrical discharge in the presence of O2. Gentile and Kushner\textsuperscript{22, 23} investigated microstreamer dynamics during plasma remediation of NO using atmospheric pressure dielectric barrier discharges. They reported that NO formation occurs through reaction with ground state N radicals, N(\textsuperscript{4}S), by the reaction N(\textsuperscript{4}S) + O\textsubscript{2} \rightarrow NO + O because local energy deposition in the streamers can produce high temperatures that initiate advection and facilitate production of NO. Kim \textit{et al.},\textsuperscript{24} Lowke and Morrow\textsuperscript{25} and Mukkavilli \textit{et al.}\textsuperscript{26} proposed a similar mechanism of NO formation. However, Aritoshi \textit{et al.}\textsuperscript{20} proposed that excited N radicals, N(\textsuperscript{2}D), are the primary species responsible for NO formation, through the reaction N(\textsuperscript{2}D) + O\textsubscript{2} \rightarrow NO + O. Herron,\textsuperscript{7} Yan \textit{et al.},\textsuperscript{8} Penetrante \textit{et al.},\textsuperscript{21} and Orlandini and Riedel\textsuperscript{27} presented similar mechanisms for NO formation. Second, the formation and conversion of byproducts are rarely reported and explained, especially for N\textsubscript{2}O. Third, the relationship between the rate of electron collision reactions and oxygen content and the selectivity of electron collision reactions for the dissociation of N\textsubscript{2} and O\textsubscript{2} are rarely reported. Finally, the critical oxygen content may change
with the initial NO concentration, but no detailed studies on the critical oxygen content have been reported.

Therefore, the goals of this work are to study the effect of O\textsubscript{2} on NO conversion in a PCDR, through experiments and simulation, to clarify the mechanism of NO\textsubscript{x} formation and conversion in the presence of O\textsubscript{2}, to understand the relationship between the rate of electron collision reactions and oxygen content, and to study the relationship between the critical oxygen content and initial NO concentration.

**Experimental**

The experimental setup is shown in Figure 1. The test gas was prepared by mixing the gas from the two sets of gas cylinders, one set with NO in N\textsubscript{2} (three concentrations were used: 655 ppm NO, 659 ppm NO, or 800 ppm NO in ultra high purity N\textsubscript{2}, US Airgas) and the other set with O\textsubscript{2} in N\textsubscript{2} (four concentrations were used, approximately: 5\% O\textsubscript{2}, 10\% O\textsubscript{2}, 15\% O\textsubscript{2} and 30\% O\textsubscript{2} in ultra high purity N\textsubscript{2}, USAirgas). These gases were mixed through a careful flow rate control to obtain the desired concentrations of NO and O\textsubscript{2} in nitrogen fed to PCDR shown in Table 1. The PCDR feed was prepared and maintained at ambient temperature (~300 K). The pressure in the PCDR was maintained at 217 kPa with control valves on the outlet gas lines. The oxygen concentration at the PCDR outlet was analyzed using a Hewlett Packard 5890 series II Gas Chromatograph (GC) with a thermal conductivity detector (TCD) and an Alltech CTR I column (outer tube with 6 ft × 1/4″ packing of activated molecular sieve and inner tube with 6 ft × 1/8″ packing of porous polymer mixture). The outlet gas was collected in 300 ml stainless steel cylinders (as shown in Figure 1) and analyzed for stable nitrogen oxides using a Spectrum 2000 Perkin-Elmer Fourier transform infrared spectrometer (FTIR) with a narrow-band mercury cadmium telluride (MCT) detector.
The PCDR used in this work consisted of a high-voltage power supply with control unit and pulser/reactor assembly, as explained previously in detail. The high voltage controller contained electronic and gas controls required to regulate the high voltage charging power supply as well as the pulsed power delivered to the reactor gas. The pulser/reactor assembly contained the pulsed power generator and the pulsed corona discharge reaction chambers. The reactor had ten parallel reaction tubes, each 914 mm in length and 23 mm in diameter, with a stainless steel wire, 0.58 mm in diameter, passing axially through the center of each tube. The wire was positively charged and the tube was grounded. The gas flowing through the reactor tube was converted to a plasma by high voltage discharge from the reactor anodes. One tube was fitted with UV-grade quartz windows for diagnostics and plasma observation. The energy delivered to the reactor per pulse can be calculated either from time integral of the product of the measured pulse discharge voltage (V) and current (I) or from \((1/2)CVc^2\), where C is the pulse forming capacitance, 800 pF; \(Vc\) is the constant charge voltage, 19.2 ± 1 kV, in the pulse forming capacitance before discharge. The discrepancy between the calculated values for energy per pulse using these two methods is measured to be less than 3%. Since the current can fluctuate and be shifted in phase relative to voltage, and since the delay times of the voltage sensor and current sensor cannot be measured accurately, the second method should be more reliable. Therefore, the second method, \((1/2)CVc^2\), is used to calculate energy input per pulse in this work.

The power consumed, \(W\) (J \(\cdot\) s\(^{-1}\)), is calculated as the product of the input energy per pulse and the pulse frequency. The specific energy input, \(Es\) (kJ \(\cdot\) m\(^{-3}\)), is defined as

\[
es = \frac{W}{1000 \cdot u} \tag{1}
\]

where \(u\) is gas flowrate (m\(^3\) \(\cdot\) s\(^{-1}\)). The system design permitted variation and measurement of the applied voltage and frequency and of the reactor current and voltage.
The plasma reactor described above was modeled using a lumped kinetic model that describes the evolution of all species, reported elsewhere.\textsuperscript{5}

**Results and Discussion**

**Experimental observations**

Figure 2 shows the FTIR spectra for NO conversion in N\textsubscript{2} (Figure 2(a)) and in 4.60\% O\textsubscript{2} in N\textsubscript{2} (Figure 2(b)) at a pulse frequency of 200 Hz and applied voltage of \textasciitilde 20 kV. Similar FTIR spectra were obtained during NO conversion with the other oxygen concentrations shown in Table 1. Only NO, NO\textsubscript{2} and N\textsubscript{2}O were detected in these spectra of the outlet gas from the PCDR. Other nitrogen oxides, such as N\textsubscript{2}O\textsubscript{5} (peaks expected at 787.90-793.89 cm\textsuperscript{-1} and 1217.09-1305.73 cm\textsuperscript{-1}),\textsuperscript{29} and O\textsubscript{3} (peaks expected at 980-1080 cm\textsuperscript{-1})\textsuperscript{29} were not detected. The FTIR detection limit is 5 ppm for both nitrogen oxides and ozone. Herron\textsuperscript{7} simulated the NO reaction in dry air and found that N\textsubscript{2}O\textsubscript{5} should be formed as a terminal product, but no experimental data support this conclusion.

Figures 3(a), (b) and (c) show the evolution of NO, NO\textsubscript{2} and N\textsubscript{2}O concentrations, respectively, as functions of specific energy inputs. In the absence of O\textsubscript{2}, the NO concentration decreases quickly to zero with increasing specific energy input (filled squares in Figure 3(a)). The NO\textsubscript{2} concentration initially increases to a maximum with increasing specific energy input, and then decreases to zero at the same specific energy input at which the NO concentration reaches zero (filled squares in Figure 3(b)). The N\textsubscript{2}O concentration also increases to a maximum and then decreases to a constant value with increasing specific energy input (filled squares in Figure 3(c)). Figure 3(d) shows the NO\textsubscript{x} conversion as a function of specific energy input. The NO\textsubscript{x} conversion can be defined as the fraction of NO converted to N\textsubscript{2}, expressed as follows:
\[ X_{NO_x} = \frac{C_{i,NO} - C_{o,NO} - C_{o,NNO_2} - 2 \times C_{o,N_2O}}{C_{i,NO}} \times 100\% \] (2)

where \( C_i \) is the concentration of a given species at the reactor inlet (ppm) and \( C_o \) is the concentration of a given species at the reactor outlet (ppm). In the absence of \( O_2 \), the overall \( NO_x \) conversion initially increases linearly with increasing specific energy input until reaching a constant value at 98.5 ± 0.5\% because of the difficulty of converting \( N_2O \) (filled squares).\(^4,\,5,\,9\)

This behavior of \( NO_x \) concentrations in pure \( N_2 \) can be explained quantitatively using the reaction mechanism developed previously.\(^4,\,5,\,9\)

However, when oxygen is present, the \( NO \) conversion and byproduct formation is more complex. At low \( O_2 \) concentrations, for example 2.28\% \( O_2 \) (open circles in Figure 3(a)), the \( NO \) concentration decreases quickly with increasing specific energy input for low specific energies (<100 kJ/m\(^3\)), but at high specific energy input (>100 kJ/m\(^3\)), it decreases slowly with increasing specific energy input. \( NO \) is not fully converted at the highest specific energy tested. At high \( O_2 \) concentrations (≥4.60\% \( O_2 \), open triangles in Figure 3(a)), the \( NO \) concentration initially decreases with increasing specific energy input until it reaches a minimum, after which it increases slowly with increasing specific energy input. Figure 3(b) shows that the \( NO_2 \) concentration forms a shallow maximum at the two lower oxygen concentrations, while it increases continually with increasing specific energy at the two higher oxygen concentrations. \( NO_2 \) cannot be completely converted in the presence of \( O_2 \) at the same specific energy inputs at which \( NO_2 \) is completely converted in the absence of \( O_2 \). In contrast to \( N_2O \) in the absence of oxygen, Figure 3(c) shows that there is no maximum for \( N_2O \) formation in the presence of oxygen. The \( N_2O \) concentration increases continuously with increasing specific energy input. At a given specific energy input, the amount of \( NO_2 \) and \( N_2O \) formed increases with increasing oxygen content, as shown in Figures 3(b) and (c), respectively. The \( NO_x \) conversion shown in
Figure 3(d) changes from a positive value to a negative value for all oxygen concentrations greater than ~2.5%. According to Eq. (2), a positive NO\textsubscript{x} conversion means that some NO is converted to N\textsubscript{2} and O\textsubscript{2}. However, a negative NO\textsubscript{x} conversion means that the amount of NO\textsubscript{x} formed is greater than the amount of NO reduced to N\textsubscript{2}/O\textsubscript{2}. The amount of NO\textsubscript{x} formed increases with increasing oxygen concentration. This phenomenon will be further discussed in terms of the lumped model.\textsuperscript{5}

**Electron Collision Reactions**

The collisions of energetic electrons produced by the electrical discharge with gas molecules produce chemically active species, such as radicals and ions, which contribute to NO\textsubscript{x} formation and conversion.\textsuperscript{30} The initial selectivity analysis developed recently\textsuperscript{4} was used to identify the chemically active species produced by electron collision reactions that are important in NO\textsubscript{x} formation and conversion. For this analysis, electron interactions with species other than N\textsubscript{2} and O\textsubscript{2} were not considered since their concentrations relative to N\textsubscript{2} and O\textsubscript{2} are always very low.\textsuperscript{5, 30} Further, McLarnon and Penetrante\textsuperscript{17} found that charged species do not contribute significantly to NO\textsubscript{x} conversion. Our previous investigation\textsuperscript{4} on NO\textsubscript{x} conversion in non-thermal nitrogen plasma confirmed that cations, such as N\textsubscript{2}\textsuperscript{+}, do not contribute to NO\textsubscript{x} conversion. Therefore, reactions with ions are not considered in this analysis.

As reported recently,\textsuperscript{4} the possible chemically active species formed from electron collision reactions with nitrogen include N\textsubscript{2}(A\textsuperscript{3}\Sigma\textsubscript{u}\textsuperscript{+}), N\textsubscript{2}(B\textsuperscript{3}\Pi\textsubscript{g}), N\textsubscript{2}(B\textsuperscript{1}\Sigma\textsubscript{u}\textsuperscript{−}), N\textsubscript{2}(a\textsuperscript{1}\Sigma\textsubscript{u}\textsuperscript{−}), N\textsubscript{2}(a\textsuperscript{1}\Pi\textsubscript{g}), N\textsubscript{2}(W\textsuperscript{1}\Delta\textsubscript{u}), N\textsubscript{2}(C\textsuperscript{2}\Pi\textsubscript{u}), N\textsubscript{2}(E\textsuperscript{3}\Sigma\textsubscript{g}\textsuperscript{+}), N(\textsuperscript{4}S), and N(\textsuperscript{2}D). An initial selectivity analysis of systematic experiments performed in absence of O\textsubscript{2} showed that the active species which play an important role in NO\textsubscript{x} conversion are N\textsubscript{2}(A\textsuperscript{3}\Sigma\textsubscript{u}\textsuperscript{+}) and N(\textsuperscript{4}S).\textsuperscript{4} Other active species are mainly quenched to the ground state by the nitrogen background gas. However, at percent-level O\textsubscript{2} concentrations,
the situation may be different because these active species contribute to O₂ dissociation or NOₓ formation by the following reactions (at 300 K):

\[
\begin{align*}
N_2(A^3\Sigma_u^+) + O_2 & \rightarrow N_2 + O + O \quad k = 1.51 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1} \quad (R1)^{31} \\
N_2(B^3\Pi_g) + O_2 & \rightarrow N_2 + O + O \quad k = 1.20 \times 10^{14} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1} \quad (R2)^{32} \\
N_2(C^3\Pi_u) + O_2 & \rightarrow N_2 + O + O \quad k = 1.81 \times 10^{14} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1} \quad (R3)^{33} \\
N_2(a'1\Sigma_u^-) + O_2 & \rightarrow N_2 + O + O \quad k = 1.69 \times 10^{13} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1} \quad (R4)^{34} \\
N_2(a^1\Pi_g) + O_2 & \rightarrow N_2 + O + O \quad k = 2.59 \times 10^{14} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1} \quad (R5)^{35} \\
N(2D) + O_2 & \rightarrow NO + O \quad k = 3.13 \times 10^{12} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1} \quad (R6)^{36} \\
N(4S) + O_2 & \rightarrow NO + O \quad k = 5.91 \times 10^{7} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1} \quad (R7)^{37}
\end{align*}
\]

Therefore, the chemically active species produced by electron collision reactions with nitrogen may be consumed by four parallel processes:

1. **Natural radiation accompanying optical emission:**

   \[ A^* \rightarrow A + h\nu \quad R_I = k_I C_{A^*} \]

2. **Quenching with the background gas N₂:**

   \[ A^* + N_2 \rightarrow A + N_2 \quad R_q = k_q C_{A^*} C_{N_2} \]

3. **Dissociative quenching or reaction with background gas O₂:**

   \[ A^* + O_2 \rightarrow \text{products} \quad R_d = k_d C_{A^*} C_{O_2} \]

4. **Reaction with NOₓ (conversion of NOₓ):**

   \[ A^* + NO_x \rightarrow \text{products} \quad R_r = k_r C_{A^*} C_{NO_x} \]

In these chemical equations, A* represents any active species; \( k_I \), \( k_q \), \( k_d \) and \( k_r \) are the rate constants of radiation, quenching, dissociative quenching of O₂, and NOₓ conversion, respectively; and \( R_i \) is the reaction rate of reaction type i. The initial selectivity of these four parallel processes can be defined as
where $S_I$, $S_q$, $S_d$ and $S_r$ are the initial selectivities to radiative emission reactions, quenching reactions, O$_2$ dissociation, and NO$_x$ conversion reactions, respectively.

The analysis of initial selectivity is an effective method to examine the significance of the active species. Only the active species which contribute predominantly to NO$_x$ formation and conversion need to be considered. In this work, the highest NO$_x$ concentration in the presence of O$_2$ is less than 600 ppm, while the lowest O$_2$ concentration is 2.28% (mol/mol) in the N$_2$ balance gas. At 217 kPa and 300K, these concentrations of NO$_x$, O$_2$ and N$_2$ are $5.21 \times 10^{-8}$ mol/cm$^3$, $1.98 \times 10^{-6}$ mol/cm$^3$, and $8.49 \times 10^{-5}$ mol/cm$^3$, respectively. Substituting these concentrations and the rate constants for consumption of active species (A*) by radiation, quenching, dissociative quenching of O$_2$, and NO$_x$ conversion (summarized in our previous work$^4$) in equations 3a through 3d, yields the initial selectivities for the four parallel processes presented in Table 2. These results indicate that all of the electronic excited states of molecular nitrogen contribute predominantly to O$_2$ dissociation or quenching. Moreover, with increasing O$_2$ concentration, the contribution of these active species to O$_2$ dissociation further increases.

Therefore, only N(2D), which is an excited atomic N radical, and N(4S), which is the ground state atomic N radical, may directly contribute to NO formation through reactions R6 and
However, a simple comparison shows that \( \text{N}^{(4S)} \) cannot contribute significantly to NO formation regardless of the \( \text{N}^{(4S)} \) concentration. Under the most conservative circumstance of low NO concentration (e.g. 50 ppm NO in the presence of O\(_2\) in the reactor, shown in Figure 3(a)), the rate of NO formation by R7 is about 500 times lower than the rate of NO decomposition by reaction \( \text{N}^{(4S)} + \text{NO} \rightarrow \text{N}_2 + \text{O} \), which has a rate constant of \( 1.87 \times 10^{13} \text{ cm}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1} \). Therefore, \( \text{N}^{(4S)} \) atoms are mainly consumed in reactions with NO and NO\(_2\). As a result, the mechanism of NO formation is predominantly through \( \text{N}^{(2D)} \) in R6. With increasing oxygen concentration, the selectivity of NO formation through \( \text{N}^{(2D)} \) further increases. Cosby found that the dominant dissociation mechanism in pure N\(_2\) plasmas is \( \text{N}_2 \rightarrow \text{N}^{(2D)} + \text{N}^{(4S)} \), indicating that approximately equal amounts of \( \text{N}^{(2D)} \) and \( \text{N}^{(4S)} \) are formed. Hill et al. found that the yield of \( \text{N}^{(2D)} \) during \( \text{N}_2 \) dissociation in air corona discharges is \( \sim 67\% \), which means that \( \text{N}^{(2D)} \) is formed at twice the rate of \( \text{N}^{(4S)} \). Both of these results are consistent with the proposal that NO formation occurs through reaction with \( \text{N}^{(2D)} \) in R6, but they do not provide a consistent value for the relative proportions of \( \text{N}^{(2D)} \) and \( \text{N}^{(4S)} \).

Similar to electron collisions with nitrogen, many active species may be produced when electrons collide with molecular oxygen. Again, the active oxygen species that actually contribute to NO\(_x\) formation and conversion must be determined. The potential energy curve of molecular and atomic oxygen is reported in reference 41. Only two electronic states of O atoms \([\text{O}^{(3P)} \text{ and O}^{(1D)}]\) are energetically accessible at the experimental conditions of this study because the average electron energy in the PCDR is less than 10 eV, as supported by investigation of Eliasson and Kogelschatz. O\(^{(3P)}\) and O\(^{(1D)}\) are the ground state and the first electronic excited state of atomic O radicals, respectively. Therefore, the possible chemically active species formed from electron collision reactions with oxygen are \( \text{O}_2(a^1\Delta_g), \text{O}_2(b^1\Sigma_g^+) \),
Table 3 lists these possible interactions. Extensive literature reviews\textsuperscript{45, 46} reported no reactions with or quenching by the following molecular O\textsubscript{2} electronic excited states: O\textsubscript{2}(3\textPi\textsubscript{u}), O\textsubscript{2}(1\textPi\textsubscript{u}), O\textsubscript{2}(3\textSigma\textsubscript{g}^{-}), O\textsubscript{2}(1\textDelta\textg), O\textsubscript{2}(1\textDelta\textu), O\textsubscript{2}(1\textDelta\textg), O\textsubscript{2}(3\textPi), and O(1D), which can be consumed by natural radiation, reaction, quenching with N\textsubscript{2}, O\textsubscript{2}, or NO\textsubscript{x}.

As a result, only O(1D) or O(3P) or both are involved in the NO\textsubscript{x} formation mechanism. The rate constants for the quenching reactions of O(1D) by N\textsubscript{2} and O\textsubscript{2} (R31 and R32) are equal to or up to four times lower than the rate constants for the reactions of O(1D) and NO\textsubscript{x} (R33-R36), while the total concentration of N\textsubscript{2} and O\textsubscript{2} is 167 times higher than that of NO\textsubscript{x} (based on 600 ppm NO\textsubscript{x}). Comparison of the reaction rates of R31-32 with those of R33-36 shows that O(1D) would be quenched by the background nitrogen and oxygen because the total reaction rate of R31-32 is at least 40 times higher than R33-36 at the prevailing reactant concentrations and any assumed O(1D) concentration. Therefore, only ground state O atoms, O(3P), contribute to NO\textsubscript{x} evolution among all of the active species produced from electron collision reactions with molecular oxygen.

**Mechanism and kinetics**

The previous discussion on electron collision reactions with oxygen indicates that, although many electron collision reactions with O\textsubscript{2} occur in the PCDR, only the O\textsubscript{2} dissociation
reaction must be considered because only O atoms contribute to NO\(_x\) formation. Therefore, only
the following electron collision reaction is considered for molecular O\(_2\):

\[
e + O_2 \rightarrow O(^3P) + O(^3P) + e
\]  
(R37)

As the earlier discussion on electron collision reactions with nitrogen has shown, almost all active species can contribute to NO\(_x\) evolution, either directly through formation of NO\(_x\) by N(\(^2\)D) or indirectly through O\(_2\) dissociation reactions with these excited N\(_2\) species. Therefore, all electron collision reactions resulting in active species formation are considered:

\[
e + N_2 \rightarrow N(^4S) + N(^4S) + e
\]  
(R38)

\[
e + N_2 \rightarrow N(^2D) + N(^2D) + e
\]  
(R39)

\[
e + N_2 \rightarrow N_2(A^3\Sigma_u^+) + e
\]  
(R40)

\[
e + N_2 \rightarrow N_2(B^3\Pi_g) + e
\]  
(R41)

\[
e + N_2 \rightarrow N_2(B^3\Sigma_u^+) + e
\]  
(R42)

\[
e + N_2 \rightarrow N_2(a^1\Sigma_u^-) + e
\]  
(R43)

\[
e + N_2 \rightarrow N_2(a^1\Pi_g) + e
\]  
(R44)

\[
e + N_2 \rightarrow N_2(W^1\Delta_u) + e
\]  
(R45)

\[
e + N_2 \rightarrow N_2(C^3\Pi_u) + e
\]  
(R46)

\[
e + N_2 \rightarrow N_2(E^3\Sigma_g^+) + e
\]  
(R47)

The rate constant of electron collision reactions is a function of electron energy distribution and the cross sections of electronic excitation and molecular dissociation.\(^{26}\) However, the electron energy distribution in the plasma is complicated and not measurable because the electric field is strongly non-uniform, due to strong space-charge field effects, and is time dependent.\(^{21}\) Further, there are large discrepancies in the reported values of the cross sections of electronic excitation
and molecular dissociation. Therefore, a calculation for all of these rate constants of electron collision reactions with N₂ is not feasible.

In our kinetic model, there are two parameters that describe the rate constant of each electron collision reaction, α and β, as shown in the following equation:

\[
k[e] = \beta \sqrt{\frac{1}{\alpha P}} W^{0.75} \exp\left(-\frac{\alpha P}{W}\right)
\]

where P is the system pressure and W is the power input. This expression, based on a Maxwellian distribution function for the electron velocity, semi-empirically describes the rate of electron collision reactions through a pseudo-first order rate constant by combining the true rate constant with the electron concentration. This implies that 20 model parameters would be needed to describe the ten electron collision reactions with N₂ (R38-R47), too many to produce meaningful results. However, the net effect of electron collision reactions R40-R47 is the dissociation of oxygen because all electronic excited states of molecular nitrogen predominantly contribute to O₂ dissociation or are selectively quenched, as shown in Table 2. Thus, a reasonable simplifying assumption is to model the net result of electron collision reactions R40-R47 as the single electron collision reaction R37. The contribution of all molecular nitrogen electronic excited states to O₂ dissociation is presumably far lower than that of direct electron collision reactions with O₂ because the dissociation energy per oxygen molecule, 5.2eV/O₂, is much less than the critical electronic excitation energy of all N₂ electronic excited states (Figure 1 in Reference 4).

In addition to R37, R38 and R39 (electron collision reactions that form N(4S) and N(2D), respectively) are the only electron collision reactions assumed to be important for NOₓ conversion and formation in N₂/O₂ plasma. Both R38 and R39 are included due to the disagreement in previous reports on the relative amounts of N(4S) and N(2D) formed.
Many series and parallel reactions among active species, N₂, O₂ and NOₓ are possible to follow the electron collision reactions. For example, Penetrante et al.⁶ used 287 reactions to simulate NOₓ evolution in a very simple system, NO in N₂. In the present analysis, a total of 28 reactions (shown in Table 4) were selected to simulate NOₓ evolution based on a rough selectivity analysis to determine the controlling reactions by assuming that the slowest reaction among series reactions is the controlling step, while the fastest reaction among parallel reactions is the controlling step. These 28 reactions for NOₓ evolution were analyzed for the NO/N₂/O₂ reaction system.

For such a system, six model parameters must be determined for the three electron collision reactions (R37-39) for the NO in N₂/O₂ system. There are ten components (O, N, N(²D), NO NO₂, N₂O, NO₃, O₃, O₂, N₂) in this reaction system, as shown in Table 4. Therefore, there are ten equations for each of the eight power inputs, which leads to a total of 80 equations used to determine the six parameters (αᵢ and βᵢ, i = 1-3) for a experimental system of 2.28% O₂ + 355 ppm NO in N₂ using the previously reported optimization method.⁵ Figure 4 shows measured and correlated NO, NO₂, and N₂O concentrations for the experiments listed in Table 1. The correlated curves in Figure 4 represent the experimental data, which confirms that the reaction mechanism in Table 4 is a reasonable hypothesis of NOₓ evolution in N₂/O₂ plasma. The concentrations of N₂ and O₂ at the outlet of the reactor used in the model calculations were obtained from nitrogen and oxygen material balances.

No O, N, O₃, NO₃, or N₂O₅ were detected at the outlet of the reactor. The absence of the atomic radicals is consistent with their reactivity, but the absence of the other three molecules was investigated using the model. The lack of ozone in the reactor effluent (Figure 2) can be explained by reaction R65. During all experimental conditions in the presence of oxygen, the NO
concentration is greater than 50 ppm (Figure 3(a)). Assuming that the NO concentration is 50 ppm \((4.34 \times 10^{-9} \text{ mol/cm}^3)\), O\(_3\) conversion, calculated from the rate constant for R65, is shown in Figure 5 as a function of gas residence time. O\(_3\) can be completely converted in 0.1 s of residence time in the reactor. Therefore, NO and O\(_3\) do not coexist in the system. By the same reasoning, NO\(_3\) is undetectable because of reaction R66. The simulation results show that the ozone concentration is less than 1 ppm and the NO\(_3\) concentration is less than 0.001 ppm for all experimental conditions. N\(_2\)O\(_5\) is not formed in detectable quantities because the low NO\(_3\) concentration limits the reaction of NO\(_2\) + NO\(_3\) \(\rightarrow\) N\(_2\)O\(_5\). These model results explain why nitrogen oxides other than NO, NO\(_2\) and N\(_2\)O are undetectable in our experiments.

Model parameters obtained for different O\(_2\) concentrations for the three electron collision reactions (R37-R39) are shown in Figure 6. For each electron collision, model parameter \(\alpha\) remains constant with oxygen concentration (Figure 6(a)). However, model parameter \(\beta\) decays with oxygen concentration as a power function (Figure 6(b)-(d)). Applying a least square regression analysis to these data, \(\beta\) is found to be inversely proportional to the mole fraction of oxygen to a different power for each electron collision reaction:

For R37: \[ \beta = 2.00 \times 10^{-5} \cdot x_{O_2}^{-0.817} \] (5a)

For R38: \[ \beta = 4.00 \times 10^{-7} \cdot x_{O_2}^{-0.314} \] (5b)

For R39: \[ \beta = 5.55 \times 10^{-7} \cdot x_{O_2}^{-0.0726} \] (5c)

where \(x_{O_2}\) is the mole fraction of oxygen. All model parameters \(\beta\) for electron collision reactions R37-R39 are oxygen concentration dependent because the expression for the rate constant of electron collision reactions involves the effect of electron concentration, as shown in Eq. (4). However, electron concentration changes with oxygen concentration in the plasma, as observed
Figure 7(a) shows the rate constants of electron collision reactions R37-R39 (calculated from Eq. (4)) as a function of O₂ concentration at 100 W power input. The rate constant of electron collision reactions decrease with increasing oxygen concentration. Oxygen is electronegative; it has a strong electron affinity (0.45 eV). The presence of O₂ as a reactant reduces the discharge current by capturing electrons and therefore reduces the electron concentration during discharge due to the electron attachment process, as observed by Sathiamoorthy et al., Kanazawa et al., and Mok et al., which results in the decreasing values in the rate constants observed in Figure 7(a).

Figure 7(b) shows the ratio of the rate constant of electron collision reaction with oxygen to the rate constants of electron collision with nitrogen as a function of oxygen mole fraction at different power inputs. The rate constant for N₂ dissociation is approximately two orders of magnitude less than that for O₂ dissociation. McLarnon and Penetrante used theoretical calculations (the Boltzmann code ELENDIF) to estimate the rate constant of electron collision reactions. When they compared the ratio of the rate constants of electron collision reactions with oxygen and nitrogen, they found similar results, which support the validity of our lumped model analysis. At a constant oxygen concentration, Figure 7(b) also shows that the rate constant ratio weakly increases with increasing power input because oxygen has a lower dissociation energy compared to nitrogen dissociation, as discussed earlier.

Substituting the expressions for β from Eq. 5(a)-(c) in Eq.(4), the expressions for the rate of electron collision reactions for R37-R39 become

\[ R_{37} = 2.00 \times 10^{-5} \cdot x_{O_2}^{0.183} \cdot \sqrt{\frac{1}{\alpha P}} \cdot W^{0.75} \cdot \exp\left(-\frac{\alpha P}{W}\right) \cdot \frac{P}{RT} \] (6a)

\[ R_{38} = 4.00 \times 10^{-7} \cdot x_{O_2}^{0.314} \cdot (1 - x_{O_2}) \cdot \sqrt{\frac{1}{\alpha P}} \cdot W^{0.75} \cdot \exp\left(-\frac{\alpha P}{W}\right) \cdot \frac{P}{RT} \] (6b)
\[ R_{39} = 5.55 \times 10^{-7} \cdot x_{O_2}^{-0.6726} \cdot (1-x_{O_2}) \cdot \sqrt{\frac{1}{\alpha P}} \cdot W^{0.75} \cdot \exp\left(\frac{-\alpha P}{W}\right) \cdot \frac{P}{RT} \]  

where \( R_n \) is the rate of reaction \( n \), \( R \) is the gas constant, and \( T \) is gas temperature. These equations indicate that the rate of the electron-oxygen collision reaction increases with increasing oxygen concentration, while the rate of electron-nitrogen collision reactions decreases with increasing oxygen content. Figure 8(a) shows these rate trends for the three electron collision reactions as a function of \( O_2 \) concentration. Using the definition of selectivity given by Eq.3(a)-(d), selectivities for the three parallel electron collision reactions R37-R39 are shown in Figure 8(b). The selectivity of R37 increases with increasing oxygen concentration, while the selectivity of R38 and R39 decreases with increasing oxygen concentration, which is consistent with the results in Figure 8(a). The oxygen reaction (R37) selectivity is always far higher than the selectivity of nitrogen reactions (R38 and R39) over the range of oxygen concentrations examined in this work, which is consistent with the results reported by Penetrante et al. They found that discharge plasma conditions with mean electron energy of less than 10 eV are optimum for the dissociation of \( O_2 \) in preference of \( N_2 \) because a significant fraction of the input power is consumed by dissociation of \( O_2 \). This suggests that most of NO would be converted into \( NO_2 \) by the reaction with \( O \) (R28) in the presence of \( O_2 \).

In addition, the similar selectivity of electron collision reactions R38 and R39 indicates that the branch ratio for \( N(^4S) \) and \( N(^2D) \) formation through electron collision reactions with \( N_2 \) is approximately one, which is consistent with the results reported by Cosby, who found that \( e + N_2 \rightarrow N(^4S) + N(^2D) \) is the dominant dissociation mechanism. In hindsight, the similar nitrogen reaction selectivities suggest that this single reaction could be used to replace both R38 and R39 to decrease the number of parameters in the model by two. Evaluation of the model
with only four parameters ($\alpha$ and $\beta$ for each of the electron collision reactions, R37 and $e + N_2 \rightarrow N(^4S) + N(^2D)$) confirmed that such a model is as accurate as the six parameter model.

**Critical O$_2$ concentration for NO$_x$ formation and conversion**

The reaction mechanism of NO$_x$ conversion in the presence of oxygen, shown in Table 4, suggests that NO is converted to N$_2$ and O$_2$ through reduction with N($^4S$) and N($^2D$) (R48 and R56) and is formed through oxidation with N($^2D$) (R6). Therefore, the O$_2$ concentration at which the production of NO by N($^2D$) counterbalances the reduction of NO by N($^4S$) and N($^2D$) is a critical value. Figure 9 shows an example of the lumped model calculation results, in which the NO$_x$ conversion, defined in Eq. (2), changes as a function of oxygen concentration for an inlet concentration of 350 ppm NO at different specific energy inputs. The same model parameters as those discussed in the previous section were used in this calculation for the three electron collision reactions R37-R39 (Figure 5). NO$_x$ conversion of zero implies that the reduction of NO to N$_2$ and O$_2$ is counterbalanced by the formation of NO, resulting in a constant total NO$_x$ concentration in the reactor. The results in Figure 9 show that the NO$_x$ conversion for all specific energy inputs converges to zero at almost the same oxygen concentration (~2.5%), which is consistent with the previous experimental observation (Figure 3(d)). At lower oxygen concentrations, NO$_x$ conversion is positive, which means that NO is being converted to N$_2$ and O$_2$ faster than it is being produced. At higher oxygen concentrations, NO$_x$ conversion is negative, which means that NO is formed through reaction R6 faster than it is decomposed. The oxygen concentration at which NO$_x$ conversion is zero is defined as the critical oxygen concentration.

Figure 9 shows that, in general, at a given specific energy input, NO$_x$ conversion initially decreases with increasing oxygen concentration and reaches a minimum negative value (i.e., when the NO$_x$ formation rate is maximum). This minimum in NO$_x$ conversion occurs because
the rate of R6 is controlled by the concentration of both O2 and N(2D). At low oxygen concentrations, the effect of increasing oxygen concentration is dominant. However, increasing oxygen concentration causes the nitrogen concentration to decrease, which leads to a decrease of the N(2D) concentration. When the increase in oxygen concentration is unable to compensate for the decrease in N(2D) concentration (at O2 mole fractions of about 0.13), the observed minimum in NOx conversion occurs.

The consumption of N(2D) occurs predominantly through R6, R56 and R58. The rate of R57 is negligible because the concentration of N2O is very low, as shown in Figure 4(c). At oxygen concentrations below the critical concentration, reactions R56 and R58 prevail, resulting in net NO conversion. However, at oxygen concentrations above the critical concentration, R6 prevails, resulting in net NO formation. The formation rate of N(2D) increases with increasing specific energy input, as shown in Eq.6(c). Therefore, at a given oxygen concentration, NOx conversion increases with increasing specific energy input below the critical concentration, while NOx conversion decreases (corresponding to NOx formation) with increasing specific energy input above the critical concentration, as shown in Figure 9.

Figure 10 shows the critical oxygen concentration as a function of initial NO concentration modeled at six specific energy inputs. The critical oxygen concentration increases with initial NO concentration. Consumption of N(2D) by NO conversion through R56 increases with initial NO concentration, which results in a decrease of N(2D) consumption to form NO through R6. Therefore, higher oxygen concentrations are required to increase the reaction rate of R6 in order to counterbalance the reaction rate of R56. Figure 10 also shows that the critical concentrations for different specific energy inputs at the same initial NO concentration are approximately equal, which is consistent with the convergence point shown in Figure 9.
Conclusions

In general, oxygen reduces NO\textsubscript{x} conversion and increases its formation in a pulsed corona discharge reactor. Ozone and nitrogen oxides other than NO, NO\textsubscript{2} and N\textsubscript{2}O are not detected at the outlet of the reactor in our experiments. NO is mainly converted to NO\textsubscript{2} by chemical oxidation in the presence of oxygen. Initial selectivity analysis shows that three electron collision reactions are important for NO\textsubscript{x} reactions in O\textsubscript{2}/N\textsubscript{2}, although subsequent analysis shows that only two are required to accurately model the system. The rate constants of these electron collision reactions, calculated for different oxygen concentrations from a kinetic model, decrease with increasing oxygen concentration. The rate constant of O\textsubscript{2} dissociation by electron collision reaction is almost two orders of magnitude higher than that of N\textsubscript{2} dissociation by electron collision because oxygen has a lower dissociation energy compared to nitrogen. A reaction mechanism proposed for NO\textsubscript{x} conversion and formation in O\textsubscript{2} and N\textsubscript{2} plasma leads to a good agreement between the model data and experimental data. NO is converted to N\textsubscript{2} and O\textsubscript{2} through reduction reactions and is formed through an oxidation reaction in the presence of oxygen in the PCDR. The mechanism of NO formation occurs mainly by the reaction of N(\textsuperscript{2}D) radicals with molecular oxygen: N(\textsuperscript{2}D) + O\textsubscript{2} → NO + O. The critical oxygen concentration, which is defined as the oxygen concentration with zero net NO\textsubscript{x} conversion, increases with increasing initial NO concentration.

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acknowledge experimental assistance provided by Dr. S. Legowski and Mr. R. Borgialli.

**Literature cited**


2 Sathiamoorthy G, Kalyana S, Finney WC, Clark RJ, Locke BR. Chemical Reaction Kinetics
and Reactor Modeling of NOx Removal in a Pulsed Streamer Corona Discharge Reactor.

3 Zhou Q, Yao SC, Russell A, Boyle J. Flue gas nitrogen oxide (NOx) reduction using ammonia

4 Zhao G-B, Hu X, Argyle MD, Radosz M. N Atom Radicals and N$_2$(A$^3\Sigma_u^+$) Found to be

5 Zhao G-B, Hu X, Yeung MC, Plumb OA, Radosz M. Nonthermal Plasma Reactions of Dilute

6 Penetrante BM, Hsiao MC, Merritt BT, Vogtlín GE, Wallman PH. Comparison of Electrical

7 Herron JT. Modeling Studies of the Formation and Destruction of NO in Pulsed Barrier

8 Yan K, Kanazawa S, Ohkubo T, Nomoto Y. Oxidation and Reduction Processes During NOx
19:421-443.

9 Zhao G-B, Garikipati SVBJ, Hu X, Argyle MD, Radosz M. Effect of Reactor Configuration on

10 Dinelli G, Civitano L, Rea M. Industrial Experiments on Pulse Corona Simultaneous


34 Piper LG. Quenching Rate Coefficients for N₂(a¹Σ⁺). *J. Chem. Phys.* 1987; 87:1625-1629.

35 Marinelli WJ, Kessler WJ, Green BD, Blumberg WAM. Quenching of N₂(a¹Πg, v'=0) by N₂, O₂, CO, CO₂, CH₄, H₂, and Ar. *J. Chem. Phys.* 1989; 90:2167-2173.


45 http://gaphyor.lpgp.u-psud.fr/gaphyor.


**Table Captions**

Table 1. Experiments at 217 kPa

Table 2. Initial selectivity of consumption of active species of nitrogen by radiation, quenching, \( \text{O}_2 \) dissociation and NO\(_x\) conversion

Table 3. Chemical reactions and rate constants relevant to active species of oxygen

Table 4. Chemical reactions and rate constants for NO\(_x\) in N\(_2\)/O\(_2\)
Table 1. Experiments at 217 kPa

<table>
<thead>
<tr>
<th>System Flowrate (m³/s)</th>
<th>Residence time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>659 ppm NO + N₂</td>
<td>1.81 × 10⁻⁴</td>
</tr>
<tr>
<td>2.28% O₂ + 355 ppm NO + N₂</td>
<td>2.64 × 10⁻⁴</td>
</tr>
<tr>
<td>4.60% O₂ + 358 ppm NO + N₂</td>
<td>2.54 × 10⁻⁴</td>
</tr>
<tr>
<td>7.07% O₂ + 428 ppm NO + N₂</td>
<td>2.58 × 10⁻⁴</td>
</tr>
<tr>
<td>13.6% O₂ + 437 ppm NO + N₂</td>
<td>2.54 × 10⁻⁴</td>
</tr>
</tbody>
</table>

Table 2. Initial selectivity of consumption of active species of nitrogen by radiation, quenching, O₂ dissociation and NOₓ conversion

<table>
<thead>
<tr>
<th>Active species</th>
<th>k₁ (s⁻¹)</th>
<th>kₐC₂N₂(s⁻¹)</th>
<th>kₙC₂O₂(s⁻¹)</th>
<th>kᵣCₙOₓ(s⁻¹)</th>
<th>S₁ (%)</th>
<th>S₂ (%)</th>
<th>S₃ (%)</th>
<th>S₄ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂(A³Σ_u⁺)</td>
<td>0.526</td>
<td>154</td>
<td>2.99 × 10⁶</td>
<td>4.08 × 10⁷</td>
<td>~ 0</td>
<td>~ 0</td>
<td>88.0</td>
<td>~ 12.0</td>
</tr>
<tr>
<td>N₂(B³Π_g)</td>
<td>2 × 10⁵</td>
<td>1.54 × 10⁶</td>
<td>2.38 × 10⁸</td>
<td>1.26 × 10⁷</td>
<td>~ 0</td>
<td>86.0</td>
<td>13.3</td>
<td>0.7</td>
</tr>
<tr>
<td>N₂(B²Σ_u⁻)</td>
<td>2.60 × 10⁴</td>
<td>1.54 × 10⁹</td>
<td>2.38 × 10⁸</td>
<td>1.26 × 10⁷</td>
<td>~ 0</td>
<td>86.0</td>
<td>13.3</td>
<td>0.7</td>
</tr>
<tr>
<td>N₂(a¹Σ_u⁻)</td>
<td>43.5</td>
<td>9.68 × 10⁶</td>
<td>3.35 × 10⁷</td>
<td>1.13 × 10⁷</td>
<td>~ 0</td>
<td>17.8</td>
<td>61.5</td>
<td>20.7</td>
</tr>
<tr>
<td>N₂(a¹Π_g)</td>
<td>1.80 × 10⁴</td>
<td>1.12 × 10⁹</td>
<td>5.13 × 10⁸</td>
<td>1.13 × 10⁷</td>
<td>~ 0</td>
<td>68.1</td>
<td>31.2</td>
<td>0.7</td>
</tr>
<tr>
<td>N₂(W¹Δ_u)</td>
<td>6.50 × 10²</td>
<td>5.11 × 10⁸</td>
<td>[-]</td>
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<td>~ 0</td>
<td>96.5</td>
<td>[-]</td>
<td>3.5</td>
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<tr>
<td>N₂(C¹Π_u)</td>
<td>2.73 × 10⁴</td>
<td>5.11 × 10⁸</td>
<td>3.58 × 10⁸</td>
<td>[-]</td>
<td>3.0</td>
<td>57.0</td>
<td>39.9</td>
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<tr>
<td>N₂(E³Σ_g⁻)</td>
<td>5.26 × 10³</td>
<td>5.11 × 10⁸</td>
<td>[-]</td>
<td>[-]</td>
<td>~ 0</td>
<td>100</td>
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<td>[-]</td>
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<tr>
<td>N(²D)</td>
<td>1.07 × 10⁵</td>
<td>8.66 × 10⁵</td>
<td>6.20 × 10⁶</td>
<td>1.88 × 10⁶</td>
<td>~ 0</td>
<td>9.7</td>
<td>69.3</td>
<td>21.0</td>
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<tr>
<td>N(²S)</td>
<td>0</td>
<td>0</td>
<td>118</td>
<td>9.74 × 10⁵</td>
<td>0</td>
<td>0</td>
<td>~ 0</td>
<td>100</td>
</tr>
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Table 3. Chemical reactions and rate constants relevant to active species of oxygen

<table>
<thead>
<tr>
<th>Chemical reaction</th>
<th>Rate constant*</th>
<th>Source</th>
<th>No.</th>
</tr>
</thead>
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<tr>
<td><strong>O$_2$(a'Δg) reactions</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O$_2$(a'Δg) → O$_2$ + hv</td>
<td>3.70 × 10$^{-4}$</td>
<td>Schofield$^{47}$</td>
<td>R8</td>
</tr>
<tr>
<td>O$_2$(a'Δg) + N$_2$ → O$_2$ + N$_2$</td>
<td>8.43 × 10$^{4}$</td>
<td>Atkinson et al.$^{48}$</td>
<td>R9</td>
</tr>
<tr>
<td>O$_2$(a'Δg) + O$_2$ → O$_2$ + O$_2$</td>
<td>9.63 × 10$^{5}$</td>
<td>Atkinson et al.$^{48}$</td>
<td>R10</td>
</tr>
<tr>
<td>O$_2$(a'Δg) + NO → O$_2$ + NO</td>
<td>1.51 × 10$^{13}$</td>
<td>Smirnov et al.$^{33}$</td>
<td>R11</td>
</tr>
<tr>
<td><strong>O$_2$(b'Σg$^+$) reactions</strong></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>O$_2$(b'Σg$^+$) → O$_2$ + hv</td>
<td>9.09 × 10$^{-2}$</td>
<td>Schofield$^{47}$</td>
<td>R12</td>
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<td>O$_2$(b'Σg$^+$) + N$_2$ → O$_2$ + N$_2$</td>
<td>1.26 × 10$^{9}$</td>
<td>Atkinson et al.$^{48}$</td>
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<td>O$_2$(b'Σg$^+$) + O$_2$ → O$_2$ + O$_2$</td>
<td>2.47 × 10$^{7}$</td>
<td>Atkinson et al.$^{48}$</td>
<td>R14</td>
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<td>O$_2$(b'Σg$^+$) + NO → O$_2$ + NO</td>
<td>2.41 × 10$^{10}$</td>
<td>Smirnov et al.$^{33}$</td>
<td>R15</td>
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<td><strong>O$_2$(c'Σu$^-$) reactions</strong></td>
<td></td>
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</tr>
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<td>O$_2$(c'Σu$^-$) → O$_2$ + hv</td>
<td>10$^{-4}$</td>
<td>Schofield$^{47}$</td>
<td>R16</td>
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<td>O$_2$(c'Σu$^-$) + N$_2$ → O$_2$ + N$_2$</td>
<td>1.93 × 10$^{12}$</td>
<td>Copeland et al.$^{49}$</td>
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<tr>
<td>O$_2$(c'Σu$^-$) + O$_2$ → O$_2$ + O$_2$</td>
<td>3.13 × 10$^{12}$</td>
<td>Copeland et al.$^{49}$</td>
<td>R18</td>
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<td><strong>O$_2$(C$_3$∆u) reactions</strong></td>
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<tr>
<td>O$_2$(C$_3$∆u) → O$_2$ + hv</td>
<td>10$^{-5}$</td>
<td>Schofield$^{47}$</td>
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<td>O$_2$(C$_3$∆u) + N$_2$ → O$_2$ + N$_2$</td>
<td>1.81 × 10$^{11}$</td>
<td>Kossyi et al.$^{50}$</td>
<td>R20</td>
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<td>O$_2$(C$_3$∆u) + O$_2$ → O$_2$ + O$_2$</td>
<td>1.75 × 10$^{11}$</td>
<td>Kossyi et al.$^{50}$</td>
<td>R21</td>
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<td><strong>O$_2$(A$_3$Σu$^+$) reactions</strong></td>
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<tr>
<td>O$_2$(A$_3$Σu$^+$) → O$_2$ + hv</td>
<td>5</td>
<td>Schofield$^{47}$</td>
<td>R22</td>
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<tr>
<td>O$_2$(A$_3$Σu$^+$) + N$_2$ → O$_2$ + N$_2$</td>
<td>5.60 × 10$^{9}$</td>
<td>Kenner and Ogryzlo$^{51}$</td>
<td>R23</td>
</tr>
<tr>
<td>O$_2$(A$_3$Σu$^+$) + O$_2$ → O$_2$ + O$_2$</td>
<td>1.75 × 10$^{11}$</td>
<td>Kenner and Ogryzlo$^{52}$</td>
<td>R24</td>
</tr>
<tr>
<td>O$_2$(A$_3$Σu$^+$) + N$_2$O → O$_2$ + N$_2$O</td>
<td>2.83 × 10$^{12}$</td>
<td>Schofield$^{47}$</td>
<td>R25</td>
</tr>
</tbody>
</table>
### O$_2$(B$^3\Sigma_g^+$) reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
<th>Source</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_2$(B$^3\Sigma_g^+$) → O$_2$ + hv</td>
<td>2.50 × 10$^7$</td>
<td>Schofield$^{47}$</td>
<td>R26</td>
</tr>
</tbody>
</table>

### O(3P) reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
<th>Source</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(3P) + O$_2$ → O$_3$</td>
<td>1.76 × 10$^{10}$</td>
<td>Atkinson et al.$^{48}$</td>
<td>R27</td>
</tr>
<tr>
<td>O(3P) + NO → NO$_2$</td>
<td>2.45 × 10$^{12}$</td>
<td>Atkinson et al.$^{48}$</td>
<td>R28</td>
</tr>
<tr>
<td>O(3P) + NO$_2$ → NO$_3$</td>
<td>2.03 × 10$^{12}$</td>
<td>Atkinson et al.$^{48}$</td>
<td>R29</td>
</tr>
</tbody>
</table>

### O(1D) reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
<th>Source</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(1D) → O$_2$ + hv</td>
<td>6.76 × 10$^{-3}$</td>
<td>Cosby$^{53}$</td>
<td>R30</td>
</tr>
<tr>
<td>O(1D) + N$_2$ → O(3P) + N$_2$</td>
<td>1.57 × 10$^{13}$</td>
<td>Herron and Green$^{31}$</td>
<td>R31</td>
</tr>
<tr>
<td>O(1D) + O$_2$ → O(3P) + O$_2$</td>
<td>2.41 × 10$^{13}$</td>
<td>Herron and Green$^{31}$</td>
<td>R32</td>
</tr>
<tr>
<td>O(1D) + NO → products</td>
<td>2.41 × 10$^{13}$</td>
<td>Herron and Green$^{31}$</td>
<td>R33</td>
</tr>
<tr>
<td>O(1D) + NO$_2$ → NO + O$_2$</td>
<td>8.43 × 10$^{13}$</td>
<td>Herron and Green$^{31}$</td>
<td>R34</td>
</tr>
<tr>
<td>O(1D) + N$_2$O → NO + NO</td>
<td>4.33 × 10$^{13}$</td>
<td>Herron and Green$^{31}$</td>
<td>R35</td>
</tr>
<tr>
<td>O(1D) + N$_2$O → N$_2$ + O$_2$</td>
<td>2.65 × 10$^{13}$</td>
<td>Herron and Green$^{31}$</td>
<td>R36</td>
</tr>
</tbody>
</table>

* The units of the rate constants are s$^{-1}$ for radiation reactions and cm$^3$·mol$^{-1}$·s$^{-1}$ for bimolecular reactions.
### Table 4. Chemical reactions and rate constants for NOx in N2/O2

<table>
<thead>
<tr>
<th>Chemical reaction</th>
<th>Rate constant ( \text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1} )</th>
<th>Source</th>
<th>No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( e + O_2 \rightarrow O(^3P) + O(^3P) + e )</td>
<td>( k_{37} = \frac{\beta_1}{[e]} \sqrt{\frac{1}{\alpha_1 P}} W^{0.75} \exp(-\frac{\alpha P}{W}) )</td>
<td>This work</td>
<td>R37</td>
</tr>
<tr>
<td>( e + N_2 \rightarrow N(^4S) + N(^4S) + e )</td>
<td>( k_{38} = \frac{\beta_2}{[e]} \sqrt{\frac{1}{\alpha_2 P}} W^{0.75} \exp(-\frac{\alpha P}{W}) )</td>
<td>This work</td>
<td>R38</td>
</tr>
<tr>
<td>( e + N_2 \rightarrow N(^2D) + N(^2D) + e )</td>
<td>( k_{39} = \frac{\beta_3}{[e]} \sqrt{\frac{1}{\alpha_3 P}} W^{0.75} \exp(-\frac{\alpha P}{W}) )</td>
<td>This work</td>
<td>R39</td>
</tr>
<tr>
<td>( N(^4S) + NO \rightarrow N_2 + O(^3P) )</td>
<td>( 1.87 \times 10^{13} )</td>
<td>Atkinson et al.</td>
<td>R48</td>
</tr>
<tr>
<td>( N(^4S) + NO_2 \rightarrow N_2O + O(^3P) )</td>
<td>( 1.81 \times 10^{12} )</td>
<td>Atkinson et al.</td>
<td>R49</td>
</tr>
<tr>
<td>( N(^4S) + NO_2 \rightarrow N_2 + O_2 )</td>
<td>( 4.21 \times 10^{11} )</td>
<td>Kossyi et al.</td>
<td>R50</td>
</tr>
<tr>
<td>( N(^4S) + NO_2 \rightarrow N_2 + 2O(^3P) )</td>
<td>( 5.48 \times 10^{11} )</td>
<td>Kossyi et al.</td>
<td>R51</td>
</tr>
<tr>
<td>( N(^4S) + NO_2 \rightarrow 2NO )</td>
<td>( 1.38 \times 10^{12} )</td>
<td>Kossyi et al.</td>
<td>R52</td>
</tr>
<tr>
<td>( N(^4S) + N(^4S) + N_2 \rightarrow N_2 + N_2 )</td>
<td>( 1.59 \times 10^{15} ) [N2]</td>
<td>Kossyi et al.</td>
<td>R53</td>
</tr>
<tr>
<td>( N(^4S) + O(^3P) + N_2 \rightarrow NO + N_2 )</td>
<td>( 3.68 \times 10^{15} ) [N2]</td>
<td>Kossyi et al.</td>
<td>R54</td>
</tr>
<tr>
<td>( N(^4S) + O_2 \rightarrow NO + O(^3P) )</td>
<td>( 5.91 \times 10^{7} )</td>
<td>Fernandez et al.</td>
<td>R7</td>
</tr>
<tr>
<td>( N(^4S) + O_3 \rightarrow NO + O_2 )</td>
<td>( 6.02 \times 10^{7} )</td>
<td>Barnett et al.</td>
<td>R55</td>
</tr>
<tr>
<td>( N(^2D) + O_2 \rightarrow NO + O(^3P) )</td>
<td>( 3.13 \times 10^{12} )</td>
<td>Herron</td>
<td>R6</td>
</tr>
<tr>
<td>( N(^2D) + NO \rightarrow N_2 + O(^3P) )</td>
<td>( 3.61 \times 10^{13} )</td>
<td>Herron</td>
<td>R56</td>
</tr>
<tr>
<td>( N(^2D) + N_2O \rightarrow NO + N_2 )</td>
<td>( 1.32 \times 10^{12} )</td>
<td>Herron</td>
<td>R57</td>
</tr>
<tr>
<td>( N(^2D) + N_2 \rightarrow N + N_2 )</td>
<td>( 1.02 \times 10^{10} )</td>
<td>Herron</td>
<td>R58</td>
</tr>
<tr>
<td>( O(^3P) + O_2 + N_2 \rightarrow O_3 + N_2 )</td>
<td>( 2.03 \times 10^{14} ) [N2]</td>
<td>Atkinson et al.</td>
<td>R59</td>
</tr>
<tr>
<td>( O(^3P) + O_2 + O_2 \rightarrow O_3 + O_2 )</td>
<td>( 2.17 \times 10^{14} ) [O2]</td>
<td>Atkinson et al.</td>
<td>R60</td>
</tr>
<tr>
<td>( O(^3P) + O_1 \rightarrow O_2 + O_2 )</td>
<td>( 4.82 \times 10^{9} )</td>
<td>Atkinson et al.</td>
<td>R61</td>
</tr>
<tr>
<td>( O(^3P) + NO \rightarrow NO_2 )</td>
<td>( 2.45 \times 10^{12} )</td>
<td>Atkinson et al.</td>
<td>R28</td>
</tr>
<tr>
<td>( O(^3P) + NO_2 \rightarrow NO_3 )</td>
<td>( 2.03 \times 10^{12} )</td>
<td>Atkinson et al.</td>
<td>R29</td>
</tr>
<tr>
<td>( O(^3P) + NO_2 \rightarrow NO + O(^3P) )</td>
<td>( 5.85 \times 10^{12} )</td>
<td>Atkinson et al.</td>
<td>R62</td>
</tr>
<tr>
<td>( O(^3P) + NO_3 \rightarrow NO_2 + O_2 )</td>
<td>( 1.02 \times 10^{13} )</td>
<td>Atkinson et al.</td>
<td>R63</td>
</tr>
<tr>
<td>( O(^3P) + O(^3P) + N_2 \rightarrow O_2 + N_2 )</td>
<td>( 1.10 \times 10^{15} ) [N2]</td>
<td>Kossyi et al.</td>
<td>R64</td>
</tr>
<tr>
<td>( NO + O_3 \rightarrow NO_2 + O_2 )</td>
<td>( 1.08 \times 10^{10} )</td>
<td>Atkinson et al.</td>
<td>R65</td>
</tr>
<tr>
<td>( NO + NO_3 \rightarrow NO_2 + NO_2 )</td>
<td>( 1.57 \times 10^{13} )</td>
<td>Atkinson et al.</td>
<td>R66</td>
</tr>
<tr>
<td>( NO + NO + O_2 \rightarrow NO_2 + NO_2 )</td>
<td>( 7.25 \times 10^{9} ) [O2]</td>
<td>Atkinson et al.</td>
<td>R67</td>
</tr>
<tr>
<td>( NO_2 + O_3 \rightarrow NO_3 + O_2 )</td>
<td>( 2.11 \times 10^{7} )</td>
<td>Atkinson et al.</td>
<td>R68</td>
</tr>
</tbody>
</table>
Figure Captions

Figure 1. Experimental set up
(1) gas cylinder, NO + N₂; (2) gas cylinder, O₂ in N₂; (3) valve; (4) rotameter; (5) pressure gague; (6) pulsed corona discharge reactor; (7) gas bomb; (8) gas chromatograph

Figure 2. FTIR spectra at 200 Hz showing the product distribution; (a) 659 ppm NO + N₂, (b) 4.60% O₂ + 358 ppm NO + N₂

Figure 3. Experimental results
(a) NO evolution with specific energy input; (b) NO₂ evolution with specific energy input; (c) N₂O evolution with specific energy input; (d) NOx conversion with specific energy input.

◼: 659 ppm NO + N₂
○: 2.28% O₂ + 355 ppm NO + N₂; △: 4.60% O₂ + 358 ppm NO + N₂
◇: 7.07% O₂ + 428 ppm NO + N₂; ×: 13.6% O₂ + 437 ppm NO + N₂

Figure 4. Experimental data and correlated data for varying oxygen content.
(a) 2.28% O₂ + 355 ppm NO + N₂, (b) 4.60% O₂ + 358 ppm NO + N₂, (c) 7.07% O₂ + 428 ppm NO + N₂, (d) 13.6% O₂ + 437 ppm NO + N₂

Experimental data: ■ (NO), ○ (NO₂), ▲ (N₂O); Calculated data: —— (NO), −−−− (NO₂), −⋯− (N₂O)

Figure 5. Ozone conversion through reaction R65 as a function of residence time assuming 50 ppm NO in the gas.

Figure 6. Model parameters as a function of O₂ concentration
Model parameter α for electron collision reactions (a); Model parameter β for electron collision reaction R37 (b), R38 (c), R39 (d). (◼) R37, (●) R38, (▲) R39, (—) regression results

Figure 7. Rate constants of electron collision reactions R37-R39 as a function of O₂ concentration at 100 W power input (a); Ratio of rate constant of electron collision reaction with O₂ and N₂ as a function of O₂ concentration at different power inputs (b)

Figure 8. Rates of electron collision reactions R37-R39 as a function of O₂ concentration at 100 W power input (a); Selectivity of electron collision reactions R37-R39 as a function of O₂ concentration at 100 W power input (b)

Figure 9. NOx conversion as a function of O₂ concentration for inlet concentration of 350 ppm NO at different specific energy input

Figure 10. Critical O₂ concentration as a function of NO concentration at different specific energy input
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Figure 9. NO\textsubscript{x} conversion as a function of O\textsubscript{2} concentration for inlet concentration of 350 ppm NO at different specific energy input.

Figure 10. Critical O\textsubscript{2} concentration as a function of NO concentration at different specific energy input.