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Nonthermal Aftertreatment of Diesel Engine Exhaust

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NONTHERMAL AFTERTREATMENT OF DIESEL ENGINE EXHAUST

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OBJECTIVES

The ultimate objective of this work has been to develop a nonthermal plasma process to reduce NO_x in diesel exhaust gas. A secondary objective has been to study the possibility of particulate matter (soot) reduction by the same technique. Our early work revealed a fundamental difficulty with this NO_x reduction approach in the gas environment of the diesel engine exhaust. These observations necessitated a thorough study of the unfavorable chemistry in the hope that knowledge of the chemical mechanism would offer an opportunity to make the approach useful for NO_x reduction. Whereas fundamental understanding of the mechanism has been obtained, we have not found any measure that would make the approach meet its original objective.

BACKGROUND INFORMATION

Emission standards for diesel engines will be tightened in several stages over the next ten years. Particularly stringent is a proposed NO_x standard of only 2.5 g/bhph for California in 2004. This amount is half of the current federal NO_x standard of 5 g/bhph.

Practical NO_x reduction for diesel applications is difficult because the presence of a large excess of oxygen in the exhaust renders existing three-way catalysts ineffective. The only established processes for NO_x reduction from a gas like diesel exhaust use ammonia or ammonia-like additives in conjunction with either high temperatures or catalysts. These processes have been developed for stationary combustion facilities and are not well suited for mobile sources such as diesel trucks. Consequently, the tightening NO_x emission standard has stimulated NO_x aftertreatment research throughout the world.

Several groups have taken a nonthermal plasma approach to offgas aftertreatment.[1] These approaches rely on the generation of reactive species by the nonthermal plasma and their subsequent chemical reactions with the pollutants. Our research has focused on the generation of N radicals from the nitrogen gas because this radical is known to react rapidly with NO to form molecular nitrogen.[2] In this respect the approach is similar to the conventional ammonia-based $DeNO_x$ process that relies on the NH_2 radical to convert NO to N_2.

APPROACH

The test unit used in our study of NO_X reduction by pulsed plasma discharges has been described elsewhere.[3] Fig.1 shows a schematic diagram of this apparatus. Gas sources used in this work were both an 8-hp 1-cylinder Yanmar diesel engine and gas cylinders with the desired components blended to the desired gas composition. The effect of the discharge reactor was determined by analyzing the effluent gas and comparing it to the known inlet gas.

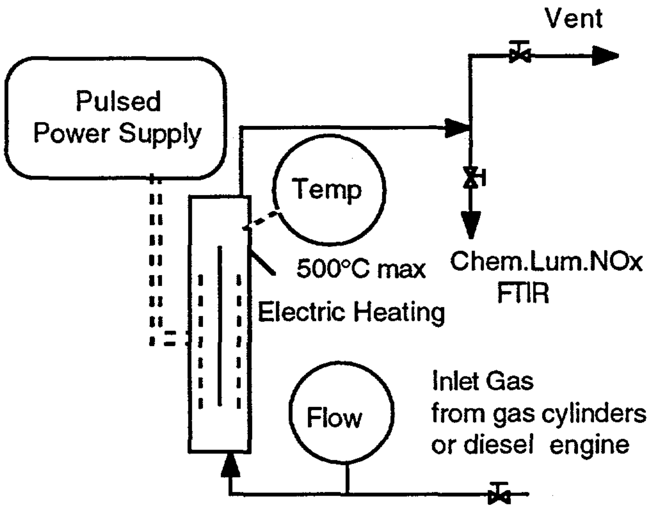
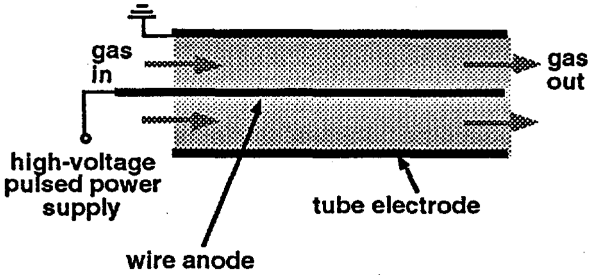


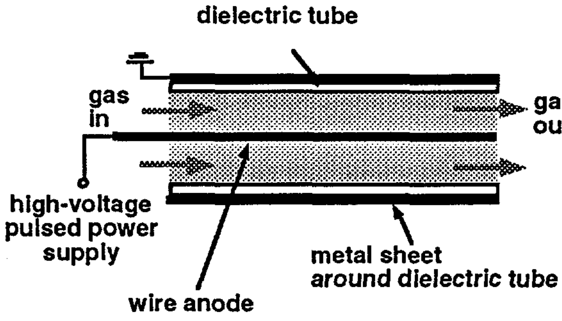
Figure 1. Experimental Apparatus

Fig.2 shows the three different types of discharge reactors tested in this work. Fig. 2 (a) is a pulsed corona reactor consisting of a wire (1.5 mm diameter) in a 300 mm long metal pipe with an inner diameter of 60 mm. The outer electrode defines a volume of 0.86 liter. The power supply is a magnetic pulse compression system capable of delivering up to 15-35 kV output into 100 ns pulses at a repetition rates from 10 Hz to 2 kHz. The resultant current ranges from milliamperes to hundreds of amperes. Both the voltage and current profiles are recorded. The measured current consists of both the discharge current and the current associated with charging the capacitance of the reactor. To obtain the energy deposition into the plasma, the capacitor charging current is subtracted from the total current before integration of the voltage current product. The integral yields the pulse energy. In the experiments either pulse energy or pulse repetition rate was varied to vary the power input to the processor. For the data analysis energy input is expressed in energy units (Joules) per feed gas volume (standard liters).

(a) Pulsed corona reactor



(b) Dielectric barrier reactor



(c) Dielectric pellet-bed reactor

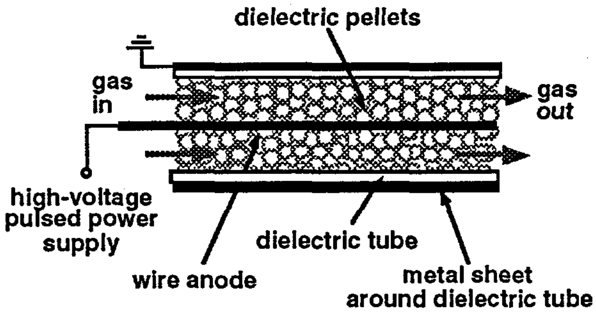


Figure 2. Experimental Discharge Reactors Tested

The dielectric-barrier discharge reactor in Fig.2(b) combines the fast-rising, strongly non-uniform applied electric field of a corona reactor with the self-extinguishing microdischarge pulses of the dielectric. The reactor consists of a wire (1.5 mm diameter) in a 300 mm long dielectric (alumina) tube with inner and outer diameters of 28 mm and 35 mm, respectively. The middle 150 mm of the dielectric tube has aluminum foil coating the outside to form the outer electrode.

The dielectric-pellet bed reactor of Fig 2(c) is the same as the previous dielectric-barrier reactor, except that it is packed with alumina beads. The diameter of the alumina beads is around 4 - 6 mm. The reason for using this reactor was to determine whether the dielectric packing could lead to an enhancement of the electric field experienced by the microdischarges and if the radical production efficiency would be improved.

RESULTS

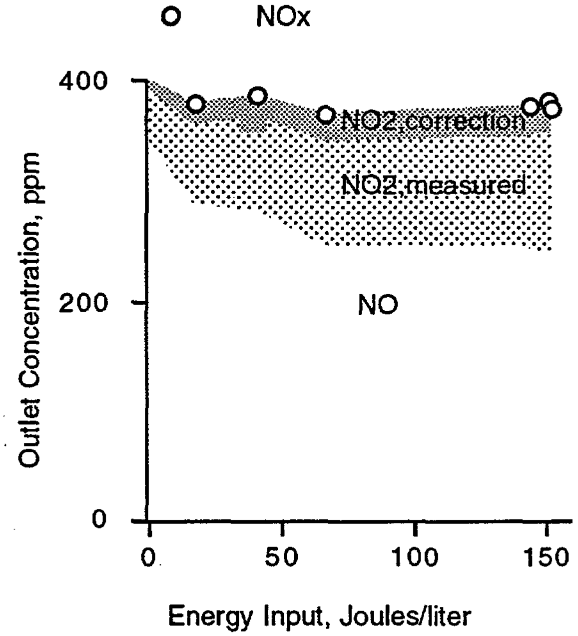


Figure 3. **Pulsed plasma processing of diesel engine exhaust (13% O_2, 5% CO_2, 5% H_2O) Temperature 300°C. Residence time 0.5 s.**

Fig.3 shows a result obtained with the pulsed-corona reactor fed by real diesel exhaust. The processor outlet gas composition is reproduced as an area graph so as to allow easy read out of total NO_x. The important conclusion from the results shown in Fig.3 is that pulsed-corona processing does not decrease total NO_x, it merely converts some NO to NO_2. NO_2 concentration measurement by means of a steel preconverter followed by chemiluminescent NO detection was found to be difficult requiring a correction to the indicated value. We determined that our steel converter only converted NO_2 to NO with 80% efficiency . Without a correction the indicated NO_2 value would be 20% low, a significant error for cases were most of the total NO_x is in the form of NO_2 (At lower temperature or with hydrocarbons present most of the NO was converted to NO_2 by the nonthermal plasma). The steel converter had an even poorer conversion efficiency for other nitrogen oxides like nitric acid. Our FTIR measurements allowed us to measure the higher oxides of nitrogen and provided a redundant measure of NO and NO_2 to confirm the consistency of the chemiluminescent scheme. Such redundancy was considered necessary when using the disappearance of NO_x as a measure of NO decomposition.

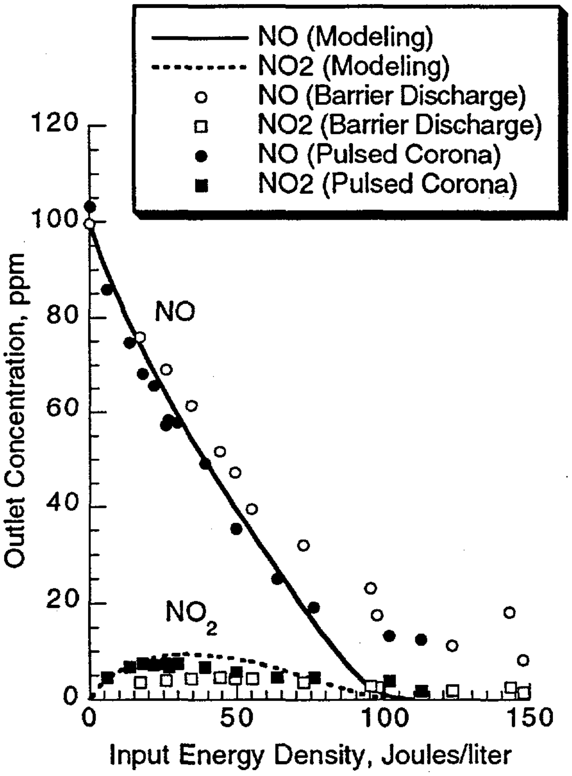


Figure 4. **Electrical Discharge Processing of 100 ppm NO in N_2. Temperature 100°C. Residence Time 0.8 s.**

The results in Fig.3 were obtained at the relatively high temperature of 300°C. At lower temperatures such as 100°C the pulsed corona produced higher conversions of NO to NO_2 and further conversion of the NO_2 to HNO_3. This HNO_3 proved hard to quantify because it adsorbed strongly on all steel surfaces even when heated. Hence, steady state outlet concentrations were hard to obtain at 100°C and impossible at ambient temperature. However, the conclusion from experiments at 100°C was that no decrease in total NO_x was observed with discharge processing.

With the other reactor types of Fig.2 we reproduced the results of Fig.3: Under no processing conditions did we detect a reduction in the total concentration of total nitrogen oxide species. This finding lead to detailed study of the effect of gas composition on NO_x reduction by electrical discharges.

Fig.4 shows the effect of input electrical energy on the decomposition of 100 ppm NO in N_2. This decomposition leads to formation of N_2 and O_2 (the latter reaction product quantified in the experiments) in accordance with the following stoichiometry:

$$2\,NO \longrightarrow N_2 + O_2 \qquad (1)$$

Another finding with respect to the results in Fig.4 is the identical behavior of the pulsed-corona and the dielectric-barrier reactors (not shown are similar results obtained with the dielectric-pellet bed reactor). This equivalence between the three reactor types was found for the entire experimental matrix of this work. This matrix spanned a broad range of gas compositions, energy inputs, temperatures and residence times. Our interpretation of this equivalence is that there is a fundamental constraint in electron energies despite the different types of discharges.

The presence of O_2 in the gas altered the chemistry dramatically. This effect is shown in Fig.5 where the inlet gas contained an increasing level of O_2 while input energy density was fixed at 50 Joules/liter (this level corresponds to approximately 8% of diesel engine output assuming a 100% conversion of mechanical to electrical energy). The total NO_x curve illustrates that there is no decomposition by the time O_2 reaches 3%. Hence, O_2 inhibits the favorable chemistry of the pure N_2 case.

The NO_x chemistry for electrical discharge reactors has been modeled based on kinetic data for electron-molecule and molecule-molecule interactions. A result representing the former is shown in Fig.6 where the percent of input electrical energy dissipated into various electron-impact processes in dry air are presented as a function of electron mean energy (this mean energy being a function of effective field strength in the discharge). The main chemical kinetics relationships are reproduced in Appendix A for the O_2-N_2 background gas mixture.

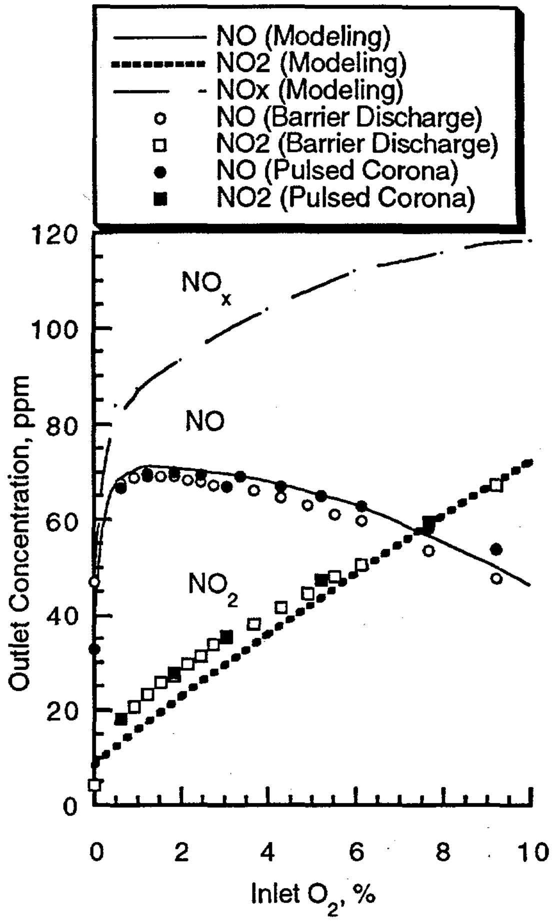
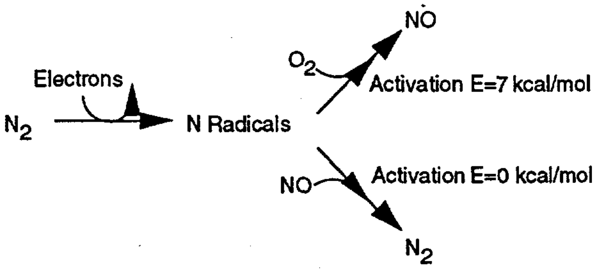


Figure 5. **Electrical Discharge Processing of 100 ppm NO in N_2/O_2 Mixtures. Temperature 100°C. Residence Time 0.8 s. Input Energy 50 Joules/liter**

The model calculations imply that the O_2 effect shown in Fig 5 is due to a fundamental competition for the main reactant, the N radical in accordance with the following simplified reaction scheme:



The lower favorable reaction path is much faster than the upper unfavorable reaction path up to a temperature of about 680°C for typical diesel exhaust thanks to a much lower activation energy. However, our initial postulation that the discharge NO_x chemistry would occur much below 680°C seems incorrect. Instead, we now postulate that the discharge leads to transient heating of the discharge channel that results in an effective temperature much above the ambient gas temperature. The increased temperature accelerates the upper reaction path and the two are roughly balanced in the experiments with O_2 concentrations above about 3%. In addition, there are corresponding unfavorable reaction paths between N and H_2O and CO_2 explaining the inhibiting effects of these gases that were observed in experiments devoted to these diesel exhaust components. Also, bulk temperature effects found experimentally support the above model: High bulk temperature favored NO production over NO reduction.

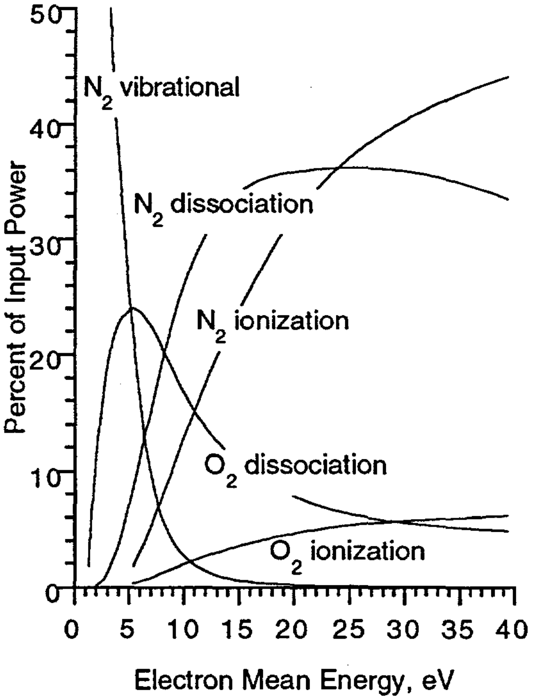


Figure 6. **Computed Energy Dissipation as a Function of Electron Mean Energy.**

ELECTRON BEAMS

In light of the energy dissipation results in Fig. 6 heating of the discharge channel is no surprise because the vibrational mode dominates at the low electron energies associated with atmospheric pressure discharges (approximately 2-5 eV for the discharges in our reactors). An obvious remedy of the heating effect would be to raise the electron mean energy and this, in fact was the driving force behind our search for better discharge reactors. However, this search failed in that all three reactors produced essentially the same results. Hence, it seems that the only possibility of significantly increasing the electron mean energy is to use Ebeam technology, i.e. accelerate electrons in a low-pressure tube outside the exhaust and inject the electrons through a window into the exhaust. We considered this strategy interesting enough to devote some of our attention to Ebeam NO_x chemistry.

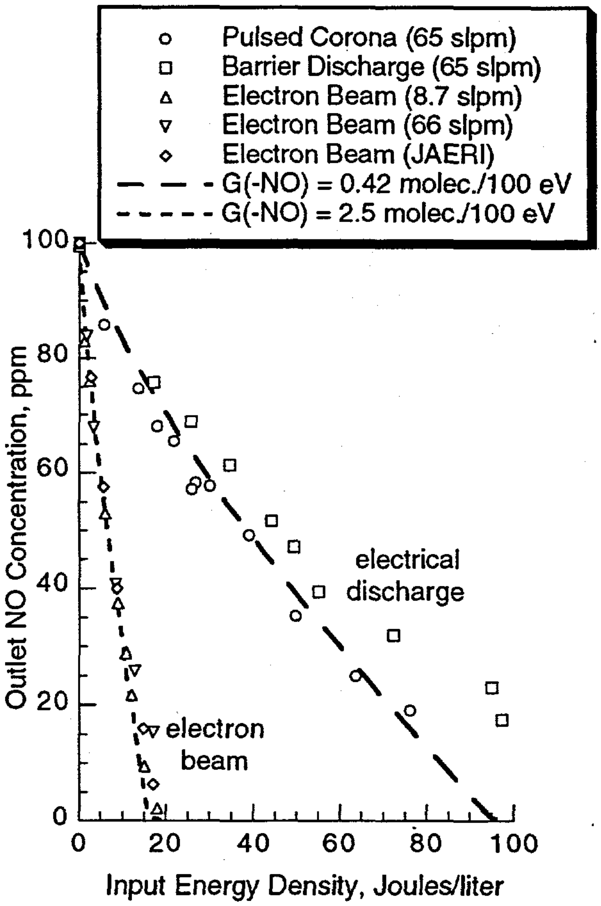


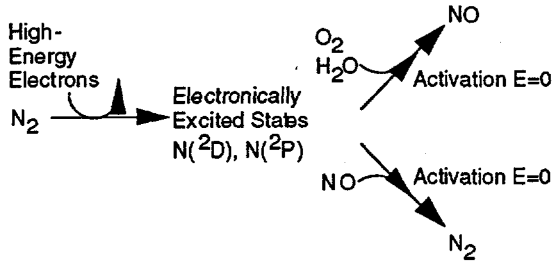
Figure 7. **Electron Beam vs. Electrical Discharge Processing of 100 ppm NO in N_2. Temperature 100°C.**

Fig.7 shows a comparison between Ebeam results[4] and the discharge results of Fig.4 replotted here for easy comparison. This figure shows that the Ebeam is about six times more energy efficient than the electrical discharges in terms of energy deposited into the gas (electrical conversion efficiencies may alter this comparison if the "yardstick" is wall-plug power). This favorable result can be explained by reference to Fig.6. At higher electron mean energy more N radicals are formed, thus the favorable impact on the NO reducing reaction:

$$N + NO \rightarrow N_2 + O \qquad (2)$$

Further analysis of the energy dissipation diagram of Fig.6 leads to the conclusion that heating effects should largely be absent in the Ebeam case since the vibrational excitation mode has decreased to zero. Consequently, one might expect that O_2 in the bulk gas would not be a problem for Ebeam-driven chemistry as it was in the electrical discharge case. However, work carried out at Japan Atomic Energy Research Institute[5] shows an O_2 effect almost identical to that of the electrical discharges shown in Fig.5. The Ebeam-driven NO decomposition was also completely inhibited by the presence of 3% O_2.

The O_2 effect on Ebeam-driven NOx chemistry cannot be explained by simple thermal effects. Rather, our explanation here is the generation of electronically excited N radicals that react readily with O_2, H_2O and CO_2 to form NO without thermal excitation, viz.:



This effect makes the otherwise favorable Ebeam-driven NO_x chemistry difficult for the diesel exhaust gas composition. We are currently investigating if it is possible to quench the electronically excited N radicals without producing NO.

CONCLUSIONS

We have studied the effect of electrical discharges on gas mixtures simulating diesel engine exhaust by modeling and by experiment. Our results have shown that the discharges can convert NO_x to N_2 using the nitrogen itself as a reductant, but only in gases containing essentially no O_2 or other O-containing species. We explain the O_2 effect by a competing reaction between the reactant N and the O-specie leading to production of NO rather than reduction. Under a fairly wide range of operating conditions the production and reduction branches are approximately balanced so that the net result is constant NO, or more accurately, constant NO_x since some NO is converted to NO_2 in the apparatus.

We have also found that the different reactor types of this work produced very similar results implying that the underlying discharge field strengths must have been similar. This in turn means that regardless of imposed field strengths, the electrons are influenced by space charge shielding that brings the effective field strength down to a level close to that of breakdown.

FUTURE WORK

The electrical discharge reactors have been found to initiate combustion-type chemistry at temperatures lower than thermal ignition temperature. This feature could be applied to the regeneration of particulate filters or to the oxidation of gaseous hydrocarbons from various sources.

ACKNOWLEDGMENTS

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Appendix A. Some of the reactions involved in the $NO/N_2/O_2$ kinetics.

Reaction*	k_0	b	E/R	Literature source
N(4S) + NO => N2 + O(3P)	3.40E-11	0.0	0.	!Baulch et al. (1980)
N(2D) + NO => N2 + O(1D)	6.30E-11	0.0	0.	!Schofield (1979)
N(2P) + NO => N2 + O(1D)	3.00E-11	0.0	0.	!Schofield (1979)
N(4S) + NO2 => N2O + O(3P)	3.00E-12	0.0	0.	!Atkinson et al. (1989)
N(4S) + N2O => N2 + NO	1.67E-11	0.0	10000.	!Hanson & Salimian (1984)
N(2D) + N2O => N2 + NO	1.20E-11	0.0	570.	!Schofield (1979)
N(2P) + N2O => N2 + NO	4.00E-14	0.0	0.	!Schofield (1979)
N(4S) + O2 => NO + O(3P)	1.50E-11	0.0	3600.	!DeMore et al. (1990)
N(2D) + O2 => NO + O(1D)	3.50E-13	0.5	0.	!Schofield (1979)
N(2P) + O2 => NO + O(1D)	2.00E-11	0.0	0.	!Schofield (1979)
N(2D) + N2 => N(4S) + N2	9.40E-13	0.0	510.	!Schofield (1979)
2N(4S) + M => N2 + M	1.10E-33	0.0	0.	!Pravilov et al. (1992)
N(2P) + N(4S) => 2N(4S)	1.00E-12	0.0	0.	!Schofield (1979)
N(4S) + O(3P) + M => NO + M	5.46E-33	0.0	-155.	!Campbell & Gray (1973)
N(2D) + O(3P) => N(4S) + O(3P)	2.00E-12	0.0	0.	!Schofield (1979)
N(2P) + O(3P) => N(4S) + O(3P)	1.00E-11	0.0	0.	!Schofield (1979)
O(3P) + NO + M => NO2 + M	9.10E-28	-1.6	0.	!Atkinson et al. (1992)
O(1D) + NO => N + O2	8.50E-11	0.0	0.	!Heidener & Husain (1973)
O(3P) + NO2 => NO + O2	6.50E-12	0.0	-120.	!Atkinson et al. (1992)
O(1D) + NO2 => NO + O2	2.30E-11	0.0	0.	!Heidener & Husain (1973)
O(3P) + N2 => NO + N	3.00E-10	0.0	38370.	!Hanson & Salimian (1984)
O(3P) + O2 + O2 => O3 + O2	2.96E-33	-0.28	0.	!Atkinson et al. (1992)
O(3P) + O2 + N2 => O3 + N2	4.75E-27	-2.8	0.	!Atkinson et al. (1992)
O(1D) + O2 => O(3P) + O2	3.20E-11	0.0	67.	!Atkinson et al. (1992)
O(3P) + O(3P) + M => O2 + M	5.21E-35	0.0	-900.	!Tsang & Hampson (1986)
O(1D) + O(3P) => 2O(3P)	2.55E-12	0.0	0.	!Sobral et al. (1993)
O(3P) + O3 => 2O2	8.00E-12	0.0	2060.	!Atkinson et al. (1992)
O(1D) + O3 => 2O(3P) + O2	2.40E-11	0.0	0.	!Atkinson et al. (1992)
O(1D) + O3 => 2O2	2.40E-11	0.0	0.	!Atkinson et al. (1992)
O3 + NO => NO2 + O2	1.80E-12	0.0	1370.	!Atkinson et al. (1992)

*Reaction rate constant k expressed as $k_0 \, T^b \exp(-E/RT)$ (in units of $cm^3/(molec\text{-}s)$ for 2-body reactions, $cm^6/(molec^2\text{-}s)$ for 3-body reactions). $N(^4S)$ denotes the ground-state nitrogen atom, while $N(^2D)$ and $N(^2P)$ are electronically excited nitrogen atoms. $O(^3P)$ and $O(^1D)$ denote the ground-state and electronically excited oxygen atoms, respectively.