MODELING OF ATMOSPHERIC PRESSURE PLASMA PROCESSING
OF GASES AND SURFACES

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Atmospheric pressure plasma based processes have become indispensable components of numerous industrial applications owing to their high efficiencies and low costs. In this work, we computationally investigate the applications of dielectric barrier discharges (DBDs), one of the commonly used atmospheric pressure plasma devices, to the remediation of nitrogen oxides (NO$_x$) from diesel exhausts and to the surface treatment of polypropylene (PP) for improved adhesion. We determine the kinetics of these processes in order to develop methods to optimize their energy efficiencies.

Unburned hydrocarbons (UHCs), inevitably present in diesel exhausts, significantly affect the plasma remediation of NO$_x$ by oxidizing NO, the major form of NO$_x$ in the exhaust, into NO$_2$. The efficiency of NO$_x$ removal increases when a given amount of energy is deposited in a large number of shorter-duration pulses as opposed to in a single pulse.

Soot particles significantly affect the plasma remediation of NO$_x$ by changing the composition of NO and NO$_2$ in the plasma. In general, NO$_x$ removal improves in the presence of soot. Heterogeneous reactions on soot also result in the production of CO. At high number densities and large diameters, soot particles significantly affect the ionization kinetics in the gas phase. When using repetitively pulsed discharges in the presence of soot, both NO$_x$ removal improves and soot oxidation increases.
Spatial dependencies can affect the energy efficiencies of remediation. Localized energy deposition in the streamer results in production of radicals in confined regions. Consumption of these radicals by UHCs limits their diffusion to outer radii thereby affecting the remediation.

Atmospheric pressure plasma processing of PP in humid air increases the surface densities of alcohol, peroxy, acid, and carbonyl groups. However, significant amounts of O₃ and NₓOᵧ are generated in the gas phase. Increasing the relative humidity results in decreased production of O₃ and increased concentrations of peroxy and acid groups on the surface. Increasing the gas temperature increases the surface concentration of peroxy radicals and decreases the concentrations of alcohol, carbonyl, and acid groups. For a given energy deposition, increasing the web speed results in decreased surface densities of peroxy, alcohol, carbonyl, and acid groups.
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1. INTRODUCTION

1.1 Introduction

Plasma-based processes have become an indispensable component for numerous industrial applications. Lower costs and higher efficiencies are some of the attractive features of plasma processing. In creating these plasmas, most of the electrical energy goes into the production of energetic electrons and excitation of feedstock gases rather than into gas heating. As a result, these plasmas contain “hot” electrons (few to tens of eV) and “cold” ions and neutral species (at or near the ambient temperature).

In recent years, a number of investigations have been performed to evaluate the potential of atmospheric pressure nonthermal plasmas for processing gases and surfaces. Some applications include remediation of toxic gases [1-5], processing of polymer surfaces [6-10], sterilization and decontamination of medical equipment and supplies [11,12], and production of ozone for disinfection of water supplies [13]. Advantages of atmospheric pressure processes compared to low pressure glow discharge processing include larger throughput and lower cost due to the lack of vacuum equipment and interfaces. In this work, we investigate two applications of atmospheric pressure plasmas, namely plasma remediation of NO\textsubscript{x} and plasma surface modification of polymers. Commonly used atmospheric pressure plasma devices include electron-beam [14-20], corona discharges [21-31], and dielectric barrier discharges (DBDs) [1-5,9,32-37].

In the context of toxic gas remediation of combustion effluent, the electron-beam process is a dry-scrubbing process in which the gas is irradiated with high energy (hundreds of keV) electrons. These high-energy electrons ionize the background gases,
thereby creating a plasma. In addition to the charged particles, reactive free radicals are also produced. The applicability of this process to the remediation of SO\(_x\) (oxides of sulphur) and NO\(_x\) (oxides of nitrogen) has been investigated in detail for cleaning the effluent of coal fired power plants and as high as 80% NO\(_x\) remediation and 90% SO\(_x\) remediation have been achieved.[14,38,39] The radicals in the plasma react with the toxic components and convert them into harmless or less harmful species.

In corona discharges, the geometry confines the discharge to high-field ionization regions around the powered electrodes. Several configurations are used for these devices based on the polarity and geometry of the electrodes.[30] Corona discharge devices, which typically use an asymmetric electrode pair such as point-plane, are driven by fast-rising high voltage (10s of kV) discharge pulses which typically last a few to 10s of ns. The transient nature of the plasma is controlled by the applied voltage pulse.[40] The discharge develops in the high field region near the sharp electrode and spreads out towards the opposite electrode. It is a positive corona when the electrode with the strongest curvature is electrically positive and a negative corona otherwise. At relatively low voltages the discharge extinguishes due to the build up of space charge near the sharp electrode. This space charge then disappears due to diffusion and recombination and a new discharge pulse appears. This is a self-repetitive corona and occurs in the positive and in the negative case.

DBDs (also known as silent discharges), shown schematically in Fig. 1.1, consist of planar electrodes or concentric cylindrical tubes with either one or both of the electrodes being covered with dielectric layers, separating them from the gas. The electrode spacing is typically 2-5 mm. Voltages, typically a few to tens of kV, at
frequencies ranging from a few hundreds to several thousand Hz are applied across the electrodes to produce a number of filamentary microdischarges. Typically, these microdischarges last a few to 100 ns and are 10s to 100s of µm in diameter. The discharge channels are terminated when the charge accumulation on the surface of the dielectric reduces the voltage across the gap to a value below the sustaining level.

One of the important applications of atmospheric pressure plasmas is the remediation of toxic gases, and in particular NOx. During the past decade, the removal of NOx has become a central scientific concern because of its key role in many global environmental problems such as acid rain, photochemical smog formation, and the greenhouse effect. Approximately 50% of the NOx emissions are from on road vehicles, particularly diesel engines.[41] Current measures for NOx removal include catalytic reduction, plasma remediation, and direct decomposition using reductants such as ammonia and hydrocarbons. The use of catalysts for remediation has inherent problems of poisoning requiring periodic maintenance. Direct decomposition is impractical for mobile sources. Hence, plasma remediation is being investigated for the removal of NOx (oxides of nitrogen). The critical issues in the practical implementation of atmospheric pressure plasmas for the remediation of toxic gases are twofold; electrical efficiency and generation of byproducts.

Although high levels of remediation have been achieved using e-beams, the large sizes of these devices make them impractical for mobile applications. Both corona and DBDs have been studied for remediation of toxic gases, but it still remains an open question as to which is more efficient for plasma chemical applications. For use in mobile sources such as on road vehicles, the plasma devices should ideally be
lightweight, use low voltage, and must be effective in removing the toxins without generating significant amounts of other unwanted compounds. In this regard, DBDs are known for their high-energy efficiency and reliability. They are in general compact, stable, can operate at high average power and with low voltages (a few to ten kV) compared to coronas or electron beams. Given these advantages of size, cost, and safety of the DBD over e-beam and coronas, the successful application of the DBDs will depend on the ability to arrive at optimal operating conditions for high efficiency of remediation and low byproduct formation. To this end, we have developed computer models for atmospheric pressure DBD processing of gases to study in detail the mechanisms responsible for the decomposition of the pollutant molecules in the plasma. An understanding of the plasma chemical kinetics serves as an important design tool in maximizing the energy efficiency and identifying the byproducts. By realistically modeling the exhaust gases and by understanding the process of their remediation, strategies for optimization can be proposed.

Several experimental and numerical investigations have been performed on the discharge dynamics [42,43] and the chemical kinetics [40,44,45] in DBD reactors used for diesel exhaust treatment. Typically, diesel exhausts contain N₂, O₂, H₂O, and CO₂ (mostly from the unreacted excess air and combustion products) with 100s of ppm of NOₓ (primarily NO), CO, H₂, and unburned hydrocarbons (UHCs) due to the incomplete combustion of the fuel. Since the actual exhaust composition depends on the origin of the fuel, fuel-to-air ratio, and compression ratio, investigations are usually performed on model gases. For example, Niessen et al. [46] examined ethene (C₂H₄) as an additive to a NOₓ-humid air mixture. Penetrante et al. [47] investigated the consequences of propene
(C\textsubscript{3}H\textsubscript{6}) in a NO\textsubscript{x}-air feed. Both studies showed that UHCs significantly contribute to NO oxidation. Niessen et al. [46] found that adding 2000 ppm of C\textsubscript{2}H\textsubscript{4} improved the NO removal efficiency from 60 eV to 5-10 eV with most of the remediated NO being converted to NO\textsubscript{2}. With propene addition, Penetrante et al. [47] found that, at 300 °C, almost 100% of the initial NO (500 ppm) was converted to NO\textsubscript{2}, whereas in the absence of propene, only 7% of NO was removed.

In this work, we have developed computer models to investigate the dynamics and kinetics of plasma remediation in DBDs. To address in detail the chemical processes during remediation, we have used a zero-dimensional (0-D) model called GLOBAL_KIN to capture the volumetric plasma kinetics. To investigate in further detail the dynamics and kinetics during the plasma remediation, one-dimensional (1-D) hydrodynamic models have been developed. The 1-D model is radially dependent and is applied to the study of a single microstreamer. The details of these models are discussed in Chapter 2.

In Chapter 3, GLOBAL_KIN is used to investigate the consequences of multiple pulse formats on the plasma remediation of NO\textsubscript{x} in the presence of UHCs. The gas mixture used for this investigation contained N\textsubscript{2}, O\textsubscript{2}, H\textsubscript{2}O, and CO\textsubscript{2} with ppm levels of NO\textsubscript{x} (primarily NO), CO, H\textsubscript{2}, C\textsubscript{3}H\textsubscript{6} (propene), and C\textsubscript{3}H\textsubscript{8} (propane). We found that it is more efficient with respect to remediation to deposit a given amount of energy in a large number of shorter duration pulses. With each pulse, radicals initiating the plasma chemistry are generated, and during the interpulse period, these radicals undergo reactions, thereby changing the composition of the plasma. The reaction chemistry for the follow-on pulses is different from that which would be obtained from an equivalent
energy deposition in a single or smaller number of pulses due to the accumulation of these interpulse products.

Another step towards more realistic modeling of plasma treatment of exhaust is accounting for carbonaceous particles in the exhaust. Soot particles in typical diesel exhausts have mass concentrations of 20-200 mg/m³.[48] The average geometric diameter and particle density of the soot particles depend on the combustion regime. Typical values are around 100 nm [49] and \(10^8\) cm\(^{-3}\).[48,50] which are high enough to initiate heterogeneous chemistry. Soot influences the chemistry of NO\(_x\) plasma remediation dominantly through NO\(_2\)-soot interactions [51,52] and influences the ionization kinetics through electron attachment to and ion neutralizations with the particles. The resulting changes of electron density and temperature may then affect the rates of electron-impact processes.

To address the reactions on soot surfaces, a heterogeneous reaction chemistry model was developed and incorporated into GLOBAL_KIN. The details of this model are also given in Chapter 2. In Chapter 4, results from our investigations on the consequences of soot particles on the plasma remediation of NO\(_x\) are discussed. We have performed parameterizations while varying energy deposition, UHC concentration, and soot particle number density on NO\(_x\) removal. We found that NO\(_x\) remediation improved by nearly 10% in the presence of soot. With soot, higher energies were required for the remediation of a given amount of NO.

In Chapter 5, we report on a computational investigation of the combined effects of repetitive discharge pulses and soot on NO\(_x\) remediation and soot oxidation. We investigated the consequences of varying energy deposition, inlet UHC concentration,
soot diameter, and soot particle number density on NO\textsubscript{x} remediation and soot oxidation for cases when using a single pulse and when using multiple pulses. In the absence of soot, using repetitive pulses resulted in larger conversion of NO to NO\textsubscript{2} compared to using a single pulse case. The combined effects of multiple pulses and heterogeneous chemistry on NO\textsubscript{x} remediation and soot oxidation are twofold. Improved NO\textsubscript{x} removal by the increased production of HNO\textsubscript{2}, HNO\textsubscript{3}, organic nitrates and nitrites due to the more favorable overlap in time of NO\textsubscript{2} and reactive radical densities; and increased soot oxidation because of larger NO\textsubscript{2} densities.

Spatially nonuniform energy deposition in DBDs results in spatial gradients in gas temperature and species densities. These gradients initiate advection and diffusion leading to transport of species to and from the microstreamer region. Previous studies on the dynamics and kinetics of these processes associated with the DBD processing of NO\textsubscript{x} showed a significant effect of the transport on the NO\textsubscript{x} removal.[42] However, the exhaust gases used in the investigations did not contain UHCs. In this work, we have investigated in detail the consequences of UHCs on the discharge kinetics and transport during the DBD processing of NO\textsubscript{x}. For this, we have used the 1-D radial hydrodynamic model. The results are discussed in the Chapter 6.

Another important use of atmospheric pressure plasmas is in the modification of polymer surfaces for improved wettability and adhesion. In these surface treatments, only the top 100s of Å of the material is modified, leaving the bulk polymer largely unaffected.[8] In general, the surface energy of untreated polymers is insufficient for good adhesion. For optimum adhesion, the surface energy of the polymer should be larger than that of the material to be bonded with. Similarly, for effective wetting of a
liquid on a polymer surface, the surface energy of the polymer should exceed the surface
tension of the liquid. The surface energies of some common polymers and the surface
tensions of a few commonly used inks are shown in Fig. 1.2. For example, the surface
energy of untreated PP is $\approx 27$ mJ-m$^{-2}$.[53,54] The typical surface tensions of water-based
adhesives are 44-50 mJ-m$^{-2}$ and those of water-based inks are 54-56 mJ-m$^{-2}$.[55] Plasma
surface treatment can increase the surface energy of PP above that of the surface tensions
of adhesives and inks, thereby enabling efficient sticking and printing. For example, in
studies of atmospheric pressure plasma treatment of PP in He (containing ppm levels of
O$_2$ and H$_2$O) by Massines and Gouda [53], the surface energy of PP increased from 27
mJ-m$^{-2}$ to as high as 62 mJ-m$^{-2}$. The increase was attributed primarily to the bonding of O
atoms to the PP surface.

A variety of polymers have been treated by plasmas, including polypropylene
(PP) [53,56-61], polyethylene (PE) [9,56,62-66], poly(tetrafluoroethylene) [37],
polyimide [67,68], polystyrene [66], polycarbonate [69,70], and poly($p$-phenylene
benzobisthiozol) [71]. The aim of these treatments is generally to improve the wetting
and adhesion properties of the polymers. For example, Shenton et al. [72] observed that
atmospheric pressure plasma treatment of low density PE (LDPE) and poly(ethylene
terephthalate) (PET) resulted in adhesion enhancements by factors ranging from two to
ten.

Plasma surface treatment of polymers primarily results in the oxidation of the
surface by generation of functional groups such as C-OH (alcohol), C-O-O-H
(hydroperoxide), H-C=O (aldehyde), C=O (carbonyl), C-O-C=O (ester), C-O-O (peroxy),
H-O-C=O (acid), OC(O)O (carbonate), and NH$_2$ (amine). For example, Foerch et al. [63]
observed the formation of ester, alcohol, carbonyl, and acid groups by XPS C 1s spectra while treating PE with an air plasma. Surface physicochemistry studies of air-corona-discharge-treated PP by O’Hare et al. [73] showed the presence of alcohol, peroxide, acid, ester, carbonyl, and carbonate groups on the surface. The relative concentrations of the functional groups generally depend on the operating conditions of the plasma generator such as energy deposition and gas composition for a given polymer being processed. These interrelations can be quite complex. Poncin-Epaillard et al. [58] measured $2.5 \times 10^{14}$ cm$^{-2}$ of amino groups following N$_2$ microwave plasma treatment of PP using a power of 100 W. Higher concentrations of these groups were observed on PE for treatments with short durations (higher frequency) and powers greater than 50 W.

In addition to functionalization, other phenomena such as erosion of the polymer, chain scission, and cross-linking may occur with corona treatment.[74,75] Clouet and Shi [62] used hexatriacontane ($C_{36}H_{74}$) as a representative for high-density polyethylene (HDPE) to study the gas phase products of plasma surface oxidation and erosion. They found that CO, H$_2$O, CO$_2$, and H$_2$ were the primary products in an oxygen rich plasma. Hansen et al. [76] studied the effects of atomic oxygen on polymers such as PE, PP, polyimide, and polysulfide. Emission of CO$_2$ was observed and correlated with the erosion of the polymer at a rate directly proportional to the duration of the treatment.

The erosion of the polymer occurs through chain scissions and the formation of low molecular weight oxidized materials (LMWOMs). The volatile components of LMWOM can leave the surface.[60,77] LMWOMs have been found to agglomerate into globules at the surface due to a large difference in interfacial free energy between the underlying hydrophobic substrate and the oxygenated overlayer.[78] The role of
LMWOM in the improvement of adhesion is still unresolved. Strobel et al. [60] suggest that formation of LMWOM improves adhesion for select conditions whereas Kim et al. [6] propose that excessive scission by corona plasma treatment resulting in LMWOM can lead to the formation of weak boundary layers that hinder adhesion.

The gas used for surface treatment determines the surface properties of the polymer. For example, oxygen plasma treatment generally increases the surface energy of polymers, whereas fluorine plasma treatment generally decreases the surface energy thereby making the polymer more hydrophobic and chemically inert.[8,79] Low surface energies can also be obtained by insertion of oriented methyl groups into the polymer chain.[80] In this regard, several gases have been investigated for modifying the surface properties of PP, including He [53], CO₂ [81], N₂ [54,58], NH₃ [82], and air [54,61,83]. CO₂ plasmas have been found to result in less erosion of PP compared to O₂ plasmas.[81] Studies by Massines et al. [83] on the role of gas composition in the DBD treatment of PP showed that O₂, even when present in small quantities, can significantly affect the surface chemistry and hence the level of surface transformation. For example, when ≈ 0.2% of O₂ was added to N₂, the percentage of O on the surface doubled while the percentage of N on the surface decreased by a factor of 5.[83] Meiners et al. [84] showed that exposure of PP to an Ar plasma followed by exposure to pure acetylene gas (C₂H₂) increased the surface energy from 30 mJ-m⁻² to 72 mJ-m⁻². A thin polymeric film was formed on the PP surface which both increased and stabilized the surface energy. When only an air or Ar plasma was used, the surface energy was 40 mJ-m⁻².

The nature of the discharge also affects the surface properties of the polymer. Filamentary discharges, the normal mode of operation of an atmospheric pressure
plasma, result in inhomogeneous treatment on a microscopic scale.[54] Under controlled operating conditions, stable, uniform, nonfilamentary or glow discharges, can be produced,[53] which are often effective compared to filamentary discharges for surface modification. For example, in studies of PP surface treatment at atmospheric pressure by Massines et al. [53], the surface energy increased from 27 mJ-m\(^{-2}\) to 62 mJ-m\(^{-2}\) when using glow (nonfilamentary) discharges, whereas with filamentary discharges the surface energy increased only to 45 mJ-m\(^{-2}\). The contact angle for the glow discharge treated PP was 32\(^{\circ}\) and that for the filamentary discharge treated PP was 57\(^{\circ}\) (The smaller the contact angle, the larger the wettability.).

Power deposition and web speed, which determine the total energy deposition to the surface, largely control the surface properties of the treated film.[75] Other parameters that influence the surface properties include air-gap thickness of the discharge, relative humidity (RH), gas temperature, and the structure of the polymer. For example, Hansen et al. [76] found that the rates of oxidation of branched polymers such as PP were considerably higher compared to the relatively unbranched hydrocarbon polymers such as PE for otherwise the same operating conditions.

Plasma modified polymer surfaces tend to age, a process commonly attributed to the migration of groups on the surface after treatment, surface reorientation, and exposure to oxidizing environments.[57] Aging depends on the type of polymer and the process conditions used for its treatment. For example, studies of air-corona-discharge treatment of PP by Strobel et al. [57] showed the effects of aging to be minimal. The O/C ratio on the surface did not change with aging while the wettability decreased by < 5% after 30 days. This change in the wettability was attributed to the reorientation of surface groups.
Guimond et al. [54] showed that the surface energy of PP produced by a N₂ glow discharge treatment decreased by aging. Immediately after treatment, the surface energy was ≈ 53 mJ-m⁻². After 10 days, the surface energy stabilized to ≈ 44 mJ-m⁻².

Although plasma processing of polymers is being done in industries on a large scale for more than a decade, the mechanisms responsible for the change in the surface properties of the polymers are unclear. An understanding of the basic processes and their consequences on the surface modification will be of use in arriving at optimal conditions for treatment. To this end, we have developed a pseudo-homogeneous global kinetics model for the study of DBD processing of polymer surfaces. This model is similar to that used for the study of heterogeneous reactions on soot during the plasma remediation of NOₓ. The details of this model are given in Chapter 2.

Although the model is capable of handling surface chemistries for any polymer, we have investigated in particular the plasma surface modification of polypropylene (PP), a widely used material. We have developed a surface reaction mechanism for PP and analyzed in detail the consequences of the variations in important process variables such as energy deposition, relative humidity, film speed, and process gas temperature on the surface properties of PP. Results from our computational investigations on the surface modification of PP in humid-air plasmas are in Chapter 7. We found that increasing energy deposition not only results in increased densities of peroxy and acid groups on the PP surface, but also increases byproducts such as NₓOᵧ and O₃. Increasing the RH resulted in decreased production of O₃. Increasing the gas temperature increased the surface concentration of peroxy radicals and decreased the surface concentrations of alcohol, carbonyl, and acid groups. For a given energy deposition, increasing the web
speed resulted in decreased densities of peroxy, alcohol, carbonyl, and acid groups on the PP surface.

Our concluding remarks are in Chapter 8.
Fig. 1.1. A typical dielectric barrier discharge (DBD) device.
Fig. 1.2. Surface energies of common polymers and surface tensions of liquids. For optimal wetting of a polymer surface, the surface energy of the polymer should exceed the surface tension of the liquid.
1.3 References


2. DESCRIPTION OF THE MODELS

2.1 Overview

In this chapter, the models used to investigate the atmospheric pressure plasma processing of gases and surfaces are described. The 0-D model, GLOBAL_KIN, used to investigate the volumetric plasma kinetics of NO\textsubscript{x} plasma remediation is described in Section 2.2. The modifications made to this model to address the surface kinetics on soot surfaces are discussed in Section 2.3. In Section 2.4, we describe in detail the 1-D hydrodynamic radial model used to investigate the microstreamer discharge dynamics in DBDs. Finally, in Section 2.5, we discuss the modifications made to GLOBAL_KIN to investigate the plasma surface treatment of polymers.

2.2 Zero-Dimensional Plasma Chemistry Model – GLOBAL_KIN

GLOBAL_KIN is a spatially homogenous model and consists of three main modules: a plasma chemistry module, a circuit module and a Boltzmann equation module. A schematic of the modules used in GLOBAL_KIN is given in Fig. 2.1a. From a user-defined reaction mechanism, the plasma chemistry module constructs differential equations for the evolution of the density of species, the electron temperature, and the gas temperature. The circuit module provides the E/N (electric field/number density) in the plasma. The source terms for the gas phase reactions are obtained from the species concentration and reaction rate coefficients using
\[
\frac{dn_i}{dt} = \sum_j \left\{ \left( a_{ij}^{(2)} - a_{ij}^{(1)} \right) k_j \prod_l n_l^{a_{ij}^{(l)}} \right\},
\]

(2.1)

where \( a_{ij}^{(1)} \) and \( a_{ij}^{(2)} \) denote the left-hand side (LHS) and right-hand side (RHS) stoichiometric coefficients of species \( i \) in reaction \( j \). \( n_i \) is the density of species \( i \), \( k_j \) is the rate constant of reaction \( j \) which depends on the gas temperature and is calculated using Arrhenius expressions for reactions involving only heavy species. The rate constants of electron-impact reactions are obtained as a function of electron temperature by solving the two-term spherical harmonic expansion of Boltzmann's equation for the electron energy distribution and parameterizing them for several values of E/N.[1]

The external discharge circuit used to deposit energy in the plasma is shown in Fig. 2.1b. The discharge region is modeled as a resistor \( R_p \) and the dielectrics on the electrodes are represented by the capacitor \( C_s \) in series with \( R_p \). The inductor \( L \) is added to obtain the desired \( LC \) time constant for the circuit. A ballast resistance \( R_s \) may be used to control the energy deposition in the plasma. The storage capacitor, \( C_{sto} \) is initially charged to the applied voltage. Typical values for the circuit parameters in Fig. 2.1b are:

- Applied voltage = 10-20 kV
- \( C_{sto} = 200 \times 10^{-9} \) F
- \( C_p = 20 \times 10^{-9} \) F
- \( C_s = 5.5 \times 10^{-15} \) F
- \( L = 30 \times 10^{-9} \) H.
Initially, the voltage across the plasma is equal to the voltage across the storage capacitor. As current flows through the discharge, the capacitor $C_s$ in series with the plasma charges up thereby robbing voltage from the discharge region. When the voltage across the plasma falls below sustaining, the discharge is extinguished.

The electron temperature is determined by the energy gained by Joule heating, and the energy lost in elastic and inelastic collisions,

$$
\frac{d}{dt} \left( \frac{3}{2} n_e k_B T_e \right) = \mathbf{j} \cdot \mathbf{E} - \sum_i \frac{3}{2} n_e \nu_{mi} \left( \frac{2m_e}{M_i} \right) k_B \left( T_e - T_i \right) + \sum_i n_e k_i N_i \Delta \varepsilon_i .
$$

(2.7)

$n_e$ is the electron density, $T_e$ is the electron temperature, $\mathbf{j}$ and $\mathbf{E}$ are the current density and the electric field in the discharge, $\nu_{mi}$ is the electron momentum transfer collision frequency with species $i$, $m_e$ is the electron mass, and $M_i$ and $T_i$ are the mass and temperature of species $i$. For the $l^{th}$ electron impact process, $k_l$ is the reaction rate coefficient, $N_i$ is the density of the gas phase collision partner, and $\Delta \varepsilon_i$ is the change in the electron energy.

The average gas temperature $T_g$ is obtained by accounting for heating from elastic and inelastic collisions with electrons, enthalpy of heavy particle reactions,

$$
\frac{d}{dt} \left( N_c p T_g \right) = \sum_i \frac{3}{2} n_e \nu_{mi} \left( \frac{2m_e}{M_i} \right) k_B \left( T_e - T_i \right) + \sum_j n_e k_j N_j \Delta \varepsilon_j - \sum_j \Delta H_j .
$$

(2.8)
where \( N \) is the total gas density, \( c_p \) is the specific heat, \( \Delta H_j \) is the change in enthalpy of the \( j^{th} \) reaction, and \( d_{\text{gap}} \) is the electrode separation. The first and second terms in Eq. 2.8 account for heating due to momentum transfer collisions with electrons and dissociative electron impact processes which produce Frank-Condon heating.

The final set of ordinary differential equations (Eqs. 2.1, 2.7, and 2.8) is then integrated in time using VODE [2], a stiff equation solver. The time steps chosen for integration are dynamically adjusted to capture the dynamics of the system at any particular time and spans > \( 10^9 \) orders of magnitude. In order to capture the features of multiple discharges, the model is run for a series of current pulses and afterglow time periods. The total number of pulses is divided equally over the residence time used for the single pulse case. The energy deposition is varied by either changing the applied voltage, the dielectric thickness, or the dielectric permittivity.

### 2.3 Model for Reaction Kinetics at Soot Surfaces

To investigate the consequences of heterogeneous reactions on soot particles on the plasma remediation of NO\(_x\), a heterogeneous chemistry model was developed and incorporated into GLOBAL_KIN. In this model, the reactive medium around a given soot particle is described using a quasi-homogeneous model which distinguishes two regions in the gas volume surrounding one particle: a homogenous bulk gas phase and a gas-surface boundary layer. (See Fig. 2.2) Using this assumption, the concentration profile in the boundary layer is linear between the gas phase and surface of the particles, and is mainly driven by diffusion and surface reactions. All the particles have the same diameter, \( d_s \), that corresponds to the average of the actual particle diameter distribution.
The soot particles are characterized by their diameter and by the surface density of available adsorption sites. The soot particle number density, $n_p$, is a constant since additional particle nucleation does not take place. The only physical change that particles undergo is a decrease of their diameter due to oxidation reactions. Gas phase species are characterized by their density in the bulk of the gas phase, $n_{sg}$, and near the surface of the soot particles, $n_{ss}$.

The time-evolution of the bulk density of species $i$ is given by

$$\frac{dn_{ig}}{dt} = W_{ig} + W_{is}$$

(2.9)

where $n_{ig}$ and $W_{ig}$ are the bulk density and the net production rate by gas-phase reactions of species $i$. $W_{is}$ denotes the net production term of species $i$ by heterogeneous processes on the soot particles. This term is nonzero only for species involved in the surface reactions.

For large particle diameters, $d_s > 80$ nm, the continuum approach is valid and the source term $W_{is}$ is directly related to the diffusion rate of species $i$ at the soot surface,

$$W_{is} = \left( -D_i \frac{n_{ig} - n_{is}}{\delta} \right) \left( \pi d_s^2 n_p \right),$$

(2.10)

where $D_i$ is the diffusion coefficient of species $i$ and $\delta$ the boundary layer thickness. The first term of Eq. 2.10 is the rate of diffusion of species $i$ to the soot particle. The second term is the soot geometric surface per unit volume of the gas phase. The diffusion
boundary layer thickness may be estimated from a standard correlation for mass transfer between a fluid and an immersed sphere. For the conditions of interest,

\[ Nu = 2.0 + 0.60 \, Re^{1/2} \, Sc^{1/3} \]  

(2.11)

where, \( Nu = d_s / \delta \) is the Nusselt number, \( Re = \rho v d_s / \mu \) is the Reynolds number and \( Sc = \mu / \rho D_s \) is the Schmidt number.[3] \( \rho, v \) and \( \mu \) denote the mass density, velocity and the viscosity of the gas phase. For the conditions considered in this work \( Re \) and \( Sc \) are small, and so the boundary layer thickness is nearly equal to the particle radius.

Since gas phase chemistry is neglected in the boundary layer, the time variation of the density near the soot particle is governed by the balance between the flux of species entering the boundary layer by diffusion and the consumption or production of species by heterogeneous reactions at the soot surface. The mass balance in the boundary layer is,

\[ \frac{d}{dt} \left[ \frac{1}{2} (n_{ig} + n_{is}) \delta V_\delta \right] = D_i \frac{n_{ig} - n_{is}}{\delta} \pi d_s^2 \delta + (R_{di} - R_{ai}) S_s, \]  

(2.12)

where \( S_s \) is the specific surface of the soot particles and \( V_\delta \) is the volume of the boundary layer. \( R_{di} \) and \( R_{ai} \) are the rates of desorption and adsorption per unit surface of soot for species \( i \). The consumption rate by adsorption reactions is

\[ R_{ai} = \sum_j \left( a_{ij}^{(1)} \gamma_j v_i n_{is} \right), \]  

(2.13)
where \( \gamma_j \) is the adsorption probability for the \( j^{th} \) process and \( v_i \) the thermal speed of species \( i \) at the surface of the soot particle, 
\[
v_i = \sqrt{\frac{8kT_g}{\pi m_i}}.
\]
The production rate of species \( i \) due to desorption reactions is
\[
R_{di} = \sum_j a_{ij}^{(2)} k_j N_{is} \text{.}
\] (2.14)

where \( k_j \) is the rate of the \( j^{th} \) desorption reaction and \( N_{is} \) is the surface density of the adsorbed species. The surface used in the computation of desorption and adsorption rates is the true surface area, \( S_s \), of the soot, 
\[
S_s = \pi d_{sp}^2 N_{sp},
\]
where \( d_{sp} \) is the spherule diameter and \( N_{sp} \) is the number of spherules contained in each particle. This is consistent with the measurements of the adsorption probability and the surface density of the total adsorption sites.[4-6] The soot specific surface \( S_s \) was determined from experiments reporting that the particles are composed of \( \approx 20 \) nm elementary spherules having a fractal structure.[7] A fractal dimension of \( f = 2.8 \) was chosen based on work by Mitchell and Frenklach.[8]

The number of spherules, \( N_{sp} \), contained in each particle is [9]
\[
N_{sp} = \left( \frac{d_s}{d_{sp}} \right)^f.
\] (2.15)

The specific surface of the soot particles is assumed to be equal to the total surface of all the spherules. For estimating diffusion fluxes, the geometric surface was used.
The surface densities of the adsorbates are obtained from

\[
\frac{dN_{i-\text{s}}}{dt} = \sum_j \left( a_{ij}^{(2)} \gamma_j v_i \frac{n_i'}{4} - \sum_j \left( a_{ij}^{(1)} k_i N_{i-\text{s}} \right) \right),
\]

(2.16)

where the first sum is over adsorption reactions, the second sum is over the desorption reactions and \( n_i' \) is the density of the gas-phase species involved in the adsorption reaction.

A single type of adsorption site was used for all adsorbates. The total surface density of adsorption sites for OH and O has been reported to be \( \approx 10^{15} \text{ cm}^{-2} \) [10] which is similar to that for the adsorption sites of NO2.[5] We therefore used \( 10^{15} \text{ cm}^{-2} \) for the total surface density of the adsorption sites.

When the soot particle diameters are small and produce a Knudsen number, \( \lambda_{\text{mfp}} / d_s > 1 \), the continuum approach is no longer valid. Diffusion is fast enough to insure a constant concentration in the boundary layer, \( n_{i-\text{s}} = n_{i-\text{g}} \). [11] There is consequently no need for an equation for the densities of gas phase species near the soot particles. The rate of surface reactions \( W_{i-\text{s}} \) is

\[
W_{i-\text{s}} = (R_{di} - R_{ai})S_s n_p,
\]

(2.17)

where the factor \( S_s n_p \) is the soot surface per unit volume.
The calculation of $R_{ai}$ is different from that in the continuum regime since the rarefaction around the particle must be taken into account. In this case, $R_{ai}$ is given by [11]

$$R_{ai} = \sum_j \frac{2D_j}{8D_i / \gamma_j v_i + d_j / (1 + 2\Delta / d_j)} n_i,$$

(2.18)

where $\Delta$ is the mean distance between the point of last collision in the gas phase and the particle center.

The final set of ordinary differential equations (Eqs. 2.7-2.9, 2.12, and 2.16) are then integrated in time using VODE.[2] At each step during the time integration in the model, the decrease of the soot mass is computed and the corresponding surface and diameter are adjusted assuming that the fractal dimension, and therefore the number of spherules, remain constant. The soot number density also remains constant. When the size of the particle decreases to the point that the flow around the particles is not continuum (Eq. 2.13), Eqs. 2.17 and 2.18 are used to provide the heterogeneous rates.

Soot particle charging by the attachment of charged species may affect the ionization kinetics, and therefore the electron temperature and density, in DBDs. Particle charging in plasmas has been mostly investigated at low pressure where the Orbit Motion Limited (OML) theory may be used.[12] The validity of OML theory requires that $d_p << \lambda_D << \lambda_{mfp}$, where $d_p$ is the particle diameter, $\lambda_D$ is the Debye length of the plasma and $\lambda_{mfp}$ is the electron/ion mean free path between collisions. For these conditions, the motion of charged species in the plasma sheath around the particle is collisionless and is
mainly governed by the interaction potential between the particles and electrons or ions. In this case, the sheath potential and currents to the particles are functions only of the plasma density, electron temperature and ion temperature.

Unfortunately, the assumptions for the OML theory are violated by atmospheric plasmas. During the current pulse the electron density $n_e$ and temperature $T_e$ are $10^{12}$-$10^{13}$ cm$^{-3}$ and 3-4 eV, which produces a Debye length of the order of $10^{-3}$ cm. The electron mean free path, based on N$_2$ is $\approx 3 \times 10^{-5}$ cm and so the sheath is collisional.

To estimate an upper limit to the particle charging during the short current pulse, we considered the charging due to ion collection and electron attachment to the soot. The collection frequency of electrons by the soot is determined by assuming that the electron density in the sheath follows a Boltzmann distribution with respect to the electrical potential. The charging rate is then

$$\frac{dQ_s}{dt} = -q \frac{n_{eg} \exp(qV_s / kT_e)}{4} \left( \frac{8kT_e}{\pi m_e} \right) d_s^2 + \sum_i n_{ig} \frac{1 - \exp(q_i V_s / kT_i)}{4} \left( \frac{8kT_i}{\pi m_i} \right) d_s^2$$

(2.19)

where $d_s$ and $Q_s$ denote the diameter and the electrical charge for the soot particles, $q$ is the elementary charge, and $k$ is Boltzmann’s constant. $m_e$, $n_{eg}$ and $T_e$ are the electron mass, density in the bulk plasma, and temperature respectively. $m_i$, $n_{ig}$, $q_i$, and $T_i$ are the ion mass, density in the bulk plasma, charge, and temperature respectively. The sum is over ions. $V_s$ is the particle potential and may be estimated from the particle charge by modeling the particle as a spherical capacitor,


\[ V_s = \frac{2qQ_s}{4\pi\varepsilon_0 d_s}. \]  

\[ (2.20) \]

2.4 One-Dimensional Plasma Chemistry and Hydrodynamics Model

In the 1-D model, we include the radial dependence of the microstreamers and the surrounding volume and solve for the species densities based on chemical kinetics, and diffusive and advective transport. In actual devices, the streamers have axial variations as well. However, these variations tend to be significant only for times less than a few tens of ns. At processing times of interest for our study, which are at least tens of ms, streamer properties can likely be homogeneous along the axial direction, and hence, their variations in that direction can be neglected. The model developed for this study is based on the 1-D microdischarge simulation described previously in Ref. [13]. The model differs from that in Ref. [13] in that it employs a different technique to obtain the final set of ODEs and a different integration method.

For computational purposes, the DBD is represented as being composed of a uniformly spaced array of identical, radially symmetric microdischarges. Each microdischarge and its surrounding volume is discretized into a set of concentric cylinders (cells) with increasing inter cylinder spacing. Typically, 50-100 radial points are used in the model.

The model is composed of four modules: a circuit module, a Boltzmann’s equation solver module, a plasma chemistry module, and a transport module. A schematic of the modules in the 1-D model is given in Fig. 2.3a and the external circuit used to drive the plasma is shown in Fig. 2.3b. The discharge is represented by a parallel set of resistors, each accounting for the cell containing plasma at a particular mesh point.
The circuit module calculates the voltage across the plasma, which is then used to obtain the E/N in each of the cells. The rate coefficients for electron impact reactions are obtained by solving the two-term spherical harmonic expansion of Boltzmann's equation for the electron energy distribution and parameterizing them for several values of E/N.[1] The plasma chemistry module provides the rates for change of species densities based on chemical kinetics. The changes in species densities as a result of motion between the mesh points are addressed in the transport module. The equations we solve in the transport module are:

\[
\frac{\partial \rho}{\partial t} = \nabla \cdot (\rho \vec{v}), \quad (2.21)
\]

\[
\frac{\partial (\rho \vec{v})}{\partial t} = -\nabla P - \nabla \cdot (\rho \vec{v} \vec{v}) - \nabla \cdot \vec{\tau}, \quad (2.22)
\]

\[
\frac{\partial (c_p \rho T)}{\partial t} = \vec{j} \cdot \vec{E} - \sum_i \left( \frac{dN_i}{dt} \right) \Delta H_i + \sum_i \frac{3}{2} n_e v_{mi} \left( \frac{2m_e}{M_i} \right) k_B (T_e - T_i) + \nabla \cdot \kappa \nabla T - \nabla \cdot (c_p \rho T \vec{v}) - P(\nabla \cdot \vec{v}) + 2\mu(\nabla \cdot \vec{v})^2, \quad (2.23)
\]

where \( \rho \) is the mass density, \( \vec{v} \) is the velocity, \( P \) is the thermodynamic pressure (assuming ideal gas behavior), \( \vec{\tau} \) is the viscosity tensor, \( c_p \) is the heat capacity, and \( \kappa \) is the thermal conductivity. \( \vec{j} = \sigma \vec{E} \) (\( \sigma \) is the plasma conductivity) is the current density, \( H_i \) is the enthalpy of heavy particle species \( i \), and \( \mu \) is the viscosity. The viscosity and thermal conductivity of the gas are obtained using Lennard-Jones parameters and applying the mixture rules as described in Hirshfelder et al.[14]
The densities of individual species are obtained by solving separate continuity equations,

$$\frac{\partial N_i}{\partial t} = -\nabla \cdot \left( N_i \nabla \rho - \rho D_i \nabla \left( \frac{N_i}{\rho} \right) \right) + W_{0D},$$  \hspace{1cm} (2.24)$$

where $D_i$ is its diffusion coefficient, and $W_{0D}$ is the source function due to electron impact and heavy particle reactions. For charged heavy species, we used ambipolar diffusion coefficients. Spatially dependent time derivatives are constructed using conservative finite difference donor cell techniques on a staggered mesh ($\rho, N_i$, and $T$ are obtained at cell vertices whereas $\rho \vec{v}$ is obtained at cell boundaries). The resulting ordinary differential equations for electron temperature (Eq. 2.7), continuity (Eq. 2.21), momentum (Eq. 2.22), gas energy (Eq. 2.23), and species densities (Eqs. 2.24) along with those for circuit parameters are integrated in time using VODE.[2] Typically the effect of advection is significant only during and slightly after the current pulse. At times later than 1 $\mu$s (typically, the current pulses last a few 10s of ns), the effects of advection are minimal and are neglected. At such times, species transport is by diffusion only. To capture the features of repetitive pulses, the model is run for a series of current pulses and afterglow periods.

2.5 Model for Reaction Kinetics on Polymer Surfaces

A schematic of a typical corona device used for plasma surface modification is shown in Fig. 2.4a. The device consists of two parallel dielectric plates backed by metal
electrodes across which typically 10s of kV sinusoidal pulses at 10s of kHz are applied to produce discharges in air. The discharges are in the form of microstreamers which are typically 10s – 100s of µm in diameter, lasting a few – 100s of ns.[13] Typical web speeds are 10s – 100s m-min⁻¹ and the polymer usually spends a maximum of a few seconds in the discharge. Energy depositions are usually 0.1 – a few J-cm⁻². Although the plasma equipment used industrially for polymer processing are typically called corona discharges, due to the dielectrics on the electrodes and the capacitance of the polymer, the devices function as DBDs.

To address the reactions on and near the polymer surface, a heterogeneous model was developed and incorporated into GLOBAL_KIN. The reaction set typically includes: electron-impact processes in the gas phase which result in ionization, dissociation, excitation, electron-ion recombination, and attachment; heavy species reactions in the gas phase that result in neutral chemistry, charge exchange, and ion-ion neutralization; reactions of gas phase species with species on the surface; and reactions between surface species.

In addition to the terms used in the estimation of the average gas temperature as given in Eq. 2.8, a term for heat transfer to surfaces is now included,

\[
\frac{d}{dt} \left( Ne_p T_g \right) = \sum_{i}^{3} n_e v_{mi} \left( \frac{2m_e}{M_i} \right) k_B (T_e - T_i) + \sum_{j} n_e k_j N_j \Delta e_j - \sum_{j} \Delta H_j - h_{\text{eff}} \frac{T_g - T_w}{d_{\text{gap}}},
\]  

(2.25)
where \( h_{\text{eff}} \) is the effective heat transfer coefficient with the discharge walls having temperature \( T_w \). We approximated that \( h_{\text{eff}} = 2.3 \text{ W-cm}^{-2}\text{-K}^{-1} \), based on flow over a flat plate.[3]

The reaction mechanism for plasma-polymer interactions is implemented using a quasi-homogeneous model which distinguishes two regions above the polymer surface; a homogeneous bulk gas phase and a gas-surface boundary layer, as shown in Fig. 2.4b. The radical concentration profile in the boundary layer is mainly driven by diffusion and surface reactions. A gas phase species \( i \) is characterized by its density in the bulk of the gas phase, \( n_{ig} \), and near the surface of the polymer, \( n_{is} \). The state of the polymer is characterized by the fractional occupancy of its surface sites by different species.

The time-evolution of the bulk density of species \( i \) is given by

\[
\frac{dn_{ig}}{dt} = W_{ig} + W_{id}, \tag{2.26}
\]

where \( W_{ig} \) and \( W_{id} \) are the net rate of production of species \( i \) by gas phase reactions and the rate of accumulation of species \( i \) in the bulk gas phase by diffusion from the polymer surface. \( W_{id} \) is nonzero only for species involved in the surface reactions.

The source term \( W_{id} \) is proportional to the rate of diffusion to the polymer surface,

\[
W_{id} = \left( -D_i \frac{n_{ig} - n_{is}}{\delta} \right) \left( \frac{S}{V} \right), \tag{2.27}
\]
where $D_i$ is the diffusion coefficient, $\delta$ the boundary layer thickness, $S$ is the polymer geometric surface area, and $V$ is the volume of the bulk plasma. The diffusion boundary layer thickness may be taken to be a few mean free paths ($\approx \mu m$ for air at 1 atm). For the conditions of this study, diffusion is not the rate limiting step and hence the thickness of the diffusion boundary layer is not critical.

Since gas phase chemistry is neglected in the boundary layer, the time variation of the density near the polymer surface is governed by the balance between the flux of species entering the boundary layer by diffusion and the consumption or production of species by heterogeneous reactions at the polymer surface. The mass balance in the boundary layer is

$$
\frac{d}{dt} \left[ \frac{1}{2} (n_{ig} + n_{is}) V_B \right] = D_i \frac{n_{ig} - n_{is}}{\delta} S + \left( R_{di} - R_{ai} \right) S, \quad (2.28)
$$

where $V_B$ is the volume of the boundary layer. $R_{di}$ and $R_{ai}$ are the rates of desorption and adsorption (or abstraction) per unit surface of polymer for species $i$. The rate of consumption by adsorption (or abstraction) reactions is

$$
R_{ai} = \sum_j \left( a^{(1)}_{ij} - a^{(2)}_{ij} \right) \gamma_j v_i \frac{n_{is}}{4}, \quad \gamma_j = \gamma_{j0} \frac{\rho_j}{\rho_o}, \quad (2.29)
$$

where $\gamma_j$ is the adsorption probability for the $j^{th}$ process, and $v_i$ the thermal speed of species $i$ at the surface of the polymer, $v_i = \sqrt{\frac{8kT_g}{\pi M_i}}$. $\gamma_{j0}$ is the adsorption probability per
unit area, \( \rho_j \) is the density of surface sites available to reaction \( j \) and \( \rho_o \) is the density of surface sites on a virgin polymer surface. \( a_j^{(1)} \) and \( a_j^{(2)} \) denote the LHS and RHS stoichiometric coefficients of species \( i \) in reaction \( j \). The production rate of species \( i \) due to desorption reactions is

\[
R_{di} = \sum_j \left( a_{ij}^{(2)} k_j N_{ls} \right),
\]

(2.30)

where \( k_j \) is the rate of the \( j^{th} \) desorption reaction, and \( N_{ls} \) is the surface density of the adsorbed species.

The densities of the surface species are obtained from

\[
\frac{dN_{ls}}{dt} = \sum_j \left( a_{ij}^{(2)} \gamma_j N_{is} \frac{n_i}{4} \right) - \sum_j \left( a_{ij}^{(1)} k_j N_{ls} \right) + \sum_j \left( a_{ij}^{(1)} - a_{ij}^{(1)} \right) k_j \prod_{l} N_{ls}^{a_{ij}^{(1)}},
\]

(2.31)

where the first sum is over adsorption or abstraction reactions, the second is over desorption reactions, and the third is over reactions between surface species. \( n_i \) is the density of the gas phase species involved in the adsorption or abstraction reaction.

The ordinary differential equations for electron temperature (Eq. 2.7), gas temperature (Eq. 2.25), species densities (Eqs. 2.26, 2.28, and 2.31) along with those for circuit parameters are integrated in time using VODE.[2]
Fig. 2.1. (a) Block diagram of the 0-D model – GLOBAL_KIN. (b) Schematic of the circuit used in the 0-D model. The plasma created in the DBD is represented by the resistor $R_p$ and the dielectrics on the electrodes are represented by the capacitor $C_s$ in series with $R_p$. $R_s$ is a ballast resistor. $C_{sto}$ is a storage capacitor, $C_p$ is a peaking capacitor in parallel with $R_p$, and $L$ is an inductor.
Fig. 2.2. Schematic of the quasi-homogeneous gas-phase model used in GLOBAL_KIN to account for soot particles. The region surrounding the soot is divided into two zones—a homogeneous bulk gas phase and a gas-surface boundary layer. Species in the bulk plasma diffuse to the soot surface through the boundary layer. Gaseous products of the heterogeneous reactions desorb from the soot surface to return to the bulk through the boundary layer.
Offline Boltzmann Solver → Lookup Table of $k$ vs. $T_e$ → Plasma Chemistry → Transport Module → VODE ODE Solver

Fig. 2.3. 1-D Model. (a) Modules in the 1-D radial hydrodynamic and plasma chemistry model. (b) External circuit. The discharge region and its surrounding area are represented by a set of resistors in parallel.
Fig. 2.4. Model for plasma polymer surface treatment. (a) Schematic of the plasma polymer surface treatment process. A plasma is created in air by applying 10s of kV sinusoidal pulses at 10s kHz across a few mm gap. The polymer web traverses the plasma region at speeds of 10s - a few 100s of m-min⁻¹. Typically, the residence time of the polymer in the plasma is at most a few s. (b) Quasi homogeneous model for species transport to the polymer surface. Two zones above the PP surface are considered – a diffusion boundary layer and homogeneous bulk plasma. Species produced in the bulk plasma diffuse through the boundary layer, react with the polymer surface, and the products diffuse back to the bulk through the boundary layer.
2.7 References

3. REPETITIVELY PULSED PLASMA REMEDIATION OF NO\textsubscript{x} IN THE PRESENCE OF UNBURNED HYDROCARBONS

3.1 Introduction

We previously established that unburned hydrocarbons (UHCs), inevitably present in diesel exhausts, significantly affect the NO\textsubscript{x} chemistry during the plasma remediation of NO\textsubscript{x} in diesel exhausts.[1] Industrial systems for plasma processing of toxic gases typically operate at sufficiently high repetition rates that a given sample of gas is subjected to several discharge pulses. Pulses with short rise-time and high amplitude voltage have been found to be advantageous due to their ability to rapidly produce high E/N (electric field/number density).[2] It has also been found that it is more efficient with respect to remediation to deposit a given amount of energy in a large number of shorter duration pulses.[3] With each pulse, radicals initiating the plasma chemistry are generated and during the interpulse period, these radicals undergo reactions thereby changing the composition of the plasma. The reaction chemistry for the follow-on pulses is different from that which would be obtained from an equivalent energy deposition in a single or smaller number of pulses due to the accumulation of these interpulse products.

In this chapter, we discuss the consequences of interpulse chemistry on the plasma remediation of NO\textsubscript{x} in a DBD reactor. The reaction mechanism for the NO\textsubscript{x}-propene-propane mixture is summarized in Section 3.2. NO\textsubscript{x} processing with multiple pulse formats is discussed in Section 3.3. Briefly, we found that with multiple pulses, approximately 10 ppm of methyl nitrate (CH\textsubscript{3}ONO\textsubscript{2}) and 16 ppm of ethyl nitrate (C\textsubscript{2}H\textsubscript{5}ONO\textsubscript{2}) was formed, whereas less than 1 ppm of each were produced with a single
pulse. The efficiency of NOx remediation improved from 240 eV per molecule for a single pulse to 185 eV per molecule when the same energy (58 J/L) was distributed over 20 pulses. Concluding remarks are in Section 3.4.

3.2 Reaction Mechanism for NOx-C3H6-C3H8

For this study, we considered nearly 80 electron impact reactions and 360 reactions involving heavy species. The species used in the model are listed in Appendix A. The reactions for NOx both in the absence and in the presence of propane and propene are given in Appendix B. The reaction mechanism for NOx remediation can be described by two trees; reactions with and without UHCs. The detailed mechanism for NOx in the absence of UHCs is described in Ref. 3. In summary, in the absence of UHCs, NOx is remediated primarily by two channels,

\[
\text{Reduction:} \\
\text{NO} + N \rightarrow N_2 + O, \quad k = 3.41 \times 10^{-11} \exp(-24/T) \text{cm}^3 \text{s}^{-1}, \\
\quad k_{298} = 3.2 \times 10^{-11} \text{cm}^3 \text{s}^{-1}, \quad (3.1)
\]

\[
\text{Oxidation:} \\
\text{NO} + O_3 \rightarrow NO_2 + O_2, \quad k = 4.3 \times 10^{-12} \exp(-1598/T) \text{cm}^3 \text{s}^{-1}, \\
\quad k_{298} = 2.1 \times 10^{-14} \text{cm}^3 \text{s}^{-1}, \quad (3.2a)
\]

\[
\text{NO} + O + M \rightarrow NO_2 + M, \quad k = 6.71 \times 10^{-32} (T / 298)^{-1.41} \text{cm}^6 \text{s}^{-1}, \quad (3.2b)
\]

\[
\text{NO} + HO_2 \rightarrow NO_2 + OH, \quad k = 3.5 \times 10^{-12} \exp(+240/T) \text{cm}^3 \text{s}^{-1}, \\
\quad k_{298} = 7.8 \times 10^{-12} \text{cm}^3 \text{s}^{-1}, \quad (3.2c)
\]
NO + OH + M → HNO₂ + M,

\[ k = 8.64 \times 10^{-31} (T / 298)^{-2.51} \exp(34 / T) \text{cm}^6 \text{s}^{-1}, \quad k_{298} = 9.7 \times 10^{-31} \text{cm}^6 \text{s}^{-1}, \quad (3.2d) \]

NO₂ + OH + M → HNO₃ + M,

\[ k = 4.62 \times 10^{-29} (T / 298)^{-5.49} \exp(-1183 / T) \text{cm}^6 \text{s}^{-1}, \quad k_{298} = 8.7 \times 10^{-31} \text{cm}^6 \text{s}^{-1}. \quad (3.3) \]

\( k \) is the rate coefficient and \( k_{298} \) is its value at \( T = 298 \) K. O, N, and OH are produced by electron impact reactions with O₂, N₂, and H₂O respectively.

\[ \text{e} + \text{O}_2 \rightarrow \text{O} + \text{O} + \text{e}, \quad (3.4) \]

\[ \text{e} + \text{N}_2 \rightarrow \text{N} + \text{N} + \text{e}, \quad (3.5) \]

\[ \text{e} + \text{H}_2\text{O} \rightarrow \text{OH} + \text{H} + \text{e}. \quad (3.6) \]

O₃ is produced by the reaction of O with O₂,

\[ \text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}, \quad k = 3.4 \times 10^{-34} (T / 298)^{-1.2} \text{cm}^6 \text{s}^{-1}. \quad (3.7) \]

HO₂ is produced by the reaction of H with O₂,

\[ \text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}, \quad k = 1.78 \times 10^{-32} (T / 298)^{-0.8} \text{cm}^6 \text{s}^{-1}. \quad (3.8) \]

H by itself is formed by the electron impact dissociation of H₂O (Eq. 3.6) and by the reaction of O with OH,
\[ O + OH \rightarrow O_2 + H, \quad k = 4.55 \times 10^{-12} (T/298)^{0.4} \exp(372/T) \text{cm}^3\text{s}^{-1}, \]

\[ k_{298} = 1.6 \times 10^{-11} \text{cm}^3\text{s}^{-1}. \quad (3.9) \]

In the absence of UHCs, the consumption of NO\(_x\) mainly occurs through the oxidation channel. This is due to the fact that the rates of producing O and OH are higher compared to N because of the lower dissociation energy of H\(_2\)O and O\(_2\) compared to N\(_2\).

For example, the contributions of each of the above channels to NO remediation in a mixture with 8% O\(_2\), 6% H\(_2\)O, 7% CO\(_2\), 400 ppm CO, 260 ppm NO, 133 ppm H\(_2\) and balance N\(_2\) are given in Fig. 3.1. At 30 J/L, the reduction channel (Eq. 3.1) accounts for only 8% of the total NO remediation. Oxidation by O\(_3\) is the dominant consumption pathway for NO (Eq. 3.2a).

The reaction mechanism for NO\(_x\) in the presence of propane (C\(_3\)H\(_8\)) and propene (C\(_3\)H\(_6\)) is discussed in detail in Ref. 1 and is summarized in Fig. 3.2. In the presence of the UHCs, C\(_3\)H\(_6\) and C\(_3\)H\(_8\), new pathways for NO oxidation are introduced, most of which primarily result in the formation of NO\(_2\). The reactivity of propane is smaller compared to propene as approximately only 5% propane is consumed at the end of a typical process [40 J/L] compared to 50% for propene. Briefly, the initiating processes for the C\(_3\)H\(_6\) and C\(_3\)H\(_8\) chains are reactions with O and OH.

\[ \text{OH} + \text{H}_3\text{C}–\text{CH}═\text{CH}_2 \rightarrow (0.35) \text{H}_3\text{C}–\text{CH(OH)}–\text{CH}_2 \]

\[ + (0.65) \text{H}_3\text{C}–\text{CH}–\text{CH}_2\text{OH}, \]

\[ k = 4.85 \times 10^{-12} \exp(504/T) \text{cm}^3\text{s}^{-1}, \quad k_{298} = 2.6 \times 10^{-11} \text{cm}^3\text{s}^{-1}, \quad (3.10) \]
The hydroxyalkyl and alkyl radicals formed by the reactions in Eqs. 3.10, 3.15 and 3.16 then quickly react with O2 to form the peroxy radicals,

\[ \text{H}_3\text{C}−\text{CH(OH)}−\text{CH}_2 + \text{O}_2 \rightarrow \text{H}_3\text{C}−\text{CH(OH)}−\text{CH}_2\text{OO}, \quad k = 3.82 \times 10^{-12} \text{ cm}^3\text{s}^{-1}, \quad (3.17) \]

\[ \text{H}_3\text{C}−\text{CH}−\text{CH}_2\text{OH} + \text{O}_2 \rightarrow \text{H}_3\text{C}−\text{CH(OO)}−\text{CH}_2\text{OH}, \quad k = 1.16 \times 10^{-11} \text{ cm}^3\text{s}^{-1}, \quad (3.18) \]

\[ \text{H}_3\text{C}−\text{CH}_2−\text{CH}_2 + \text{O}_2 \rightarrow \text{H}_3\text{C}−\text{CH}_2−\text{CH}_2\text{OO}, \quad k = 8 \times 10^{-12} \text{ cm}^3\text{s}^{-1}, \quad (3.19) \]

\[ \text{H}_3\text{C}−\text{CH}−\text{CH}_3 + \text{O}_2 \rightarrow \text{H}_3\text{C}−\text{CH(OO)}−\text{CH}_3, \quad k = 1.1 \times 10^{-11} \text{ cm}^3\text{s}^{-1}. \quad (3.20) \]

These peroxy radicals (R−OO) then react with NO to convert it into NO2,

\[ \text{R}−\text{OO} + \text{NO} \rightarrow \text{R}−\text{O} + \text{NO}_2, \quad (3.21) \]
where R is the alkyl or hydroxyalkyl part of the peroxy radical.

Some amount of NO remediation is also achieved through the formation of organic nitrates and nitrites. For example, CH$_3$O, formed from a two-step reaction beginning with CH$_3$, reacts with NO to form CH$_3$ONO (methyl nitrite).

\[
\text{CH}_3 + \text{O}_2 + \text{M} \rightarrow \text{CH}_3\text{O}_2 + \text{M}, \quad k = 4.41 \times 10^{-31} (T/298)^{-3} \text{ cm}^6\text{s}^{-1}, \tag{3.22}
\]

\[
\text{CH}_3\text{O}_2 + \text{NO} \rightarrow \text{CH}_3\text{O} + \text{NO}_2, \quad k = 4.2 \times 10^{-12} \exp(180/T) \text{ cm}^3\text{s}^{-1},
\]

\[
k_{298} = 7.7 \times 10^{-12} \text{ cm}^3\text{s}^{-1}, \tag{3.23}
\]

\[
\text{CH}_3\text{O} + \text{NO} \rightarrow \text{CH}_3\text{ONO}, \quad k = 2.0 \times 10^{-11} \text{ cm}^3\text{s}^{-1}. \tag{3.24}
\]

CH$_3$ is primarily produced by the reaction in Eq. 3.13. CH$_3$O also reacts with NO$_2$ to form CH$_3$ONO$_2$ (methyl nitrate).

\[
\text{CH}_3\text{O} + \text{NO}_2 \rightarrow \text{CH}_3\text{ONO}_2, \quad k = 8.32 \times 10^{-12} \text{ cm}^3\text{s}^{-1}. \tag{3.25}
\]

Similar chemistry is observed when C$_2$H$_5$O, formed from C$_2$H$_5$, reacts with NO to generate C$_2$H$_5$ONO (ethyl nitrite),

\[
\text{C}_2\text{H}_5 + \text{O}_2 + \text{M} \rightarrow \text{C}_2\text{H}_5\text{O}_2 + \text{M}, \quad k = 8.02 \times 10^{-26} (T/298)^{-8.24} \exp(-2150/T) \text{ cm}^6\text{s}^{-1},
\]

\[
k_{298} = 5.0 \times 10^{-29} \text{ cm}^6\text{s}^{-1}, \tag{3.26}
\]

\[
\text{C}_2\text{H}_5\text{O}_2 + \text{NO} \rightarrow \text{C}_2\text{H}_5\text{O} + \text{NO}_2, \quad k = 3.1 \times 10^{-12} \exp(330/T) \text{ cm}^3\text{s}^{-1},
\]
\[ k_{298} = 9.4 \times 10^{-12} \text{ cm}^3 \text{s}^{-1}, \quad (3.27) \]

\[ \text{C}_2\text{H}_5\text{O} + \text{NO} \rightarrow \text{C}_2\text{H}_5\text{ONO}, \quad k = 2.0 \times 10^{-11} \text{ cm}^3 \text{s}^{-1}. \quad (3.28) \]

\[ \text{C}_2\text{H}_5 \text{ is produced by the reaction of O with C}_3\text{H}_6 \text{ (Eq. 3.14). C}_2\text{H}_5\text{O also reacts with NO}_2 \text{ to form C}_2\text{H}_5\text{ONO}_2 \text{ (ethyl nitrate).} \]

\[ \text{C}_2\text{H}_5\text{O} + \text{NO}_2 \rightarrow \text{C}_2\text{H}_5\text{ONO}_2, \quad k = 1.32 \times 10^{-11} \text{ cm}^3 \text{s}^{-1}. \quad (3.29) \]

3.3 **Plasma Processing of NO\textsubscript{x} in the Presence of UHCs Using Single and Multiple Pulse Formats**

To validate the model, comparisons were made of computed results to experiments conducted by Khacef et al. [4] for DBD processing of NO in the presence of hydrocarbons. The 1 atm, 530 K gas feed contained 500 ppm NO, 500 ppm C\textsubscript{3}H\textsubscript{6}, 10% O\textsubscript{2} and 10% H\textsubscript{2}O, with the balance being N\textsubscript{2}. The reactor was a cylindrical wire-to-cylinder apparatus with a 0.5 cm gap. Comparison conditions were a repetition rate of 100 Hz and residence time of 0.1 s. Exit NO and NO\textsubscript{2} densities as a function of energy deposition are shown in Fig. 3.3(a). With increasing energy deposition, the NO density decreases while that of NO\textsubscript{2} initially increases and then decreases. The decrease is attributable to a decrease in its rate of formation from reactions involving NO. The computed NO densities agree well with the experiments whereas agreement for the case of NO\textsubscript{2} is within 15–20%. Given the agreement with the NO density, the less good agreement for NO\textsubscript{2} is attributable to the disposition of N atoms from NO forming NO\textsubscript{2} and other N containing products, and the destruction of NO\textsubscript{2}. For example, the density of
the dominant N-containing products HNO$_3$, HNO$_2$, CH$_3$ONO$_2$ and CH$_3$ONO, are shown in Fig. 3.3(b). The rate coefficient for formation of the major product, HNO$_3$, has an uncertainty of $\approx 25\%$ [5], and this uncertainty accounts for a large proportion of the disagreement.

The gas mixture discussed in the remainder of this chapter contains 8\% O$_2$, 6\% H$_2$O, 7\% CO$_2$, 400 ppm CO, 260 ppm NO, 133 ppm H$_2$, 500 ppm propene (C$_3$H$_6$) and 175 ppm propane (C$_3$H$_8$) with the balance being N$_2$. This composition was chosen to assist comparison to experiments conducted at Ford Research Laboratories using a DBD device. [6] The processed gas in the experiments was analyzed with a chemiluminescent NO$_x$ analyzer and a Fourier transform infrared (FTIR) spectrometer.

A baseline was obtained by performing simulations for a single pulse having a duration $\approx 10^{-7}$s. The electron density ($n_e$) and temperature ($T_e$) as a function of time for the base case are shown in Fig. 3.4a. The maximum electron density is $\approx 10^{13}$ cm$^{-3}$ at which time $T_e \approx 3$ eV. When the voltage is switched off, electron densities decay due to dissociative attachment with H$_2$O (69\%), O$_2$ (20\%), CO$_2$ (3\%), dissociative recombination with H$_3$O$^+$·H$_2$O (2\%) and nondissociative attachment with O$_2$ (6\%).

\begin{align*}
e + \text{H}_2\text{O} & \rightarrow \text{H}^- + \text{OH}, \\
e + \text{O}_2 & \rightarrow \text{O}^- + \text{O}, \\
e + \text{CO}_2 & \rightarrow \text{CO} + \text{O}^-, \\
e + \text{H}_3\text{O}^+·\text{H}_2\text{O} & \rightarrow \text{H} + \text{H}_2\text{O} + \text{H}_2\text{O}, \\
e + \text{O}_2 + \text{M} & \rightarrow \text{O}_2^- + \text{M}.
\end{align*}
O\textsuperscript{-}, H\textsuperscript{-} and O\textsubscript{2}\textsuperscript{-} then neutralize with positive ions, dominated by H\textsubscript{3}O\textsuperscript{+}·H\textsubscript{2}O to form neutral products,

\begin{align}
O\textsuperscript{-} + H\textsubscript{3}O\textsuperscript{+}·H\textsubscript{2}O & \rightarrow OH + H\textsubscript{2}O + H\textsubscript{2}O, \quad k = 3.0 \times 10^{-6} \text{ cm}^3 \text{s}^{-1}, \\
H\textsuperscript{-} + H\textsubscript{3}O\textsuperscript{+}·H\textsubscript{2}O & \rightarrow H\textsub{2} + H\textsub{2}O + H\textsub{2}O, \quad k = 3.0 \times 10^{-6} \text{ cm}^3 \text{s}^{-1}, \\
O\textsubscript{2}\textsuperscript{-} + H\textsubscript{3}O\textsuperscript{+}·H\textsubscript{2}O & \rightarrow O\textsub{2} + H + H\textsub{2}O + H\textsub{2}O, \quad k = 3.0 \times 10^{-6} \text{ cm}^3 \text{s}^{-1}.
\end{align}

After approximately $3 \times 10^{-7}$ s, ions have neutralized and recombined, and the chemistry is dominantly driven by neutral radicals, mostly OH, O, N, and HO\textsubscript{2}. The densities of OH, O, N, and HO\textsubscript{2} are shown in Fig. 3.4b for the base case. O, N, and OH are mainly generated by electron impact reactions (Eqs. 3.4-3.6). HO\textsubscript{2} is mainly produced as an end product of the NO - R\textsuperscript{-}OO radical reactions (67%), by the reaction of H with O\textsubscript{2} (11%) (Eq. 3.8) and by the reaction of HCO with O\textsubscript{2} (22%),

\[ \text{HCO} + \text{O}_2 \rightarrow \text{HO}_2 + \text{CO}, \quad k = 2.0 \times 10^{-14} \frac{(T/298)^{2.38}}{\text{exp}(768/T)} \text{ cm}^3 \text{s}^{-1}, \]

\[ k_{298} = 2.6 \times 10^{-13} \text{ cm}^3 \text{s}^{-1}. \] (3.38)

NO is dominantly consumed by conversion to NO\textsubscript{2} by the reactions with O, O\textsubscript{3}, HO\textsubscript{2}, and R–OO in proportions 2%, 1%, 38%, and 45% (Eqs. 3.2 and 3.21). Some amount of NO remediation also occurs by the reaction with OH to form HNO\textsubscript{2} (2%) (Eq. 3.2d) and by the formation of organic nitrites (8%) (Eqs. 3.24 and 3.28).

To investigate multiple pulse excitation, 20 pulses were applied over the residence time of 0.2 s at 100 Hz while keeping the total energy deposition constant. The electron
density and temperature during the first pulse and the last pulse for the base case are shown in Fig. 3.5. The lower energy deposition/pulse was obtained by decreasing the voltage. The electron density reaches a maximum of \(5 \times 10^{11} \text{ cm}^{-3}\) at which time \(T_e\) peaks to 3 eV. The current pulses are longer compared to the single pulse case in spite of the lower peak electron density because of the longer time required to avalanche due to the lower applied voltage. The lower energy deposition per pulse results in a peak electron density approximately 3% that of the single pulse which is less than 1/20 of the single pulse due to the lower ionization efficiency at lower voltage. The electron temperature does not significantly change since multistep excitation is not important for these conditions and so the ionization source is dominated by electron impact with ground state species. The electron density and the temperature for the 20th pulse are essentially the same as for the 1st pulse because of the almost constant composition of the background gas mixture.

The densities of O, N, OH, and HO\(_2\) during the first pulse are shown in Fig. 3.6a and for the 20th pulse in Fig. 3.6b. The maximum densities of O, N, OH, and HO\(_2\) are \(\approx 4.6\%\) that of the single pulse because of the lower energy deposition and lower excitation efficiency of the lower voltage. The maximum O, N, and OH densities are nearly unchanged for each of the 20 pulses since the density of the feedstock gases for the generation of O, N and OH, O\(_2\), N\(_2\) and H\(_2\)O do not change significantly. The rate of decay of O is essentially the same for the 1st and the 20th pulse whereas the rate of decay of N is slower for the 20th pulse because the density of NO, the main consumer of N atoms, has decreased by that time, as shown in Fig. 3.7. The decay of OH is more rapid during the 20th pulse compared to the 1st pulse because of the increased rate of reaction of
OH with NO₂, (Eq. 3.3) which has a higher density by the 20th pulse. The rate of decay of HO₂ is significantly smaller for the 20th pulse because the density of NO, which is the main consumer of HO₂, has decreased significantly. Unresolved HO₂ radical densities are shown in Fig. 3.6c. As the NO density decreases with each pulse, the density of HO₂ increases as its rate of consumption with NO decreases (Eq. 3.2c).

The densities of NO and NO₂ for single and multiple pulse excitation are compared in Fig. 3.7. With a single pulse, the NO density decreases from $4.2 \times 10^{15}$ cm$^{-3}$ to $1.0 \times 10^{14}$ cm$^{-3}$ at $t = 0.2$ s resulting in approximately 98% NO remediation. With multiple pulses, the exit densities of NO are higher than with a single pulse. This is due to the regeneration of NO from NO₂ by,

$$\text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2,$$

$$k = 6.5 \times 10^{-12} \exp(120/T) \text{ cm}^3 \text{s}^{-1},$$

$$k_{298} = 9.7 \times 10^{-12} \text{ cm}^3 \text{s}^{-1}.$$  \hspace{1cm} (3.39)

CH$_3$O is a transient species as shown in Fig. 3.8. It is generated by the reaction of CH$_3$O$_2$ with NO (Eq. 3.23) and consumed by reactions with NO and NO$_2$ (Eqs. 3.24 and 3.25) to produce CH$_3$ONO and CH$_3$ONO$_2$ respectively. The reaction rate coefficients for these processes are approximately the same and so their relative rates are determined by the relative concentrations of NO and NO$_2$. With a single pulse, the density of NO greatly exceeds NO$_2$ when the density of CH$_3$O is maximum. Hence, most of the CH$_3$O is lost in the reaction with NO forming CH$_3$ONO and the production of CH$_3$ONO$_2$ is low. With multiple pulses, CH$_3$O is produced during each pulse. With each successive pulse, the concentration of NO decreases and that of NO$_2$ increases. When the concentration of
NO₂ exceeds that of NO, CH₂O is consumed preferentially by NO₂ forming CH₃ONO₂ as opposed to reacting with NO. This leads to an increase in NOₓ remediation since CH₃ONO₂ is a terminal product.

With a single pulse, NO remediation is almost 98%, whereas with multiple pulses, the exit densities of NO are higher due to the regeneration from NO₂ through the reaction in Eq. 3.39. With a single pulse, the density of O decays before the density of NO₂ increases to a significant level. As a result, the regeneration process is not important. For later pulses, the densities of O and NO₂ are high at the same time, resulting in NO₂ reduction and formation of NO. This trend is shown in Fig. 3.9. During the initial pulses, NO is mainly converted to NO₂ (t < 0.05 s) and the density of NO₂ increases. At later times, as the concentration of NO₂ increases, NO and NO₂ come into a pulse-to-pulse equilibrium. After approximately 0.05 s, at the start of each pulse, NO₂ is converted to NO by the reaction with O atoms (Eq. 3.39) and at later times during the same pulse, the NO is converted back into NO₂ (Eqs. 3.2 and 3.21).

The densities of CH₃ONO₂ for single and multiple pulse formats for an energy deposition of 70 J/L are shown in Fig. 3.10. The final concentration with multiple pulses is ≈ 2.5 times that produced with a single pulse. This difference is due to the increased temporal overlap of CH₂O and NO₂ in the multiple pulse case in comparison with the single pulse.

The exit densities of NO as a function of energy deposition are shown in Fig. 3.11a. For energy depositions > 40 J/L, almost 100% of the NO is removed with a single pulse, a major fraction of (∼65%) which reappears as NO₂. With increasing energy deposition, a larger fraction of this NO₂ is converted to HNO₃. With multiple pulses, NO
conversion is lower compared to the single pulse case due to the regeneration of NO from NO\(_2\) (Eq. 3.39). The exit NO densities obtained using multiple pulses agree more closely with experimental results than with single pulses. The efficiency of these processes can be quantified by \(W\)-values. (\(W\)-value [eV/molecule] is the amount of energy required to remove one molecule of the compound. Lower values correspond to more efficient processes.) The \(W\)-values for NO\(_x\) as a function of energy deposition are also shown in Fig. 3.11a. The \(W\)-values for NO\(_x\) are lower (more efficient) with multiple pulses. At low energy deposition (\(\approx 20\) J/L), \(W\)-values are \(\approx 110\) eV for multiple pulses compared to 153 eV for a single pulse. At high energy deposition (\(\approx 60\) J/L), \(W\)-values for multiple pulses are \(\approx 185\) eV compared to 240 eV for a single pulse. The decrease in the \(W\)-values is a result of the additional removal of NO\(_x\) through the formation of larger amounts of HNO\(_2\), HNO\(_3\) and CH\(_3\)ONO\(_2\).

The densities of NO\(_2\) and CH\(_3\)ONO\(_2\) as a function of energy deposition with single and multiple pulses are shown in Fig. 3.11b. As before, the values obtained using multiple pulses agree more closely with those with experimental results. With multiple pulses, more NO\(_2\) is channeled into reactions with OH, CH\(_3\)O and O (Eqs. 3.3, 3.25 and 3.39) because, with each pulse, NO\(_2\) is present when O, OH and CH\(_3\)O have large densities. As a result, the NO\(_2\) densities are lower. With increasing energy deposition, the exit concentrations of NO\(_2\) initially increase and then decreases. The decrease is due to the increased production of O, OH and CH\(_3\)O at higher energy deposition, which then consume NO\(_2\) to produce NO, HNO\(_3\) and CH\(_3\)ONO\(_2\) respectively. The difference in CH\(_3\)ONO\(_2\) densities between single and multiple pulse formats increases with increasing energy deposition. This is because, at high energy deposition, larger quantities of CH\(_3\)O
and NO₂ are produced which results in more CH₃ONO₂ when their peak densities coincide.

The exit densities of N-containing products, HNO₂ and HNO₃ as a function of energy deposition are shown in Fig. 3.12a. The densities with multiple pulses are generally higher. HNO₂ is produced by the reaction of OH with NO (Eq. 3.2d). The higher HNO₂ density with multiple pulses is due to increase in the rate of the reaction,

\[
\text{HO}_2 + \text{NO}_2 \rightarrow \text{HNO}_2 + \text{O}_2, \quad k = 1.2 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}. \quad (3.40)
\]

Since the concentration of NO₂ increases with each pulse, high densities of HO₂ and NO₂ can coincide, a condition which does not significantly occur with a single pulse. As a result, the contribution from this reaction to HNO₂ production also increases. HNO₃ is produced by the reaction of NO₂ and OH (Eq. 3.3). With the increase in NO₂, the HNO₃ density also increases as OH and NO₂ also have high densities at the same time with multiple pulses.

The consumption of C₃H₆ as a function of energy deposition is shown in Fig. 3.12b. At higher energy deposition, C₃H₆ consumption is higher with multiple pulses due to the increased production of OH by the reaction of HO₂ with NO (Eq. 3.2c). HCO production also increases with multiple pulses due to the reaction of OH with the increasing density of HCHO,

\[
\text{OH} + \text{HCHO} \rightarrow \text{HCO} + \text{H}_2\text{O}, \quad k = 4.73 \times 10^{-12} (T/298)^{1.18} \exp(225/T) \text{ cm}^3 \text{ s}^{-1},
\]

\[
k_{298} = 1.0 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}. \quad (3.41)
\]
The production of CO therefore also increases with multiple pulses due to the increase in the production of HCO radicals, which then reacts with O₂ to produce CO (Eq. 3.38).

The final C-containing products HCHO, CH₃CHO, methyl oxirane and CHO-CHO are shown in Fig. 3.13. HCHO and CH₃CHO are generated as the end-products of the OH-initiated reactions with C₃H₆. With multiple pulses, the NO density is higher (because of the NO₂→NO conversion) which results in higher rates of reactions with peroxy radicals (Eq. 3.21). This increases the production of HCHO and CH₃CHO. The pathway leading to the production of HCHO and CH₃CHO is described in detail in Ref. 1. Briefly, the product RO of the reaction of peroxy radicals with NO (Eq. 3.21) decomposes to produce HCHO, CH₃CHO and hydroxyalkyl radicals. These hydroxyalkyl radicals further react with O₂ to produce HO₂ and more HCHO, and CH₃CHO. Methyl oxirane and CHO-CHO are products of the O atom initiated reactions with C₃H₆. Only small differences are observed in the densities of these species between single and multiple pulses because the initiating species, O, is not significantly affected by multiple pulses.

### 3.4 Concluding Remarks

The consequences of multiple discharge pulses on the plasma remediation of NOₓ in the presence of hydrocarbons was numerically investigated. When using multiple pulses, reactions occur in the latter pulses with reaction products from previous pulses which are not accessible with a single pulse. For example, less than 1 ppm of CH₃ONO₂ was formed with a single pulse whereas nearly 10 ppm was produced when the same
energy was distributed over 20 pulses. Comparison of the products of single and multiple pulse discharges showed marked differences in final concentrations of NO₂, HNOₓ, C₃H₆ and CO. \( W \)-values for NOₓ decreased from 240 eV for a single pulse to 185 eV when the same energy was distributed over 20 pulses.
Fig. 3.1. Individual contributions of various reaction channels towards the remediation of NO during the DBD processing of NO₃ in the absence of UHCs. The base gas mixture contains N₂/O₂/H₂O/CO₂ = 79/8/6/8 with 260 ppm of NO, 400 ppm of CO and 133 ppm of H₂. The energy deposition is 30 J/L. The reactor temperature and pressure are 453 K and 1 atm. In the absence of UHCs, the dominant reaction channels result in the oxidation of NO to NO₂. The reduction channel, \( \text{NO} + \text{N} \rightarrow \text{N}_2 + \text{O} \), accounts for only 8% of the NO remediation.
Fig. 3.2. Reaction mechanism for NOx in the presence of C₃H₆ and C₃H₈.
Fig. 3.3. NO and NO₂ exit densities as a function of energy deposition. Feed gas is at 260 °C and contains 500 ppm NO, 500 ppm C₃H₆, 10% O₂, 10% H₂O and balance N₂: (a) Experiment [4] and model results; (b) exit densities of major N-containing products.
Fig. 3.4. Plasma properties during the single pulse discharge processing of NO$_x$. a) $n_e$ and $T_e$. b) O, OH, N and HO$_2$. The background gas mixture is the same as in Fig. 3.1 with 500 ppm C$_3$H$_6$ and 175 ppm C$_3$H$_8$. 
Fig. 3.5. Electron density and temperature during the multiple pulse discharge processing of NOx. a) 1st of 20 pulses. b) 20th of 20 pulses. Electron densities and temperature are almost the same for all the pulses because the background gas mixture does not significantly change during the previous pulses. The gas mixture is the same as in Fig. 3.4.
Fig. 3.6. Atom and radical densities during the multiple pulse plasma processing of NO$_x$. 
a) O, OH, HO$_2$ and N during the first pulse. b) O, OH, HO$_2$ and N for the 20$^{th}$ pulse. c) 
Unresolved HO$_2$ densities during the full length of the residence time. Peak HO$_2$ 
densities increase with time owing to the decreased consumption from NO, the main 
consumer of HO$_2$. Conditions are the same as in Fig. 3.4.
Fig. 3.7. Comparison of NO, and NO$_2$ densities during the single and multiple discharge processing of NO$_x$. Conditions are the same as in Fig. 3.4. a) Single pulse. b) Multiple pulse.
Fig. 3.8. CH$_3$O, CH$_3$ONO$_2$, NO and NO$_2$ densities for single and multiple pulse discharge processing of NO$_x$. Conditions are the same as in Fig. 3.4. CH$_3$O and CH$_3$ONO$_2$ densities for a) Single pulse, b) Multiple pulse. NO, NO$_2$ and CH$_3$O densities for c) 1$^{st}$ of 20 pulses, d) 20$^{th}$ of 20 pulses. With multiple pulses, NO densities are gradually lowered and NO$_2$ densities are gradually increased. CH$_3$O is produced during each pulse and there comes a time when [NO$_2$]>[NO] and the formation of CH$_3$ONO$_2$ commences. CH$_3$O density decreases with each pulse, because the source of CH$_3$O, C$_3$H$_6$, decreases with each pulse.
Fig. 3.9. Variation of NO with NO$_2$. The curve corresponds to a time evolution. At $t < 0.05$ s, NO + O → NO$_2$ dominates over NO$_2$ + O → NO + O$_2$ due to the smaller density of NO$_2$. As a result, in each of the pulse periods after 0.05 s, there is an initial back conversion of NO$_2$ to NO and a later conversion of NO to NO$_2$. The contribution to NO formation from the initial back conversion of NO$_2$ becomes larger as the concentration of NO$_2$ increases.
Fig. 3.10. CH₃ONO₂ density as a function of time for single and multiple pulse formats. The energy deposition is 70 J/L and other conditions are the same as in Fig. 3.4.
Fig. 3.11. Effect of energy deposition on NOx remediation. a) NO and W-value for NOx. b) NO2 and CH3ONO2. Experimental values for NO (solid circles), NO2 (empty squares) and CH3ONO2 (filled squares) are also shown.[6] In general, the W-values for multiple discharge formats are lower, indicating higher efficiencies of remediation. NO2 densities in the case of multiple discharge formats are lower because of the back conversion to NO (NO2 + O → NO + O2). The differences in CH3ONO2 between single and multiple pulse formats increases with energy deposition because of the increased production of CH3O and NO2.
Fig. 3.12. Exit UHC and end product densities as a function of energy deposition. a) HNO$_2$ and HNO$_3$. b) C$_3$H$_6$ and CO. Single pulse (solid lines) and multiple pulse (dashed lines). HNO$_x$ densities are higher with multiple pulse formats due to the increased production from NO$_2$. Higher C$_3$H$_6$ conversion is observed with multiple pulse formats due to the increased production of OH from HO$_2$ (HO$_2$ + NO $\rightarrow$ NO$_2$ + OH). CO production increases with multiple pulse formats due to the increase in the production of HCO from HCHO (HCHO + OH $\rightarrow$ HCO + H$_2$O; HCO + O$_2$ $\rightarrow$ CO + HO$_2$).
Fig. 3.13. Exit hydrocarbon end product densities as a function of energy deposition. a) HCHO and CH$_3$CHO. b) Methyl oxirane and CHO-CHO. Single pulse (solid lines) and multiple pulse (dashed lines).
3.6 References


4. INTERACTIONS BETWEEN SOOT PARTICLES AND NO\textsubscript{X} DURING PLASMA REMEDIATION OF SIMULATED DIESEL EXHAUST

4.1 Introduction

In this chapter, we present results from a modeling investigation of the consequences of soot particles on the plasma chemistry in simulated diesel exhaust gas processed in a DBD reactor. The modified form of the zero-dimensional global kinetics simulation GLOBAL\textsubscript{KIN}, as described in Section 2.3, is used to address the heterogeneous chemistry on the soot surface. In this investigation, we address NO\textsubscript{x}-soot interactions, heterogeneous reactions of radicals such as O and OH with soot and the effects of soot on the ionization kinetics. We found that in the presence of soot, NO\textsubscript{x} remediation improved by nearly 10%. With soot, higher energies were required for the remediation of a given amount of NO. Since we have already discussed in detail the reaction mechanism for NO\textsubscript{x}-propene-propane in Section 3.2, only those reactions particularly germane to this study will be summarized in Section 4.2. The surface chemistry on soot particles is discussed in detail in Section 4.3. Results from our parametric studies on the NO\textsubscript{x} chemistry in the presence of soot are in Section 4.4. Section 4.5 contains our concluding remarks.

4.2 Reaction Mechanism for Gas Phase Chemistry in Simulated Diesel Exhaust

The base gas mixture contained \(\text{N}_2/\text{O}_2/\text{H}_2\text{O}/\text{CO}_2 = 79/8/6/7\) with 400 ppm of CO, 260 ppm of NO, 133 ppm of H\(_2\), 500 ppm of propene (\(\text{C}_3\text{H}_6\)) and 175 ppm of propane (\(\text{C}_3\text{H}_8\)). The last two gases are used as model UHCs. The list of species used for the simulations is given in Appendix A. All the reactions in Appendix B which involve the
species for this study are considered in the model. The reaction mechanism used in the absence of soot is discussed in detail in Chapter 3 and in Refs. 1 and 2.

The NO\textsubscript{x} chemistry is mainly driven by oxidation processes that result in the conversion of NO to NO\textsubscript{2}. The radicals initiating the chemistry, O, N and OH are produced by electron impact processes.

\begin{align*}
e + O_2 & \rightarrow O + O + e \quad (4.1) \\
e + N_2 & \rightarrow N + N + e \quad (4.2) \\
e + H_2O & \rightarrow OH + H + e \quad (4.3)
\end{align*}

NO reduction occurs through the reaction with N atoms.

\[ N + NO \rightarrow N_2 + O \quad (4.4) \]

Reactions with O atoms and OH radicals results in NO oxidation,

\begin{align*}
NO + O + M & \rightarrow NO_2 + M \quad (4.5) \\
NO_2 + OH + M & \rightarrow HNO_3 + M \quad (4.6)
\end{align*}

In the presence of UHCs, the key oxidant-species are the OH and HO\textsubscript{2} radicals and the β-hydroxyalkyl peroxy radicals (βHAPs) \textit{CH}_3\textit{CH(OO)}\textit{CH}_2\textit{OH} and \textit{CH}_3\textit{CH(OH)}\textit{CH}_2\textit{OO}. HO\textsubscript{2} is an intermediate produced by reactions of βHAPs. The βHAP radicals are produced through a two-step oxidation of propene initiated by OH, which is initially
produced by electron impact of H$_2$O (Eq. 4.3). The $\beta$-hydroxyalkyl radicals CH$_3$CHCH$_2$OH and CH$_3$CH(OH)CH$_2$ are intermediate species.

\[
\begin{align*}
C_3H_6 + OH & \rightarrow CH_3CHCH_2OH \\
C_3H_6 + OH & \rightarrow CH_3CH(OH)CH_2 \\
CH_3CHCH_2OH + O_2 & \rightarrow CH_3CH(OO)CH_2OH \\
CH_3CH(OH)CH_2 + O_2 & \rightarrow CH_3CH(OH)CH_2OO
\end{align*}
\]

The oxidation of NO then takes place following two pathways. The first one is a simple oxidation involving HO$_2$,

\[
\begin{align*}
HO_2 + NO & \rightarrow NO_2 + OH.
\end{align*}
\]

The second channel involves the $\beta$HAP radicals,

\[
\begin{align*}
CH_3CH(OO)CH_2OH + NO & \rightarrow CH_3CH(O)CH_2OH + NO_2 \\
CH_3CH(OH)CH_2OO + NO & \rightarrow CH_3CH(OH)CH_2O + NO_2
\end{align*}
\]

The radicals produced through the reactions of $\beta$HAPs with NO undergo thermal decomposition which ultimately leads to the formation of HO$_2$, formaldehyde (HCHO) and acetaldehyde (CH$_3$CHO).
\[ CH_3CH(O)CH_2OH \rightarrow CH_2OH + CH_3CHO \]  
\[ CH_2OH + O_2 \rightarrow HCHO + HO_2 \]  
\[ CH_3CH(OH)CH_2O \rightarrow CH_3CHOH + HCHO \]  
\[ CH_3CHOH + O_2 \rightarrow CH_3CHO + HO_2 \]

These reactions lead to NO→NO\(_2\) conversion. The actual NO\(_x\) remediation from the exhaust is mainly due to the oxidation of NO\(_2\) to HNO\(_3\) (Eq. 4.6) and

\[ NO + OH + M \rightarrow HNO_2 + M. \]  

The fraction of NO\(_x\) that is actually converted to HNO\(_2\) and HNO\(_3\) ranges between 10 and 20\%.[2]

### 4.3 NO\(_x\)-Soot Interactions

The gas temperatures of interest are \(\approx 453\) K and the gas residence time is usually a few tenths of a second. Under these conditions soot growth and soot nucleation are kinetically limited and may be neglected. Similarly, the soot oxidation by molecular oxygen usually observed in combustion does not take place in DBDs since gas temperatures above 700 K are typically required for such processes to be important.[3] However, soot particles may undergo oxidation when reacting with plasma generated radicals such as O and OH which are effective oxidants for carbonaceous particles even at low temperature \((T\approx 300\) K).\([4,5]\] The oxidation of soot by OH is one of the major soot consumption processes in flames, and occurs with a reaction probability of \(\approx 0.1\)
producing CO and H₂.[4] The oxidation of solid carbon by O atoms at low temperatures producing CO has been investigated only for solid graphite films. Reaction probabilities as high as 0.12 have been reported at 300 K.[5]

The interaction between NOₓ and soot takes place through adsorption and reduction processes involving NO₂. The interaction of NOₓ with carbonaceous particles was first considered in the context of atmospheric chemistry.[6-10] These studies indicated that reactions of soot with NO₂ leads to the formation of NO [8,9] and HNO₂ [10]. At low temperatures (\( T < 333 \text{ K} \) ) NO₂ once adsorbed tends to remain on the soot. The adsorption of NO₂ on n-hexane soot particles was investigated by Smith and coworkers who showed that, at 300 K, two adsorbates are formed, C-ONO and C-NO₂.[6,7,11] For temperatures higher than 350 K, a redox reaction of NO₂ occurs resulting in the desorption of NO and CO to the gas phase.

In principle, soot particles can also react with other radicals in the NOₓ chemistry. However the homogeneous gas phase chemistry of these radicals, with the exception of the βHAPs, produces loss frequencies several orders of magnitudes greater than their collision frequencies with soot particles. For example, the loss frequency of β hydroxyalkyl radicals by reaction with O₂ is approximately \( 10^8 \text{ s}^{-1} \) compared to the collision frequency with soot particles of \( \approx 10^4 \text{ s}^{-1} \) for a particle density of 5 x \( 10^8 \text{ cm}^{-3} \) and a particle diameter of 150 nm. Consequently, the concentration of these radicals is mainly governed by the gas phase chemistry and their interaction with soot may be neglected.
An exception is the $\beta$HAP radical which is consumed by NO with a frequency of $\approx 10^3$ s$^{-1}$ for a NO density of $10^{16}$ cm$^{-3}$. Since there is little data on the reaction of $\beta$HAP radicals on soot particles, parametric studies on these rate coefficients were performed.

To take into account these heterogeneous processes, we developed the following surface reaction mechanism for soot particles (denoted by $C_xH_y$):

\[
(C_xH_y) + NO_2 \rightarrow (C_{x-1}H_y)\text{-}C\text{-}NO_2 \quad (4.19)
\]

\[
(C_xH_y) + NO_2 \rightarrow (C_{x-1}H_y)\text{-}C\text{-}ONO \quad (4.20)
\]

\[
(C_xH_y) + O \rightarrow (C_{x-1}H_y)\text{-}C\text{-}O \quad (4.21)
\]

\[
(C_xH_y) + OH \rightarrow (C_{x-1}H_y)\text{-}C\text{-}OH \quad (4.22)
\]

\[
(C_{x-1}H_y)\text{-}C\text{-}NO_2 \rightarrow (C_{x-1}H_y) + NO + CO \quad (4.23)
\]

\[
(C_{x-1}H_y)\text{-}ONO \rightarrow (C_{x-1}H_y) + NO + CO \quad (4.24)
\]

\[
(C_{x-1}H_y)\text{-}C\text{-}O \rightarrow (C_{x-1}H_y) + CO \quad (4.25)
\]

\[
(C_{x-1}H_y)\text{-}C\text{-}OH \rightarrow (C_{x-1}H_{y-1}) + CO + \frac{1}{2} H_2 \quad (4.26)
\]

\[
\beta\text{HAP} + (C_xH_y) \rightarrow \beta\text{HAP}-(C_xH_y) \quad (4.27)
\]

\[
\beta\text{HAP}-(C_xH_y) \rightarrow C_xH_y + \text{Gas-phase decomposition products.} \quad (4.28)
\]

The soot is assumed to contain only H and C atoms, though actual soot may also contain O, N and S. The reaction mechanism begins with the adsorption of NO$_2$ on soot forming –C-NO$_2$ and –C-ONO complexes. Adsorption of O and OH produces –C-O and –C-OH complexes. Spontaneous desorption produces CO (and a reduction of soot mass) and NO or H$_2$. The reaction of $\beta$HAPs with soot is what we call a deactivation process. The resulting desorption products are not further important to the process and so the reactivity
of the βHAPs has been decreased. The kinetics of the adsorption reactions in Eqs. 4.19-4.22 and 4.27 is described in terms of reaction probability $\gamma_i$ ($i = 19-22, 27$ for reactions 4.19-4.22, 4.27). These probabilities depend on the surface density of free adsorption sites $[s]$. We assumed a simple linear dependence of the form $\gamma_i = \gamma_{i-0} [s]/[s]_0$ where $\gamma_{i-0}$ and $[s]_0$ are the reaction probability and the surface density of free adsorption sites at zero coverage of adsorbates. We chose $\gamma_{21-0} = 0.12$ and $\gamma_{22-0} = 0.1$ for O and OH based on Refs. 4 and 5. There is more uncertainty on the reaction probabilities for NO$_2$ ($\gamma_{19-0}$ or $\gamma_{20-0}$). Experimental studies of different carbonaceous particles have produced $\gamma_{20-0}$ of $5 \times 10^{-3} - 0.5$. We used $\gamma_{20-0} = 0.1$ from the experimental measurements of Smith and Chughtai for hexane soot as a base value.[6] The choice of this value was motivated by the fact that n-hexane soot is a good model for the soot found in diesel exhausts. However, since $\gamma_{0}(\text{NO}_2)$ may vary with the soot structure and the exhaust composition, we performed a parametric study of this parameter.

The rate constants of the desorption reactions in Eqs. 4.23 and 4.24 were deduced from the experiments of Tabor et al.[8] Frequencies of 100-500 s$^{-1}$ were determined for NO desorption following NO$_2$ adsorption on different carbonaceous particles at 300 K taking into account both the (C$_x$H$_y$)-NO$_2$ and (C$_x$H$_y$)-ONO channels. These values represent a lower limit since the gas temperature in exhausts at the point of processing is around 453 K which should result in higher desorption frequencies. Consequently, a parametric study was performed on the NO desorption frequency. Since the rate limiting step of the oxidation of soot by either O-atoms or OH-radicals is the adsorption step, an arbitrary value of $10^8$ s$^{-1}$, consistent with a fast desorption process, was used for the frequency of reactions in Eqs. 4.25, 4.26, and 4.28.
4.4 Plasma Remediation of NO\textsubscript{x} in the Presence of Soot

The gas is treated by a single discharge pulse having a duration \(\approx 10^{-7}\) s consistent with DBDs. The time evolution of the exhaust is followed for a reactor gas residence time of 0.2 s. The initial composition of the exhaust gas is \(\text{N}_2/\text{O}_2/\text{H}_2\text{O}/\text{CO}_2 = 79/8/6/7\) with 400 ppm of CO, 260 ppm of NO, 133 ppm of H\(_2\), 500 ppm of propene and 175 ppm of propane. The base case values are an energy deposition of 38 J/L, soot particle density of \(10^8\) cm\(^{-3}\) and soot particle diameters of 100 nm. The adsorption probability of NO\(_2\) and the desorption rate constants are \(\gamma_{20-0} = 0.1\) and \(k_d = 500\) s\(^{-1}\) respectively.

The fundamental processes initiating the plasma chemistry are the electron impact dissociation of O\(_2\), N\(_2\), H\(_2\)O and CO\(_2\). The electron density, \(n_e\) and temperature, \(T_e\) are shown in Fig. 4.1a for the base case conditions. \(T_e\) rises to 3 eV until electron avalanche increases the conductivity of the plasma and \(T_e\) begins to decrease. \(n_e\) reaches \(10^{13}\) cm\(^{-3}\) at which time the dielectric charges, thereby removing voltage from the gap. This reduces the electric field and \(T_e\) below the self sustaining value. The electron density then quickly decays by attachment and recombination. The densities of O, OH and N are shown in Fig. 4.1b. Electron impact on O\(_2\), N\(_2\) and H\(_2\)O produce O, N and OH respectively (Eqs. 4.1-4.3). O is also produced by the electron impact dissociation of CO\(_2\).

\[
e + \text{CO}_2 \rightarrow \text{CO} + \text{O} + e \quad (4.29)
\]

The peak O density is \(\approx 10^{15}\) cm\(^{-3}\). O is quickly consumed by O\(_2\) to form ozone.
\[ O + O_2 + M \rightarrow O_3 + M \quad (4.30) \]

N densities are smaller, \( \approx 8 \times 10^{13} \text{ cm}^3 \), due to the higher threshold energy for the dissociation of N\(_2\). N is dominantly consumed by the reaction with NO (Eq. 4.4). The peak OH density is \( \approx 10^{14} \text{ cm}^3 \). OH is dominantly consumed by reactions with UHCs (Eqs. 4.7 and 4.8). Other nonhydrocarbon species that convert NO to NO\(_2\) are HO\(_2\) (Eq. 4.11) and O\(_3\),

\[ O_3 + NO \rightarrow NO_2 + O_2. \quad (4.31) \]

The time-evolution of HO\(_2\) and O\(_3\) are shown in Fig. 4.1c. HO\(_2\) is sustained as an intermediate of the reactions of NO with the \( \beta \)HAPs (Eqs. 4.15 and 4.17) and by the reaction of HCO with O\(_2\).

\[ \text{HCO} + \text{O}_2 \rightarrow \text{HO}_2 + \text{CO} \quad (4.32) \]

The densities of NO and NO\(_2\) with and without heterogeneous reactions on the soot particles are shown in Fig. 4.2. The densities of OH and \( \beta \)HAP radicals are shown in Fig. 4.3. For \( t < 10^{-6} \text{ s} \), the species that initiate the NO\(_x\) chemistry, HO\(_2\), O\(_3\) and the \( \beta \)HAP radicals, have a low density and NO and NO\(_2\) densities remain nearly constant. For \( t > 10^{-6} \text{ s} \), homogenous reactions dominate and result in an almost total conversion of NO to NO\(_2\) when heterogeneous processes are not taken into account. When surface reactions are included, the densities of NO and NO\(_2\) critically depend on the probability of reaction.
with βHAP radicals. In the absence of βHAP deactivation, heterogeneous reactions slow down the total rate of NO→NO$_2$ conversion by the generation of NO on the particles. For example, the exit NO density is ≈50 ppm compared to ≈5 ppm when soot particles are not considered. The heterogeneously generated NO comes from the adsorption of NO$_2$ on the particles, followed by reduction of NO$_2$ and desorption. This is accompanied by a 35% decrease in NO$_2$ concentration.

When the adsorption of βHAPs is included with $\gamma_{27,0} = 1.0$, the effect of soot is more pronounced. The NO→NO$_2$ homogeneous conversion produces a minimum in the density of NO of $1.9 \times 10^{15}$ cm$^{-3}$ at $t \approx 10^{-2}$ s and then increases to $3.3 \times 10^{15}$ cm$^{-3}$, keeping NO as the major NO$_x$ species. As a result of βHAP deactivation on soot, βHAP densities decrease to $2.8 \times 10^{14}$ cm$^{-3}$ by $10^{-2}$ s (see Fig. 4.3). This decreases the rate of oxidation of NO by βHAP (Eqs. 4.12 and 4.13) which in turn decreases the rate of production of NO$_2$. The end result is a rebound in the density of NO.

The change in total NO$_x$ concentration is shown in Fig. 4.4c. The unresolved drop in NO$_x$ of ≈15 ppm when including soot chemistry without βHAP deactivation is due to the increased conversion of NO to HNO$_2$. This is facilitated by an increase of OH density when soot is included, as shown in Fig. 4.3b. When both NO$_2$-soot reactions and βHAP radical deactivation are taken into account, NO$_x$ removal decreases by ≈10%. This change is mainly due to the decrease of OH radical concentration, as shown in Fig. 4.3b. This decrease in OH is due to the decrease in the production of OH from βHAPs [pathways (4.12)-(4.14)-(4.15)-(4.11) and (4.13)-(4.16)-(4.17)-(4.11)]. Since βHAP deactivation decreases the gas-phase concentration of βHAP, the rates of the subsequent reactions in the pathways are also decreased. The rate of NO→HNO$_2$ conversion (Eq.
4.18) is proportional to the density of OH which is dominantly produced from HO2 through the reaction in Eq. 4.11. The main sources of HO2 are the reactions between βHAP radicals and NO through the reaction pathways (4.12)-(4.14)-(4.15) and (4.13)-(4.16)-(4.17). Therefore the deactivation of βHAPs leads to the decrease in HO2 and OH densities, which in turn slows the rate of homogeneous oxidation of NO and NO2.

The reaction of soot with NO2 also affects the C3H6, HCHO and CH3CHO densities as shown in Fig. 4.4. When γ27-0 = 0 for βHAPs, the C3H6 density decreases by ≈25% compared to the no soot case. This is due to the increase of the OH concentration (see Fig. 4.3b) which produces an increase in the consumption of C3H6 through the reactions in Eqs. 4.7 and 4.8. Simultaneously, the densities of formaldehyde and acetaldehyde increase by factors of 2 and 3. This is due to the higher NO density which leads to an increase in production of HCHO and CH3CHO through the reaction pathways (4.12)-(4.14)-(4.15) and (4.13)-(4.16)-(4.17). When γ27-0 = 1 for βHAPs, the decrease of the OH density lowers the reaction rate between OH and C3H6. Consequently, the C3H6 density is 12% higher than the case without soot. Smaller densities for HCHO and CH3CHO are also generated due to the lower rate of reaction of OH with C3H6, the initiating reaction for the production of these species.

The heterogeneous interaction of NO2, O and OH with soot particles leads to the formation of CO. The densities of CO with and without soot particles are shown in Fig. 4.5a. The heterogeneous production of CO starts at t≈ 10^-4 s when desorption of NO from the particles becomes important. Consequently, without βHAP deactivation, the exit CO concentration is ≈65% larger than the case without soot. The production of CO is assisted by the dynamics of NO↔NO2 exchange involving homogeneous NO→NO2.
conversion in the gas phase and heterogeneous \( \text{NO}_2 \rightarrow \text{NO} \) conversion on soot. For each cycle of this exchange (\( \text{NO}_2(gas) \rightarrow \text{NO}_2(\text{soot}) \rightarrow \text{NO}(gas) \)), one CO molecule is generated. When \( \gamma_{27-0} = 1 \) for \( \beta \text{HAP} \), the increase of CO concentration is \( \approx 20\% \) since the \( \text{NO} \leftrightarrow \text{NO}_2 \) exchange rate is slower due to the decrease of \( \beta \text{HAP} \) and \( \text{HO}_2 \) densities.

The desorption of CO produces a loss of soot mass shown in Fig. 4.5b. The mass of soot is decreased by a factor 3.5 with a diameter reduction of \( \approx 45\% \). The mass loss is initiated by reactions with \( \text{NO}_2 \) which account for \( \approx 99.9\% \) of the loss. Less soot is consumed when \( \gamma_{27-0} = 1 \) for \( \beta \text{HAP} \). In this case, the \( \beta \text{HAPs} \) are mainly consumed through deactivation on soot particles, which leads to a decrease of the \( \text{NO} \rightarrow \text{NO}_2 \) conversion rate and slower \( \text{NO} \leftrightarrow \text{NO}_2 \) exchange dynamics.

The densities of adsorbed species are shown in Fig. 4.6 for the case with no \( \beta \text{HAP} \) deactivation. The adsorption sites are not saturated. The surface densities of \( \text{NO}_2 \) adsorbates reaches a quasi-steady state value of \( \approx 6 \times 10^{14} \text{ cm}^{-2} \) at \( t \approx 10^{-3} \text{s} \) at which time the limiting step for the \( \text{NO}_2 \rightarrow \text{NO} \) heterogeneous conversion is the desorption of NO. The surface densities of O and OH are smaller compared to \( \text{NO}_2 \) due to the higher homogeneous loss frequencies of O and OH and the spontaneous desorption of \( \text{O}_{(\text{ads})} \) and \( \text{OH}_{(\text{ads})} \).

In the simulations discussed thus far, electron and ion attachment to soot were not considered. \( n_e \) and \( T_e \) are shown for particle density of \( 10^9 \text{ cm}^{-3} \) and soot diameter of 150 nm in Fig. 4.7 with and without particle charging. At this higher surface density of soot, there is \( \approx 5\% \) decrease in \( n_e \) and a small increase in \( T_e \) to increase the ionization rate to offset the electron loss to the particles. The effect is proportionally smaller for the smaller soot surface density of the base case. The consequence of these changes on the
active species in NO\textsubscript{x} chemistry is small and does not appreciably affect the results reported in this section.

The soot affects NO\textsubscript{x} chemistry through the kinetics of NO\textsubscript{2} adsorption and NO desorption. Since the adsorption probability and the soot surface may change during the treatment of the exhaust, it is instructive to parameterize the initial NO\textsubscript{2} adsorption probabilities, \([\gamma_{19-0} \text{ and } \gamma_{20-0} \text{ collectively called } \gamma_0(\text{NO}_2)]\), the NO desorption frequency \([k_d(-\text{C-ONO}) \text{ and } k_d(-\text{C-NO}_2) \text{ collectively called } k_d(\text{NO})]\) and the initial active soot surface per unit gas phase volume (the product of the soot active surface and the soot particle density, \(S_sn_p\)).

The exit densities of NO and NO\textsubscript{2} as a function of \(\gamma_0(\text{NO}_2)\) for different values of \(k_d(\text{NO})\), with \(\gamma_{27-0} = 0\) for \(\beta\)HAPs, are shown in Fig. 4.8. For low \(k_d\), NO increases monotonically with \(\gamma_0(\text{NO}_2)\). Larger rates of NO\textsubscript{2} adsorption produce more NO generation. Most of the NO is converted to NO\textsubscript{2} in the gas-phase thereby showing a monotonic decrease with \(\gamma_0(\text{NO}_2)\). For \(k_d(\text{NO}) \geq 1000\ \text{s}^{-1}\), the density of NO first increases with \(\gamma_0(\text{NO}_2)\), reaches a maximum and then decreases at high \(\gamma_0(\text{NO}_2)\) values. In the low \(\gamma_0(\text{NO}_2)\) range, the soot particles diameter does not change significantly, and the main consequence of increasing the adsorption probability is the production of more NO. Above a critical adsorption probability, the NO\textsubscript{2}-soot reaction results in a decrease of soot particle diameter as shown in Fig. 4.9a. This reduction in the specific surface area reduces the rate of NO\textsubscript{2}→NO heterogeneous conversion. Consequently, the homogenous NO→NO\textsubscript{2} conversion dominates over the heterogeneous NO\textsubscript{2}→ NO conversion, which leads to a smaller density for NO. The final NO concentration as a function of \(\gamma_0(\text{NO}_2)\) is not affected by the desorption frequency when \(k_d > 10^4\ \text{s}^{-1}\). This indicates that the
limiting step in $\text{NO}_2 \rightarrow \text{NO}$ heterogeneous conversion is the adsorption step. The decrease in soot diameter with increasing $\gamma_0(\text{NO}_2)$ is a result of the more rapid rate of heterogeneous reactions which bind with C in the soot, ultimately leading to the production of CO. As $k_d(\text{NO})$ increases, the fraction of unoccupied surface sites increases, as shown in Fig. 4.9b, thereby enabling more rapid adsorption of NO$_2$. When $k_d(\text{NO}) > 10^4 \text{ s}^{-1}$, the adsorption of NO$_2$ becomes the rate-limiting step in the oxidation of soot. This results in low surface densities of NO$_2$ and so the oxidation of soot saturates.

The variation of the total NO$_x$ density with $\gamma_0(\text{NO}_2)$ closely follows that of NO$_2$. In particular, a 15% increase in NO$_x$ remediation is obtained when $\gamma_0(\text{NO}_2)$ increases from $10^{-4}$ to 0.1. The increase in $\gamma_0(\text{NO}_2)$ also produces significant changes in CO, C$_3$H$_6$, HCHO and CH$_3$CHO densities, as shown in Fig. 4.10. These densities are almost independent on the NO$_2$ desorption frequency and values are shown for $k_d(\text{NO}_2)=10^3 \text{ s}^{-1}$. The increase of $\gamma_0(\text{NO}_2)$ in the range $10^{-4}$ - 0.1 leads to a 50% increase of CO and more than a 100% increase for HCHO and CH$_3$CHO. The concentration of C$_3$H$_6$ decreases by almost 25%. The increase of CO is a direct consequence of the increase of adsorption of NO$_2$ leading to NO and CO desorption. The increase in HCHO and CH$_3$CHO when increasing $\gamma_0(\text{NO}_2)$ is a consequence of the enhancement of NO-$\beta$HAP reactions in Eqs. 4.12 and 4.13 resulting from the increase in NO. These reactions also ultimately increase the OH density which increases the rate of reactions between OH and C$_3$H$_6$ (Eqs. 4.7 and 4.8), which then decreases the C$_3$H$_6$ density.

When $\gamma_{27-\delta}=1$ for $\beta$HAP, the densities of NO and NO$_2$ as a function of $\gamma_0(\text{NO}_2)$ have a weak dependence on $k_d$. The NO concentration increases by almost 90% when $\gamma_0(\text{NO}_2)$ is varied from $10^{-4}$ to 0.1 as shown in Fig. 4.11 while the NO$_2$ concentration
decreases. When $\beta$HAP radicals are totally quenched by the soot, the NO$_x$ chemistry is similar to that in the absence of UHCs. This results in a slower rate of NO$\rightarrow$NO$_2$ homogenous conversion, which also leads to a slower NO$_2$$\leftrightarrow$NO exchange dynamics. As a result, the effect of the NO released from the soot is less pronounced on the densities of the other species (e.g., C$_3$H$_6$) as compared to the $\gamma_{27-0} = 0$ case. The densities of HCHO and CH$_3$CHO, which are produced by NO-$\beta$HAP reactions, are almost one order of magnitude smaller than in the case for $\gamma_{27-0} = 0$ for $\beta$HAP. The production of CO is commensurately smaller.

The surface of soot particles per unit volume is one of the key-parameters in the model. The average diameter of soot particles in diesel exhaust is usually 90-120 nm while the particle density can vary by orders of magnitude depending on the combustion regime or the type of engine.[12-14] The variation of the exit NO and NO$_2$ concentration as a function of particle density are shown in Fig. 4.12a for $\gamma_o$(NO$_2$) = 0.1. The increase of $n_p$ leads to an increase of NO and a decrease of NO$_2$ due to the larger surface area available for NO$_2$ adsorption. The heterogeneous reaction chemistry becomes significant for $n_p > 5 \times 10^7$ cm$^{-3}$. NO becomes the major exit NO$_x$ species when $n_p > 2 \times 10^8$ cm$^{-3}$. The NO density saturates for $n_p > 10^9$ cm$^{-3}$ due to depletion of NO$_2$. Except for $n_p > 5 \times 10^9$ cm$^{-3}$, the increase of NO leads to a small increase in the remediation of NO$_x$ and an increase of HNO$_2$. The higher production of HNO$_2$ is due to the increase of the densities of HO$_2$ and OH whose production is assisted by the NO$_2$$\leftrightarrow$NO exchange dynamics. The increase of NO results in higher rates of reactions with $\beta$HAPs (Eqs. 4.12 and 4.13). This ultimately results in the increase in the densities of HO$_2$, HCHO and CH$_3$CHO through the reaction pathways (4.12)-(4.14)-(4.15) and (4.13)-(4.16)-(4.17) as shown in Fig.
4.12b. The increase of NO and H$_2$O$_2$ leads to an increase in OH production (Eq. 4.11) which results in more propene consumption (Eqs. 4.7 and 4.8). The increase in total particle surface area increases the concentration of carbon monoxide by a factor of 2.2 for $n_p=10^7$ cm$^{-3}$ to $10^9$ cm$^{-3}$.

The results just discussed had $\gamma_{27-0} = 0$ for $\beta$HAP. When $\gamma_{27-0} = 1$ for $\beta$HAP, the results obtained are similar to those for $\gamma_0$(NO$_2$) variation. In particular, the dynamics of the NO$_2$$\leftrightarrow$NO exchange slow down and there is no indirect effect of soot on the production of HO$_2$ and OH as observed for the $\gamma_{27-0} = 0$ case.

The consequences of energy deposition by the plasma on the NO$_x$ chemistry with and without soot are shown in Fig. 4.13. The peak O and OH densities increase linearly with increasing energy deposition. The increase in the production of these radicals increases the remediation of NO and NO$_x$. The decrease of NO with energy deposition is larger without soot particles due to the heterogeneous generation of NO with soot. Soot however, generally improves NO$_x$ remediation. This is due to the conversion of NO to HNO$_2$ through the reaction with OH (Eq. 4.18). As energy deposition increases, the exit HCHO and CH$_3$CHO densities decrease, both with and without soot, as shown in Fig. 4.13b. This is due to the fact that with increasing energy more OH is generated which consumes more NO to form HNO$_2$. Thus the amount of NO reacting with $\beta$HAPs decreases and consequently, HCHO and CH$_3$CHO which are formed from the products of the reaction of $\beta$HAP with NO also decrease.

The energy required for converting a given amount of NO to NO$_2$ before performing a catalytic reduction strongly depends on the soot particle density and is shifted to higher values when $n_p$ is increased. Plasma treatment cannot generally reduce
the NO concentration below a lower limit of \( \approx 20-40 \) ppm if a large amount of soot is present in exhausts.

### 4.5 Concluding Remarks

Results from a computational investigation of NO\(_x\) plasma remediation were used to discuss the consequences of heterogeneous chemistry on soot particles. For particle densities typical of diesel exhausts, \( n_\rho = 10^7 - 10^9 \) cm\(^{-3}\), the heterogeneous chemistry maintains the dynamic NO density which ultimately enables a higher NO\(_x\) remediation rate. The heterogeneous reactions also increase the production of carbon monoxide, formaldehyde and acetaldehyde. When the particle density is greater than \( 10^8 \) cm\(^{-3}\), there may also be additional remediation of UHCs such as propene.

The effects of soot on the NO\(_x\) reaction mechanism is summarized in Fig. 4.14. Soot influences the NO\(_x\) chemistry by changing the NO/NO\(_2\) ratio in the plasma. By regenerating the NO from NO\(_2\) and by indirectly leading to the increase of OH radicals (Eq. 4.11), soot increases the formation of HNO\(_2\). This leads to an increased NO\(_x\) remediation. The increase in OH density also increases UHC consumption (Eqs. 4.7 and 4.8). The effect of soot strongly depends on the disposition of \( \beta \)HAP radicals on particles. If \( \beta \)HAP adsorb on the particles with high probability, the homogeneous chemistry is similar to that taking place without UHCs since these important intermediate radicals are consumed by the soot (or deactivated). The soot particles affect the NO\(_x\) chemistry mainly through the NO\(_2\)\( \rightarrow \)NO heterogeneous conversion. The effect of soot is much more complex in the case when the reactivity of \( \beta \)HAP radicals on the particles is small. In such a case, the combined effect of the heterogeneous NO\(_2\) reactions and the
homogeneous reactions in Eqs. 4.12 and 4.13 are reflected in the production of HNO$_2$ (Eq. 4.18), formaldehyde [pathways (4.12)-(4.14)-(4.15) and (4.13)-(4.16)] and acetaldehyde [pathways (4.12)-(4.14) and (4.13)-(4.16)-(4.17)]. These dynamics also result in the remediation of UHCs and to the increase of CO in the exhaust.

The CO production is accompanied by a decrease in soot mass which, for most of the conditions discussed here, does not lead to a complete removal of soot particles. The soot particles also do not contain a significant amount of adsorbed NO$_x$ for the desorption frequencies used in this work. Consequently, posttreatment of these particles would not lead to regeneration of NO$_x$. The presence of soot increases the amount of energy required for a given NO$\rightarrow$NO$_2$ conversion. For exhausts with high densities of soot particles, the variation of NO conversion with energy density shows a higher asymptotic value compared to the no soot case.

This work has clarified weakness in the database which should be addressed to more accurately investigate soot dynamics. In particular, a better description of the soot structure is necessary to more accurately model the surface reaction kinetics. The effect of the heterogeneous chemistry of water adsorption on soot particles should also be investigated, and the possible interactions between different adsorbates should be taken into account. The disposition of $\beta$HAP radicals on soot is a major issue which requires further investigation.
Fig. 4.1. Time evolution of plasma parameters and plasma chemistry initiating species. a) $n_e$ and $T_e$. b) N, OH and O. c) HO$_2$ and O$_3$. Figures correspond to the base case conditions – Energy deposition of 38 J/L, initial gas mixture of N$_2$/O$_2$/H$_2$O/CO$_2$=79/6/8/7 with 400 ppm CO, 133 ppm H$_2$ and 260 ppm NO (1 atm, 453 K), soot particle number density of $10^8$ cm$^{-3}$ and diameter of 100 nm.
Fig. 4.2. Time evolution of NO\textsubscript{x} species without soot (No SOOT), with soot (SOOT, No HAP) and with soot + \( \beta \)HAP deactivation on soot (SOOT, HAP). a) NO. b) NO\textsubscript{2}. c) NO\textsubscript{x}. The presence of soot improves NO\textsubscript{x} remediation through the increased production of HNO\textsubscript{2}. With \( \beta \)HAP deactivation on soot, the exit concentration of NO\textsubscript{x} is higher compared to the no-soot case because of the decreased production of OH. Conditions are the same as for Fig. 4.1.
Fig. 4.3. Time evolution of radicals involved in NO remediation. a) $\beta$HAPs and b) OH for the cases without soot, with soot and with soot + $\beta$HAP deactivation. In the presence of soot and without $\beta$HAP deactivation, OH densities are higher and as a result aid in NO$_x$ remediation through the formation of HNO$_2$. With $\beta$HAP deactivation, the rate of reactions in the NO$_x$-soot reaction cycle is decreased leading to a decreased production of OH. Conditions are the same as for Fig. 4.1.
Fig. 4.4. Time evolution of UHCs and end-products of the remediation process. a) C$_3$H$_6$ b) HCHO and c) CH$_3$CHO for the cases without soot, with soot and with soot + βHAP deactivation. In the presence of soot and no βHAP deactivation, C$_3$H$_6$ concentrations are smaller due to the increased consumption by reactions with OH. This in turn, leads to increased production of HCHO and CH$_3$CHO, the final products of NO-βHAP reaction. With βHAP deactivation, OH production decreases leading to lesser C$_3$H$_6$ consumption and a lower production of HCHO and CH$_3$CHO. Conditions are the same as for Fig. 4.1.
Fig. 4.5. Time variation of soot oxidation products and soot properties. a) CO production for the cases without soot, with soot and with soot + βHAP deactivation. b) soot diameter and fractional reduction in soot mass. Conditions are the same as for Fig. 4.1. In the presence of soot, more CO is produced due to the oxidation of soot by NO₂. With βHAP deactivation, less NO₂ is produced due to the heterogeneous loss of βHAP on soot. As a result, less CO is produced compared to the soot-no βHAP case. However, compared to the no-soot case, CO production is increased due to the additional heterogeneous CO source by NO₂ adsorption.
Fig. 4.6. Time evolution of the adsorbed species, O, OH and NO₂. Conditions are same as for Fig. 4.1.
Fig. 4.7. Electron attachment to soot. $n_e$ and $T_e$ for a soot particle density of $10^9$ cm$^{-3}$ and an initial particle diameter of 150 nm. Other conditions are same as for Fig. 4.1. The electron temperature increases slightly in the presence of soot to increase ionization rates to account for losses to the soot.
Fig. 4.8. Exit concentrations as a function of $\gamma_o$(NO$_2$) for different values of $k_d$(NO$_2$). a) NO. b) NO$_2$. Conditions are the same as for Fig. 4.1 with no $\beta$HAP deactivation.
Fig. 4.9. Change in soot properties as a function of $\gamma_o$(NO$_2$) and $k_d$(NO$_2$). a) Soot diameter. b) Fraction of unoccupied surface sites.
Fig. 4.10. Exit densities of HCHO, CH$_3$CHO, C$_3$H$_6$ and CO as a function of $\gamma_0$(NO$_2$). With increasing adsorption probabilities of NO$_2$, the production of HCHO, CH$_3$CHO and CO increase and the consumption of C$_3$H$_6$ also increases due to the indirect increase in OH production.
Fig. 4.11. Variation of NO, NO\textsubscript{2} and CO with $\gamma_0$(NO\textsubscript{2}) for full $\beta$HAP deactivation. As $\gamma_0$(NO\textsubscript{2}) increases, more NO\textsubscript{2} is adsorbed leading to an increased gas-phase concentration of NO. This also leads to an increased oxidation of soot resulting in increased CO production. Other conditions are the same as for Fig. 4.1.
Fig. 4.12. Effect of soot particle number density on NO$_x$ / C$_3$H$_6$O$_2$. a) NO, NO$_2$, NO$_x$ and HNO$_2$. Increased soot number density increases the rate of heterogeneous NO$_2$ → NO conversion resulting in higher NO concentrations. NO$_x$ densities decrease with n$_p$ due to the increased production of HNO$_2$. b) HCHO, CH$_3$CHO, C$_3$H$_6$ and CO. Increasing n$_p$ increases the surface area for heterogeneous reactions resulting in increased production of OH which increases the rate of reaction with C$_3$H$_6$. As a result more of HCHO and CH$_3$CHO are produced. CO increases due to the increased rate of soot oxidation.
Fig. 4.13. Effect of energy deposition on NO\<sub>x</sub> / C\textsubscript{2}H\textsubscript{4}O\textsubscript{2}. a) Exit concentrations of NO, NO\<sub>x</sub> with and without soot. NO\<sub>x</sub> remediation improves in the presence of soot due to the increased production of HNO\textsubscript{2}. In the presence of soot NO is not completely remediated due to the heterogeneous back-conversion of NO\textsubscript{2} to NO. b) Exit concentrations of HCHO, CH\textsubscript{3}CHO and OH with and without soot. With increasing energy deposition, more OH is produced due to the increased rates of the dissociation of H\textsubscript{2}O. However, in the presence of soot, higher OH densities are sustained due to the increased production of HO\textsubscript{2}. 
Fig. 4.14. Summary of the effects of soot on homogeneous NO\textsubscript{x} chemistry. Heterogeneous reactions on soot surfaces result in higher NO densities in the gas-phase which increases the rates of the reactions with \(\beta\)HAPs. This leads to increased production of aldehydes and HO\textsubscript{2}. HO\textsubscript{2} further reacts with NO by HO\textsubscript{2} + NO \rightarrow NO\textsubscript{2} + OH to increase the production of OH. This increases the production of HNO\textsubscript{2} and the conversion of C\(_3\)H\(_6\) thereby improving NO\textsubscript{x} remediation and UHC consumption.
4.7 References


5. REPEITIVELY PULSED PLASMA REMEDIATION OF NO\textsubscript{x} IN SOOT LADEN EXHAUST

5.1 Introduction

In Chapter 3, we saw that interpulse chemistry significantly affects the plasma remediation of NO\textsubscript{x} and in fact, was more efficient for NO\textsubscript{x} remediation. We found that the interaction of products of previous pulses with the species during the current pulse allowed for a different chemistry in the repetitively pulsed case which ultimately improved remediation. In Chapter 4, we showed that soot particles significantly affect the NO\textsubscript{x} chemistry during plasma remediation. In this chapter, we report on a computational investigation of the combined effects of repetitive discharge pulses and soot on NO\textsubscript{x} remediation and soot oxidation. For this study, we used the modified version of GLOBAL_KIN as described in Section 2.3 to address the reaction kinetics on the soot surface. We investigated the consequences of varying energy deposition, inlet UHC concentration, soot diameter, and soot particle number density on NO\textsubscript{x} remediation and soot oxidation for cases when using a single pulse and when using multiple pulses. Results for repetitively pulsed plasma processing of NO\textsubscript{x} and oxidation of soot are discussed in Section 5.2. Concluding remarks are in Section 5.3.

5.2 Repetitively Pulsed Plasma Processing of NO\textsubscript{x} and Oxidation of Soot

The base case operating conditions are 1 atm, 453 K, gas residence time of 0.2 s (space velocity of 18,000 hr\textsuperscript{-1}) and an electrode spacing of 0.25 cm. The gas mixture is N\textsubscript{2}/O\textsubscript{2}/H\textsubscript{2}O/CO\textsubscript{2} = 79/8/6/7 with 260 ppm NO, 400 ppm CO, 133 ppm H\textsubscript{2}, and 500 ppm C\textsubscript{3}H\textsubscript{6}. The reaction set used for this study is the same as that in Chapter 4. The soot
density and diameter are $10^8$ cm$^{-3}$ and 100 nm. The energy deposition is 30 J/l (10% fuel economy for a diesel engine [1]) which, for a single pulse, corresponds to a discharge voltage of 18 kV. To address repetitively pulsed discharges, 100 Hz here, the model is executed for a series of current pulses and afterglow periods (20 for the 0.2 s residence time). The initial conditions for a discharge pulse are given by the species densities at the end of the previous afterglow. To achieve the same energy deposition with repetitive pulses, the applied voltage is 13 kV. Although there are differences in excitation rates resulting from the different voltages, these differences do not prejudice any comparisons. When varying energy deposition, either the voltage or the permittivity of the dielectric was changed.

Electron density ($n_e$) and temperature ($T_e$) are shown in Fig. 5.1 for the base case conditions when using single and multiple pulses. The current pulse lasts approximately 145 ns for the single pulse case and approximately 165 ns for the multiple pulse case. The longer current pulse when using repetitive pulses is because of the slower avalanche resulting from the lower applied voltage. Electrons, accelerated by the electric field, collide with the background gases producing positive ions and secondary electrons, dominantly by,

$$e + N_2 \rightarrow N_2^+ + e + e, \quad (5.1)$$

$$e + O_2 \rightarrow O_2^+ + e + e, \quad (5.2)$$

$$e + H_2O \rightarrow H_2O^+ + e + e, \quad (5.3)$$

$$e + CO_2 \rightarrow CO_2^+ + e + e. \quad (5.4)$$
For a single discharge pulse, the peak electron density is $\approx 10^{13}$ cm$^{-3}$ and the peak electron temperature is $\approx 3$ eV. With repetitive pulses, less energy is deposited per pulse and, as a result, the peak electron density is $\approx 0.03 \times 10^{13}$ cm$^{-3}$, while the peak electron temperature is $\approx 3$ eV. Since the current pulse is wider (165 ns) with repetitive pulses than with a single pulse (145 ns) the peak $n_e$ at high pulse repetition frequency (PRF) is less than $1/20^{th}$ of the single pulse value. The time dependences of $n_e$ and $T_e$ for the first and last pulse of the repetitive pulse case do not differ appreciably because the mole fractions of the major background gases do not change significantly.

Although the chemistry of interest is dominantly through free-radical reactions, it is nevertheless instructive to also discuss the ion chemistry. Since the ion chemistry does not significantly differ between single and repetitive pulses due to the shorter time scales for ion reactions (100s of ns), we will discuss the ion chemistry for single pulses.

The initiating reactions for ion chemistry are electron impact ionizations producing $\text{N}_2^+$, $\text{O}_2^+$, $\text{H}_2\text{O}^+$, and $\text{CO}_2^+$ (Eqs. 5.1-5.4). Nearly 46% of the $\text{N}_2^+$ formed undergoes charge exchange reactions with $\text{H}_2\text{O}$ to form $\text{H}_2\text{O}^+$,

$$\text{N}_2^+ + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^+ + \text{N}_2, \quad k = 2.0 \times 10^{-9} \text{ cm}^3\text{s}^{-1} \ [2], \quad (5.5)$$

where $k$ is the rate coefficient for the reaction. Most of the remaining $\text{N}_2^+$ (52%) dimerizes with $\text{N}_2$ to form $\text{N}_4^+$ which then charge exchanges with $\text{O}_2$ to form $\text{O}_2^+$,

$$\text{N}_2^+ + \text{N}_2 + \text{M} \rightarrow \text{N}_4^+ + \text{M}, \quad k = 1.1 \times 10^{-29} \text{ cm}^6\text{s}^{-1} \ [3], \quad (5.6)$$
\[ \text{N}_4^+ + \text{O}_2 \rightarrow \text{O}_2^+ + \text{N}_2 + \text{N}_2, \quad k = 2.5 \times 10^{-10} \text{ cm}^3 \text{s}^{-1} \] [3]. (5.7)

\( \text{O}_2^+ \) is also formed by charge exchange reactions of \( \text{H}_2\text{O}^+ \) and \( \text{CO}_2^+ \) with \( \text{O}_2 \),

\[ \text{H}_2\text{O}^+ + \text{O}_2 \rightarrow \text{O}_2^+ + \text{H}_2\text{O}, \quad k = 4.3 \times 10^{-10} \text{ cm}^3 \text{s}^{-1} \] [3], (5.8)

\[ \text{CO}_2^+ + \text{O}_2 \rightarrow \text{O}_2^+ + \text{CO}_2, \quad k = 5.6 \times 10^{-11} \text{ cm}^3 \text{s}^{-1} \] [3]. (5.9)

About 66% of the \( \text{CO}_2^+ \) is consumed by the above reaction. The remainder is lost by charge neutralization reactions with \( \text{O}^- \) and \( \text{H}^- \).

Almost all of the \( \text{O}_2^+ \) formed by the above reactions associates with \( \text{H}_2\text{O} \) to form \( \text{O}_2^+ \cdot \text{H}_2\text{O} \), which further reacts with \( \text{H}_2\text{O} \) to form \( \text{H}_3\text{O}^+ \),

\[ \text{O}_2^+ + \text{H}_2\text{O} + \text{M} \rightarrow \text{O}_2^+ \cdot \text{H}_2\text{O} + \text{M}, \quad k = 2.5 \times 10^{-28} \text{ cm}^6 \text{s}^{-1} \] [3], (5.10)

\[ \text{O}_2^+ \cdot \text{H}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{OH} + \text{O}_2, \quad k = 1.2 \times 10^{-9} \text{ cm}^3 \text{s}^{-1} \] [3]. (5.11)

\( \text{H}_3\text{O}^+ \) is also formed from \( \text{H}_2\text{O}^+ \),

\[ \text{H}_2\text{O}^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{OH}, \quad k = 1.7 \times 10^{-9} \text{ cm}^3 \text{s}^{-1} \] [3]. (5.12)

\( \text{H}_3\text{O}^+ \) reacts with \( \text{H}_2\text{O} \) to form the complex ion, \( \text{H}_3\text{O}^+ \cdot \text{H}_2\text{O} \),
\[ H_3O^+ + H_2O + M \rightarrow H_3O^+\cdot H_2O + M, \quad k = 5.0 \times 10^{-27} \text{ cm}^6 \text{s}^{-1} \quad [3]. \quad (5.13) \]

Electrons are dominantly lost by dissociative attachment to \( H_2O \) (73%), \( CO_2 \) (3%), and \( O_2 \) (24%) (both dissociative and nondissociative),

\[
\begin{align*}
&\text{e} + H_2O \rightarrow H^- + OH, \quad (5.14) \\
&\text{e} + CO_2 \rightarrow O^- + CO, \quad (5.15) \\
&\text{e} + O_2 \rightarrow O^- + O, \quad (5.16) \\
&\text{e} + O_2 + M \rightarrow O_2^- + M. \quad (5.17)
\end{align*}
\]

The densities of \( H_3O^+\cdot H_2O, N_4^+, O^- \) and \( H^- \) as a function of time are shown in Fig. 5.2. The rapid decay of \( N_4^+ \) is by reaction with \( O_2 \) forming \( O_2^- \) (Eq. 5.7). \( O^- \) and \( H^- \) neutralize less rapidly by collisions with \( H_3O^+\cdot H_2O \) to produce \( H_2O, OH \) and \( H_2 \),

\[
\begin{align*}
H_3O^+\cdot H_2O + O^- &\rightarrow H_2O + H_2O + OH, \quad k = 3.0 \times 10^{-6} \text{ cm}^3 \text{s}^{-1} \quad [3], \quad (5.18) \\
H_3O^+\cdot H_2O + H^- &\rightarrow H_2O + H_2O + H_2, \quad k = 3.0 \times 10^{-6} \text{ cm}^3 \text{s}^{-1} \quad [3]. \quad (5.19)
\end{align*}
\]

The free-radical reactions are initiated by the electron impact dissociation of the background gases producing \( N, O, OH \), and \( H \),

\[
\begin{align*}
&\text{e} + N_2 \rightarrow N + N + e, \quad (5.20) \\
&\text{e} + O_2 \rightarrow O + O + e, \quad (5.21)
\end{align*}
\]
\[ e + H_2O \rightarrow OH + H + e, \quad (5.22) \]
\[ e + CO_2 \rightarrow O + CO + e. \quad (5.23) \]

The densities of N, O, OH and H as a function of time are shown in Fig. 5.3 for a single pulse, and for the first and the last pulse of the multiple pulse case. Recalling that the current pulse is \( \approx 150 \) ns, the production of these primary radicals is dominantly from electron impact reactions. Reactions with neutral species then determine the disposition of this initial inventory of radicals. N atoms are dominantly consumed by reactions with NO, NO\(_2\), CO\(_2\) and O\(_2\),

\[ N + NO \rightarrow N_2 + O, \quad k = 3.4 \times 10^{-11} \exp(-24/T) \ cm^3 s^{-1}, \]
\[ k_{298} = 3.2 \times 10^{-11} \ cm^3 s^{-1} \ [3], \quad (5.24) \]
\[ N + NO_2 \rightarrow N_2O + O, \quad k = 2.4 \times 10^{-12} \ cm^3 s^{-1} \ [3], \quad (5.25) \]
\[ N + NO_2 \rightarrow NO + NO, \quad k = 9.9 \times 10^{-13} \ cm^3 s^{-1} \ [3], \quad (5.26) \]
\[ N + CO_2 \rightarrow CO + NO, \quad k = 3.2 \times 10^{-13} \exp(-1710/T) \ cm^3 s^{-1}, \]
\[ k_{298} = 1.0 \times 10^{-15} \ cm^3 s^{-1} \ [4], \quad (5.27) \]
\[ N + O_2 \rightarrow NO + O, \quad k = 4.4 \times 10^{-12} \exp(-3220/T) \ cm^3 s^{-1}, \]
\[ k_{298} = 7.7 \times 10^{-17} \ cm^3 s^{-1} \ [5], \quad (5.28) \]

where \( k_{298} \) is the rate constant at 298 K. When using a single pulse, the contribution to N consumption from the reactions with NO, NO\(_2\), CO\(_2\) and O\(_2\) (Eqs. 5.24-5.28) are 89.0%,

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0.2%, 5.0% and 3.0% respectively. With repetitive pulses, the contributions are 63.0%, 14.0%, 14.0% and 8.0%. The higher contribution from NO₂ for N consumption with multiple pulses is a result of an increased overlap in time of the NO₂ and N atom densities. The density of NO, a major consumer of N atoms, decreases during later pulses (explained below). As a result, the N atom densities are sustained for longer periods during the latter pulses compared to the first pulse when using repetitive pulses.

With repetitive pulses, the peak O density is \( \approx 10^{14} \text{ cm}^3 \) in any given pulse as compared with \( 2 \times 10^{15} \text{ cm}^3 \) for a single pulse. The peak O atom densities for the first and last of 20 pulses, determined largely by electron impact, are similar because the density of O₂ remains nearly a constant. O atoms are primarily consumed by reactions with C₃H₆, NO₂ and O₂,

\[
O + C_3H_6 \rightarrow \text{Methyl Oxirane}, \quad k = 1.2 \times 10^{-12} \text{ cm}^3 \text{s}^{-1} \quad [6], \quad (5.29)
\]

\[
\rightarrow C_2H_5CHO, \quad k = 1.2 \times 10^{-12} \text{ cm}^3 \text{s}^{-1} \quad [6], \quad (5.30)
\]

\[
\rightarrow CH_2CHO + CH_3, \quad k = 0.8 \times 10^{-12} \text{ cm}^3 \text{s}^{-1} \quad [6], \quad (5.31)
\]

\[
\rightarrow C_2H_5 + HCO, \quad k = 0.8 \times 10^{-12} \text{ cm}^3 \text{s}^{-1} \quad [6], \quad (5.32)
\]

\[
O + NO_2 \rightarrow NO + O_2, \quad k = 6.5 \times 10^{-12} \exp(120/T) \text{ cm}^3 \text{s}^{-1},
\]

\[
k_{298} = 9.7 \times 10^{-12} \text{ cm}^3 \text{s}^{-1} \quad [5], \quad (5.33)
\]

\[
O + O_2 + M \rightarrow O_3 + M, \quad k = 3.4 \times 10^{-34} (T / 298)^{-1.2} \text{ cm}^6 \text{s}^{-1} \quad [4]. \quad (5.34)
\]
Using single pulses, the contributions of the reactions with C\textsubscript{3}H\textsubscript{6}, NO\textsubscript{2} and O\textsubscript{2} (Eqs. 5.29-5.34) towards O consumption are 56\%, 4\% and 11\% respectively. When using repetitive pulses, the contributions are 56\%, 25\% and 12\%. The larger contribution to O consumption by the reaction with NO\textsubscript{2} with multiple pulses is due to the increased overlap in time of NO\textsubscript{2} and O atom densities. The more rapid consumption of O in the first pulse is due to the higher densities of C\textsubscript{3}H\textsubscript{6} during the first pulse compared to the last.

OH radicals are consumed primarily by reactions with C\textsubscript{3}H\textsubscript{6} forming C\textsubscript{3}H\textsubscript{6}OH (hydroxy alkyl radicals), HCHO forming HCO, NO\textsubscript{2} forming HNO\textsubscript{3} and NO forming and HNO\textsubscript{2},

\[
\text{OH} + \text{C}_3\text{H}_6 \rightarrow 0.65 \text{CH}_3\text{CHCH}_2\text{OH} + 0.35 \text{CH}_3\text{CH(OH)}\text{CH}_2, \quad k = 4.9 \times 10^{-12} \exp(504/T) \text{ cm}^3\text{s}^{-1},
\]
\[
k_{298} = 2.6 \times 10^{-11} \text{ cm}^3\text{s}^{-1} \ [6], \quad (5.35)
\]

\[
\text{OH} + \text{HCHO} \rightarrow \text{HCO} + \text{H}_2\text{O}, \quad k = 4.7 \times 10^{-12} (T/298)^{1.2} \exp(225/T) \text{ cm}^6\text{s}^{-1},
\]
\[
k_{298} = 1.0 \times 10^{-11} \text{ cm}^3\text{s}^{-1} \ [7], \quad (5.36)
\]

\[
\text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M}, \quad k = 4.6 \times 10^{-29} (T/298)^{-5.5} \exp(-1183/T) \text{ cm}^6\text{s}^{-1},
\]
\[
k_{298} = 8.7 \times 10^{-31} \text{ cm}^6\text{s}^{-1} \ [8], \quad (5.37)
\]

\[
\text{OH} + \text{NO} + \text{M} \rightarrow \text{HNO}_2 + \text{M}, \quad k = 8.6 \times 10^{-31} (T/298)^{-2.5} \exp(34/T) \text{ cm}^6\text{s}^{-1},
\]
\[
k_{298} = 9.7 \times 10^{-31} \text{ cm}^6\text{s}^{-1} \ [8]. \quad (5.38)
\]
The contributions of reactions of C_{3}H_{6}, HCHO, NO_{2} and NO (Eqs. 5.35-5.38) to OH consumption are 66%, 5%, 7% and 4% when using a single pulse. With multiple pulses, the contributions are 72%, 11%, 10% and 4%. OH consumption is more rapid in the last pulse compared to the first due to increased rates of reactions with HCHO and NO_{2} which have larger densities during the last pulse.

In the absence of UHCs, the radicals primarily responsible for the oxidation of NO to NO_{2} in the gas phase are HO_{2} and O_{3}. With UHCs, radicals such as CH_{3}CH(OH)CH_{2}OO and CH_{3}CH(OO)CH_{2}OH (β-hydroxy alkyl peroxies, in short βHAPs) are produced, which oxidize NO to NO_{2}. The reactions of HO_{2}, O_{3} and βHAPs with NO produces NO_{2}, OH and O_{2}. Products also include CH_{3}CH(OH)CH_{2}O and CH_{3}CH(O)CH_{2}OH (β-hydroxy alkoxy radicals, in short βHAs),

\[
\begin{align*}
\text{NO} + \text{CH}_{3}\text{CH(OH)CH}_{2}\text{OO} & \rightarrow \\
\text{NO}_{2} + \text{CH}_{3}\text{CH(OH)CH}_{2}\text{O}, & k = 2.7 \times 10^{-12} \exp\left(360/T\right) \text{cm}^{3} \text{s}^{-1}, \\
k_{298} = 9.0 \times 10^{-12} \text{cm}^{3} \text{s}^{-1} [6], & (5.39) \\
\text{NO} + \text{CH}_{3}\text{CH(OO)CH}_{2}\text{OH} & \rightarrow \\
\text{NO}_{2} + \text{CH}_{3}\text{CH(O)CH}_{2}\text{OH}, & k = 2.7 \times 10^{-12} \exp\left(360/T\right) \text{cm}^{3} \text{s}^{-1}, \\
k = 9.0 \times 10^{-12} \text{cm}^{3} \text{s}^{-1} [6], & (5.40) \\
\text{NO} + \text{HO}_{2} & \rightarrow \text{NO}_{2} + \text{OH}, \\
k = 3.5 \times 10^{-12} \exp\left(240/T\right) \text{cm}^{3} \text{s}^{-1}, & k_{298} = 7.8 \times 10^{-12} \text{cm}^{3} \text{s}^{-1} [6], & (5.41) \\
\text{NO} + \text{O}_{3} & \rightarrow \text{NO}_{2} + \text{O}_{2}, \\
k = 4.3 \times 10^{-12} \exp\left(-1598/T\right) \text{cm}^{3} \text{s}^{-1}, &
\end{align*}
\]
The time dependence of the densities of the βHAPs, HO2 and O3 for a single pulse and for the first and the last pulse of the high PRF case are shown in Fig. 5.4. βHAPs are produced by the reaction of O2 with hydroxy alkyl radicals (produced by the reaction in Eq. 5.35),

\[
\text{CH}_3\text{CHCH}_2\text{OH} + \text{O}_2 \rightarrow \text{CH}_3\text{CH(OO)CH}_2\text{OH}, \quad k = 1.2 \times 10^{-11} \text{ cm}^3 \text{s}^{-1} \quad [6], \quad (5.43)
\]

\[
\text{CH}_3\text{CH(OH)CH}_2 + \text{O}_2 \rightarrow \text{CH}_3\text{CH(OH)CH}_2\text{OO}, \quad k = 3.8 \times 10^{-12} \text{ cm}^3 \text{s}^{-1} \quad [6], \quad (5.44)
\]

and are mainly consumed reactions with NO to form NO2 and βHA radicals. Further reactions of βHA radicals then result in the formation of HCHO, CH3CHO and HO2,

\[
\text{CH}_3\text{CH(OH)CH}_2\text{O} \rightarrow \text{CH}_3\text{CHOH} + \text{HCHO}, \quad k = 7.9 \times 10^{13} \exp(-10517/T) \text{ s}^{-1},
\]

\[
k_{298} = 3.7 \times 10^{-2} \text{ s}^{-1} \quad [4], \quad (5.45)
\]

\[
\text{CH}_3\text{CHOH} + \text{O}_2 \rightarrow \text{CH}_3\text{CHO} + \text{HO}_2, \quad k = 1.9 \times 10^{-11} \text{ cm}^3 \text{s}^{-1} \quad [9], \quad (5.46)
\]

\[
\text{CH}_3\text{CH(O)CH}_2\text{OH} \rightarrow \text{CH}_2\text{OH} + \text{CH}_3\text{CHO}, \quad k = 9.1 \times 10^4 \text{ s}^{-1} \quad [4], \quad (5.47)
\]

\[
\text{CH}_2\text{OH} + \text{O}_2 \rightarrow \text{HCHO} + \text{HO}_2, \quad k = 2.0 \times 10^{-12} \text{ cm}^3 \text{s}^{-1} \quad [10]. \quad (5.48)
\]
The peak βHAP radical density during the first pulse of 20 pulses is \( \approx 2 \times 10^{13} \) cm\(^{-3}\). The decrease in this peak density during the 20\(^{th}\) pulse (to \( 1.5 \times 10^{13} \) cm\(^{-3}\)) is primarily a result of the decrease in the density of \( \text{C}_3\text{H}_6 \), its precursor (discussed below).

The contributions of the reactions of \( \text{O}_2 \) with \( \text{CH}_3\text{CHOH} \) and \( \text{CH}_2\text{OH} \) (Eqs. 5.46 and 5.48) to the formation of \( \text{HO}_2 \) when using multiple pulses are 27\% and 50\% respectively. Other reactions which produce \( \text{HO}_2 \) include,

\[
\begin{align*}
\text{H + O}_2 + \text{M} & \rightarrow \text{HO}_2 + \text{M}, \quad k = 1.8 \times 10^{-32} (T/298)^{-0.8} \text{ cm}^6 \text{s}^{-1} [11], \quad (5.49) \\
\text{HCO + O}_2 & \rightarrow \text{HO}_2 + \text{CO}, \quad k = 2.0 \times 10^{-14} (T/298)^{2.4} \exp(768/T) \text{ cm}^3 \text{s}^{-1}, \\
& \quad k_{298} = 2.6 \times 10^{-13} \text{ cm}^3 \text{s}^{-1} [4], \quad (5.50)
\end{align*}
\]

with their contributions being 2\% (Eq. 5.49) and 21\% (Eq. 5.50). With single pulses, the contributions to \( \text{HO}_2 \) production by \( \text{O}_2 \) reactions with \( \text{CH}_3\text{CHOH} \), \( \text{CH}_2\text{OH} \), \( \text{H} \) and \( \text{HCO} \) are 24\%, 46\%, 10\% and 20\%. The primary loss process for \( \text{HO}_2 \) radicals is the reaction with \( \text{NO} \) forming \( \text{NO}_2 \) and \( \text{OH} \) (Eq. 5.41).

\( \text{O}_3 \) is produced by the reaction of \( \text{O} \) with \( \text{O}_2 \) (Eq. 5.34) and is dominantly consumed by reaction with \( \text{NO} \) forming \( \text{NO}_2 \) (Eq. 5.42) and by reaction with \( \text{O}_2(\text{^1}\Delta) \) forming \( \text{O} \),

\[
\begin{align*}
\text{e + O}_2 & \rightarrow \text{O}_2(\text{^1}\Delta) + \text{e}, \quad (5.53) \\
\text{O}_3 + \text{O}_2(\text{^1}\Delta) & \rightarrow \text{O} + \text{O}_2 + \text{O}_2, \quad k = 5.2 \times 10^{-11} \exp(-2840/T) \text{ cm}^3 \text{s}^{-1}, \\
& \quad k_{298} = 3.8 \times 10^{-15} \text{ cm}^3 \text{s}^{-1} [9]. \quad (5.54)
\end{align*}
\]
Due to the larger rate coefficients for reactions of NO with HO₂ and βHAP radicals compared to O₃, HO₂ and βHAP radicals are more rapidly consumed than ozone. As a consequence, the O₃ density accumulates pulse to pulse, as shown in Fig. 5.4c.

The densities of NO and NO₂ as a function of time with and without soot for a single pulse are shown in Fig. 5.5. Without soot NO is mainly consumed by reactions with βHAP radicals (34%), HO₂ (36%), CH₃O₂ (3%), and C₂H₅O₂ (6%) to produce NO₂ by the reactions in Eqs. 5.39-5.41. The reaction of NO with CH₃O₂ and C₂H₅O₂ are,

\[
\text{NO} + \text{CH}_3\text{O}_2 \rightarrow \text{NO}_2 + \text{CH}_3\text{O}, \quad k = 4.2 \times 10^{-12} \exp(180/T) cm^3 s^{-1},
\]

\[
k_{298} = 7.7 \times 10^{-12} cm^3 s^{-1} [9], \quad (5.55)
\]

\[
\text{NO} + \text{C}_2\text{H}_5\text{O}_2 \rightarrow \text{NO}_2 + \text{C}_2\text{H}_5\text{O}, \quad k = 3.1 \times 10^{-12} \exp(330/T) cm^3 s^{-1},
\]

\[
k_{298} = 9.4 \times 10^{-12} cm^3 s^{-1} [4]. \quad (5.56)
\]

CH₃O₂ and C₂H₅O₂ are formed by the reactions of CH₃ and C₂H₅ with O₂,

\[
\text{CH}_3 + \text{O}_2 + \text{M} \rightarrow \text{CH}_3\text{O}_2 + \text{M}, \quad k = 4.4 \times 10^{-31} (T/298)^{-3} cm^6 s^{-1} [4], \quad (5.57)
\]

\[
\text{C}_2\text{H}_5 + \text{O}_2 + \text{M} \rightarrow \text{C}_2\text{H}_5\text{O}_2 + \text{M}, \quad k = 8.0 \times 10^{-26} (T/298)^{-8.2} \exp(-2150/T) cm^6 s^{-1},
\]

\[
k_{298} = 5.0 \times 10^{-29} cm^6 s^{-1} [12]. \quad (5.58)
\]

CH₃ and C₂H₅ are produced by the reactions of O atoms with C₃H₆ (Eqs. 5.31 and 5.32).
With soot particles, NO\textsubscript{2} undergoes heterogeneous reactions on their surface to form NO and CO,

\[ \text{NO}_2(g) \rightarrow \text{NO}_2(\text{ads}), \quad \gamma_o(\text{NO}_2)=0.1 \ [13], \quad (5.59) \]

\[ \text{NO}_2(\text{ads}) \rightarrow \text{NO}(g) + \text{CO}(g), \quad k = 10^3 \text{ s}^{-1} \ [14], \quad (5.60) \]

resulting in an increase in the NO density at later times.

The time dependences of the densities of NO and NO\textsubscript{2} with and without soot for multiple pulses are shown in Fig. 5.6a. Without soot, most of the NO is converted to NO\textsubscript{2} by reactions with βHAP radicals (42%), HO\textsubscript{2} (44%), O\textsubscript{3} (2%), CH\textsubscript{3}O\textsubscript{2} (5%) and C\textsubscript{2}H\textsubscript{5}O\textsubscript{2} (2%) (Eqs. 5.39-5.42, 5.55, and 5.56). After the fifth pulse, the density of NO is less than that of NO\textsubscript{2}. Since radicals such as N, O, OH, HO\textsubscript{2} and CH\textsubscript{3}O are produced (Eqs. 5.20-5.22, 5.49, and 5.55) with every discharge pulse, the rate of reaction of these radicals with NO\textsubscript{2} increases relative to NO whose density decreases with each pulse. Without NO, the source of NO\textsubscript{2} removed and the density of NO\textsubscript{2} decreases with each pulse. The end products of the NO\textsubscript{2} conversion include NO (Eqs. 5.26 and 5.33), HNO\textsubscript{3} (Eq. 5.37), HNO\textsubscript{2} and CH\textsubscript{3}ONO\textsubscript{2}. HNO\textsubscript{2} is formed by the reaction of HO\textsubscript{2} with NO\textsubscript{2},

\[ \text{HO}_2 + \text{NO}_2 \rightarrow \text{HNO}_2 + \text{O}_2, \quad k = 1.2 \times 10^{-13} \text{ cm}^3 \text{s}^{-1} \ [4]. \quad (5.61) \]

CH\textsubscript{3}ONO\textsubscript{2} is formed by the reaction of CH\textsubscript{3}O with NO\textsubscript{2},

\[ \text{CH}_3\text{O} + \text{NO}_2 \rightarrow \text{CH}_3\text{ONO}_2, \quad k = 8.3 \times 10^{-12} \text{ cm}^3 \text{s}^{-1} \ [4]. \quad (5.62) \]
With multiple pulses and soot, NO densities are generally higher and NO₂ densities are generally lower than without soot because of the heterogeneous conversion of NO₂ to NO on the soot surface. In any given pulse, there are three distinct phases for the evolution of the NO density as shown in Fig. 5.6b for the 12th pulse. In the first phase during the current pulse, there is a small and rapid production of NO from NO₂. In the second phase following the current pulse and lasting approximately 3 ms, the NO density decreases primarily due to gas phase reactions with βHAP radicals and HO₂ (Eqs. 5.39-5.41), resulting in conversion to NO₂. During the third phase, the NO density increases due to its heterogeneous production from the reaction of NO₂ with soot (Eqs. 5.59 and 5.60). For any given pulse, the gas phase consumption of NO is larger than its heterogeneous production, and so the NO density decreases. For pulses later than the 5th, the density of NO₂ is greater than NO. As a result, immediately following the current pulse, there is a rapid decrease in the density of NO₂ and a corresponding increase in the NO density as shown in Figs. 5.7b and 5.7c. This is due to the conversion of NO₂ to NO by reactions with O and N atoms (Eqs. 5.26 and 5.33) which are produced by electron impact reactions (Eqs. 5.20 and 5.21).

Since the density of NO decreases with every pulse, the rates of reaction of NO with βHAP radicals, O₃ and HO₂ decrease with each pulse. As a result, the rates of consumption of βHAP radicals, O₃ and HO₂ decrease with each pulse and so their densities at the end of a pulse increase with time. These trends are shown in Fig. 5.7.

In Chapter 4, we showed that the surface densities of O and OH on the soot are at least two orders of magnitude smaller than that of NO₂ and hence do not significantly
influence the heterogeneous chemistry. The time dependencies of the fraction of sites occupied by NO$_2$ when using single and multiple pulses are shown in Fig. 5.8a. With a single pulse, most of the adsorbed NO$_2$ desorbs to NO and CO. However, after a residence time of 0.2 s a significant fraction (15%) of the sites on the soot surface are still occupied by NO$_2$. When using multiple pulses, due to the smaller rate of production of NO$_2$ during any given pulse compared to a single pulse, a smaller fraction of the sites are occupied by NO$_2$. However, due to the larger densities of NO$_2$ at later times when using multiple pulses (See Fig. 5.6a.), there is an increased flux of NO$_2$ to the soot. The end result is an increased rate of soot oxidation.

The mass fractions of soot remaining as a function of time are shown in Fig. 5.8b for single and multiple pulses. The initial rates of oxidation are higher with single pulses because of the larger flux of NO$_2$ to the soot resulting from the initially larger NO$_2$ densities in the gas phase. At later times, there is a larger flux of NO$_2$ to the soot with multiple pulses (compare Figs. 5.6 and 5.7a) and, as a result, more soot oxidation occurs. This higher flux results from the conversion of NO to NO$_2$ by βHAP radicals and HO$_2$ (Eqs. 5.39-5.41). The diameters of the soot particles as a function of time for single and multiple pulses are shown in Fig. 5.8c. As a result of oxidation the diameter of the soot particles decreases to approximately 58 nm at the end of 0.2 s with a single pulse while with repetitive pulses, the exit soot diameter is 38 nm.

To investigate the consequences of complete desorption of NO$_2$ from the soot, the residence time of the gas was increased to 3 s while keeping the energy deposition and the number of pulses a constant. To maintain the 20 pulse format, the repetition rate was decreased to 7 Hz. With a single pulse almost all of the NO$_2$ desorbs from the surface as
shown in Fig. 5.9a. Due to the smaller production of NO₂ per pulse with multiple pulses, less NO₂ is adsorbed during the early pulses as shown in Fig. 5.9b. However, due to the larger flux of NO₂ at later times, more soot is ultimately oxidized using multiple pulses. For example, the diameters of the soot as a function of time for the single and repetitive pulse cases (7 Hz) are shown in Fig. 5.9c. With multiple pulses the NO₂ densities are sustained for longer times and so almost complete soot oxidation occurs. With single pulses, most of the NOₓ for times > 0.1 s is NO and so less soot oxidation occurs. The soot diameter decreases by only ≈55% for the same energy deposition.

Soot leads to circular chemistry involving interconversion between NO and NO₂, as shown in Fig. 5.10. In the absence of soot, the conversion of NO to NO₂ occurs by the reaction of NO with HO₂ which produces OH (Eq. 5.41) and by the reactions of NO with βHAP radicals which lead to HO₂ formation (Eqs. 5.39, 5.40, 5.45-5.48). The reaction of OH with C₃H₆ starts a chain reaction resulting in the formation of βHAP radicals (Eqs. 5.35, 5.43, and 5.44). Thus, the reaction of HO₂ with NO leads to the formation of βHAP radicals and that of βHAPs with NO produces HO₂. The products of the gas phase reactions converting NO to NO₂ are reactants for further NO to NO₂ conversion. With soot, heterogeneous conversion of NO₂ produces NO and as a result NO densities are sustained for longer periods of time. This leads to increased rates for the conversion of NO to NO₂ in the gas phase and a prolonged production of OH, HO₂ and βHAP radicals.

Due to the larger production of OH with soot more C₃H₆ is consumed (Eq. 5.35), as shown in Fig. 5.11a. Soot does not significantly affect C₃H₆ consumption when using single pulses as the heterogeneous conversion of NO₂ to NO occurs on time scales > 1 ms by which time most of the radicals required for the conversion of NO to NO₂ have been
consumed. As a result, the circular chemistry is less efficient. NO oxidizing radicals (for example, HO₂, O₃ and βHAP radicals) are produced during each pulse of the repetitive pulse case and so there is an increased overlap in time of the densities of NO and the oxidizing species. There is also a higher density of NO with soot. The combined effect of multiple pulses and soot is production of more OH (by the circular chemistry) which then results in increased consumption of C₃H₆, as shown in Figs. 5.12b and 5.12c.

In order to track the large dynamic ranges in densities of radicals over large dynamic ranges in time, the densities have to this point to be expressed in cm⁻³. However, it is typical for measures of remediation to be expressed in ppmv (parts per million by volume) or simply ppm for comparison with the emission standards expressed in such units. These units will be used in the following discussion. For the operating conditions of interest (1 atm, 453 K), 1 ppm = 1.62 × 10¹³ cm⁻³ (initial NO density = 260 ppm = 4.2 × 10¹⁵ cm⁻³).

Increasing energy deposition with single pulses results in increased NO conversion, as shown in Fig. 5.12a. (Energy deposition was varied by changing the applied voltage.) At 60 J/l, NO densities decrease to approximately 125 ppm resulting in an NO conversion of 52%. This higher rate of NO consumption at larger energy deposition is primarily due to the chain chemistry producing N₂ and HNO₂ by the reactions in Eqs. 5.24 and 5.38. At higher energy deposition, there is also an increased production of O atoms which generates more CH₃ and C₂H₅ by reactions with C₃H₆ (Eqs. 5.31 and 5.32). This results in increased formation of CH₃O and C₂H₅O (Eqs. 5.55 and 5.56), which then consume NO by
\[
\text{CH}_3\text{O} + \text{NO} \rightarrow \text{CH}_3\text{ONO}, \quad k = 2.0 \times 10^{-11} \text{ cm}^3\text{s}^{-1} [4], \quad (5.63)
\]

\[
\text{C}_2\text{H}_5\text{O} + \text{NO} \rightarrow \text{C}_2\text{H}_5\text{ONO}, \quad k = 2.0 \times 10^{-11} \text{ cm}^3\text{s}^{-1} [4]. \quad (5.64)
\]

The exit composition of NO\textsubscript{x} is primarily NO because of the heterogeneous conversion of NO\textsubscript{2} to NO on the soot (Eqs. 5.59 and 5.60). The fraction of sites on the soot occupied by NO\textsubscript{2} is maximum at approximately 0.15 when the NO\textsubscript{2} density peaks and subsequently decreases as the NO\textsubscript{2} flux decreases at higher energy deposition. This decrease in NO\textsubscript{2} density is largely a result of reactions with radicals such as OH, HO\textsubscript{2}, and CH\textsubscript{3}O to produce HNO\textsubscript{3}, HNO\textsubscript{2}, and CH\textsubscript{3}ONO\textsubscript{2} (Eqs. 5.37, 5.61, and 5.62). The decrease is also attributable to reactions of NO\textsubscript{2} with C\textsubscript{2}H\textsubscript{5}O\textsubscript{2} to form C\textsubscript{2}H\textsubscript{5}OONO\textsubscript{2},

\[
\text{C}_2\text{H}_5\text{O}_2 + \text{NO}_2 \rightarrow \text{C}_2\text{H}_5\text{OONO}_2, \quad k = 2.6 \times 10^{-10} (T / 298)^{-3.7} \exp(-1029 / T) \text{ cm}^3\text{s}^{-1},
\]

\[
k_{298} = 8.2 \times 10^{-12} \text{ cm}^3\text{s}^{-1} [4]. \quad (5.65)
\]

With increasing energy deposition with repetitive pulses, HO\textsubscript{2}, O\textsubscript{3} and βHAP radicals are produced on every pulse and so the heterogeneously generated NO is more effectively converted to NO\textsubscript{2}. As a result, NO densities decrease more rapidly with energy deposition, as shown in Fig. 5.12b. The reactions responsible for the decrease in the NO\textsubscript{2} density with energy deposition are similar to those for a single pulse, however the decrease is more pronounced because of the increased overlap in time of NO\textsubscript{2} and OH, CH\textsubscript{3}O, C\textsubscript{2}H\textsubscript{5}O\textsubscript{2} and HO\textsubscript{2} densities following each pulse. The fraction of sites
occupied by adsorbed NO₂ is in general larger with multiple pulses due to the larger NO₂ density.

The $W$-values for NOₓ with single and multiple pulses are shown in Fig. 5.12c. In general repetitive pulses are more efficient (lower $W$-value) compared to single pulses. At the base case energy of 30 J/l, the $W$-value for NOₓ for a single pulse is 152 eV and for multiple pulses is 120 eV. The increase in efficiency is primarily a result of increased conversion of NO₂ to HNO₃, CH₃ONO₂, C₂H₅OONO₂ and HNO₂. The densities of these nitrogen-containing products, shown in Fig. 5.13, are higher for multiple pulses as a result of the increased overlap in time of the densities of NO₂ and the participating radical species (for example, OH, CH₃O, C₂H₅O₂ and HO₂). At 60 J/l, approximately 70 ppm of HNO₂ is produced using repetitive pulses whereas only 35 ppm is formed using single pulses. At the same energy deposition, repetitive multiple pulses produce approximately 40 ppm of organic nitrates (C₂H₅OONO₂ and CH₃ONO₂) while with single pulses only 10 ppm are produced.

Important hydrocarbon products of C₃H₆ dissociation include aldehydes such as HCHO and CH₃CHO. The exit densities of HCHO and CH₃CHO as a function of energy deposition are shown in Fig. 5.13c. HCHO and CH₃CHO are produced from the reactions of the βHA radicals (Eqs. 5.45-5.48). More C₃H₆ is consumed (see Fig. 5.10) with repetitive pulses leading to an increased production of βHAP radicals (Eqs. 5.35, 5.43, and 5.44). This results in increased formation of βHA radicals (Eqs. 5.39 and 5.40) which are the precursors to HCHO and CH₃CHO production (Eqs. 5.45-5.48). The HCHO density decreases at higher energy depositions owing to consumption by reaction with OH (Eq. 5.36).
The mass fractions of soot remaining as a function of energy deposition for single and repetitive pulses are shown in Fig. 5.14a. At energy depositions > 20 J/l, the NO₂ density in the gas phase for single pulses decreases because of increased NO₂ consumption by the reactions in Eqs. 5.37, 5.61, 5.62, and 5.65. As a result, a smaller amount of soot is oxidized at higher energies. The larger NO₂ densities obtained with increasing energy deposition with repetitive pulses result in higher rates of adsorption on the soot. Consequently, more soot is oxidized. The $W$-values for soot removal (J/µg) are shown as a function of energy deposition in Fig. 5.14b. Using multiples pulse in general results in more efficient soot removal due to the sustained densities of NO₂ which oxidize the soot. The $W$-value for soot at 30 J/l is about 0.3 J/µg for multiple pulses and 0.5 J/µg for single pulses.

CO is an end product not only of soot oxidation (Eq. 5.60) but also of gas phase reactions such as the electron impact dissociation of CO₂ (Eq. 5.23) and the reaction of HCO with O₂,

$$\text{HCO} + \text{O}_2 \rightarrow \text{CO} + \text{HO}_2, \quad k = 2.0 \times 10^{-14} (T/298)^{2.4} \exp(768/T) \text{ cm}^3 \text{s}^{-1},$$

$$k = 2.6 \times 10^{-13} \text{ cm}^3 \text{s}^{-1} \text{[4]. \quad (5.66)}$$

HCO is formed by the reactions of O with C₃H₆ (Eq. 5.32) and OH with HCHO (Eq. 5.36). CO exit densities as a function of energy deposition are shown in Fig. 5.14c. Increasing energy deposition leads to increased rates of CO₂ dissociation and HCO formation (due to higher O and OH production) resulting in higher CO densities. Larger
densities of HCO are generated with repetitive pulses due to the larger production of OH. These larger densities also result in increased CO formation (Eq. 5.66).

Due to the variations in the composition of diesel fuel, the UHC concentration in exhaust gas can fluctuate. To this end, we investigated the sensitivity of NO\textsubscript{x} removal to the inlet UHC concentration when using multiple pulses. All other conditions are the same as the base case. The removal of NO\textsubscript{x} improves with increasing C\textsubscript{3}H\textsubscript{6}, as shown in Fig. 5.15. This trend is a result of increased nitrate and HNO\textsubscript{x} formation by the reactions in Eqs. 5.37, 5.61-5.65. For example, the increasing densities of HNO\textsubscript{2} with increasing C\textsubscript{3}H\textsubscript{6} are also shown in Fig. 5.15. Increased production of OH and HO\textsubscript{2} occur with soot by increased cyclic conversion between NO and NO\textsubscript{2} resulting in larger rates of HNO\textsubscript{2} formation (Eqs. 5.38 and 5.61).

The effects of soot particle number density and diameter on NO\textsubscript{x} remediation were investigated. Increasing either the diameter of the soot or its number density results in increased exit densities of NO when using single pulses, as shown in Fig. 5.16a. The increase in NO is a result of the heterogeneous conversion of NO\textsubscript{2} to NO following the larger surface area of the soot. At small soot diameters and soot densities (40 nm, 10\textsuperscript{7} cm\textsuperscript{-3}), negligible heterogeneous conversion of NO\textsubscript{2} to NO occurs and so most of the NO\textsubscript{2} produced in the gas phase exits the reactor. At large soot diameters and soot densities (200 nm, 10\textsuperscript{9} cm\textsuperscript{-3}) most of the NO\textsubscript{2} is converted to NO by heterogeneous reactions. Heterogeneous reactions occur on a time scale of ~10s of ms at which time most of the radicals which convert NO to NO\textsubscript{2} (for example, βHAPs, HO\textsubscript{2} and O\textsubscript{3}) have been consumed. As a result, the exit composition of NO\textsubscript{x} is primarily NO. Since the
heterogeneous NO\(_x\) reactions result in only the conversion of NO\(_2\) to NO, the total NO\(_x\) density remains nearly a constant, as shown in Fig. 5.16b.

The densities of NO and NO\(_x\) as a function of soot density and diameter for repetitive pulses are shown in Fig. 5.17. The production of NO consuming radicals during each pulse (see Fig. 5.7) results in the gas phase conversion of NO to NO\(_2\). As a result the NO densities are smaller compared to using a single pulse. At either small soot densities and large diameters, or at large soot densities and small diameters, the homogeneous conversion of NO to NO\(_2\) dominates the heterogeneous conversion of NO\(_2\) to NO and so most of the NO\(_x\) is NO\(_2\). However, at large soot densities and large diameters (10\(^9\) cm\(^{-3}\), 200 nm), the rates for the heterogeneous conversion of NO\(_2\) to NO exceed the rates for the homogeneous conversion of NO to NO\(_2\) and so the exit composition of NO\(_x\) is dominantly NO. The homogeneous and heterogeneous processes involving NO and NO\(_2\) result mainly in their interconversion and so the total NO\(_x\) density almost remains unaffected. The smaller NO\(_x\) density with multiple pulses is due to the increased rates of reactions of NO and NO\(_2\) with radicals such as CH\(_3\)O (Eqs. 5.62 and 5.63), C\(_2\)H\(_5\)O (Eq. 5.64), C\(_2\)H\(_5\)O\(_2\) (Eq. 5.65), OH (Eqs. 5.37 and 5.38) and HO\(_2\) (Eq. 5.61), producing CH\(_3\)ONO\(_2\), CH\(_3\)ONO, C\(_2\)H\(_5\)ONO, C\(_2\)H\(_5\)ONO\(_2\), HNO\(_2\) and HNO\(_3\). The increased rates are a result of the increased overlap in time of the densities of NO and NO\(_2\) with the radical densities.

### 5.3 Concluding Remarks

The effects of repetitive pulses and soot chemistry on the plasma remediation of NO\(_x\) using dielectric barrier discharges were investigated. In the absence of soot, using
repetitive pulses resulted in higher conversion of NO to NO₂ compared to using a single pulse case. Single pulses with soot result in an initial gas phase oxidation of NO to NO₂, followed by a heterogeneous conversion of NO₂ to NO on the soot. Due to the larger gas phase NO₂ density using repetitive pulses, there is an increased flux of NO₂ to the soot surface, resulting in increased soot oxidation and larger rates of heterogeneous conversion of NO₂ to NO. At 30 J/l, using single pulses with and without soot produced about 30% NOₓ removal. The final NOₓ was primarily NO₂ (almost 100%) in the absence of soot whereas with soot the NOₓ was 88% NO and 12% NO₂. When using multiple pulses, 30 J/l resulted in 35% NOₓ removal in the absence of soot and 37% with soot. The $W$-value for soot oxidation at 30 J/l improved from 0.5 J/µg with a single pulse to 0.3 J/µg with multiple pulses. The combined effects of multiple pulses and heterogeneous chemistry on NOₓ remediation and soot oxidation are twofold. Improved NOₓ removal by the increased production of HNO₂, HNO₃, organic nitrates and nitrites due to the more favorable overlap in time of NO₂ and reactive radical densities; and increased soot oxidation because of larger NO₂ densities.
5.4 Figures

Fig 5.1. Plasma parameters for single and repetitive pulses. a) $n_e$, $T_e$ for a single pulse. b) $n_e$, $T_e$ during the 1st pulse of 20 pulses. c) $n_e$, $T_e$ for the last pulse of 20 pulses. Conditions are 1 atm, 453 K, $N_2/O_2/H_2O/CO_2 = 79/8/6/7$ with 260 ppm NO, 400 ppm CO, 133 ppm H$_2$, and 500 ppm C$_3$H$_6$. Gas residence time is 0.2 s and the gas gap is 2.5 mm. The applied voltage for the single pulse case is 18 kV and that for 20 pulses is 13 kV for total energy deposition of 30 J/l. Following the current pulse (around 150 ns), electrons are lost primarily by attachment to H$_2$O and O$_2$. 
Fig. 5.2. Time dependence of the densities of charged species during the single pulse plasma processing of NOx. The dominant positive ion is H$_3$O$^+$·H$_2$O and the dominant negative ions are O$^-$ and H$^-$, which are primarily lost by charge neutralizations with each other. The conditions are the same as for Fig. 5.1.
Fig. 5.3. Time dependence of N, O, OH and H densities. (a) Single pulse. (b) 1st of 20 repetitive pulses. (c) 20th of 20 pulses. Conditions are same as for Fig. 5.1. Electron impact reactions with N₂, O₂, H₂O and CO produce N, O, OH and H.
Fig. 5.4. Time dependencies of the NO consuming radicals βHAPs, HO2 and O3. (a) Single pulse. (b) 1st of 20 repetitive pulses. (c) 20th of 20 pulses. Due to the depletion of NO with every pulse the residual radical densities increase with multiple pulses. O3 being the least reactive of the three with NO has a larger residual density.
Fig. 5.5. NO and NO$_2$ densities as a function of time for a single pulse with and without soot. With soot, the heterogeneous reaction of NO$_2$ regenerates NO in the gas phase. This reaction occurs on a time scale of $\sim$10s ms when most of the NO consuming radicals are depleted. As a result, NO accumulates.
Fig. 5.6. NO and NO₂ densities as a function of time for repetitive pulses with and without soot. (a) NO and NO₂ densities for all pulses. (b) NO density during the 12th pulse. (c) NO₂ density during the 12th pulse. The heterogeneous conversion of NO₂ on soot increases the gas phase density of NO and decreases the NO₂ density. After about 5 pulses, there are three distinct phases for NO evolution. Initial conversion of NO₂ to NO by reaction with O and N atoms, homogeneous conversion of NO to NO₂ by reaction with radicals such as βHAPs, HO₂ and O₃, and heterogeneous generation of NO from NO₂.
Fig. 5.7. Densities of NO consuming radicals. (a) βHAPs. (b) O$_3$. (c) HO$_2$. Since the density of NO decreases with each pulse, the rate of reaction of NO with these radicals decreases. As a result, their residual densities increase with time.
Fig. 5.8. Surface properties of soot with single and multiple pulses as a function of time. (a) Fraction of sites adsorbed with NO₂. (b) Soot mass fraction. (c) Diameter of soot
After a few ms, heterogeneous conversion of NO₂ on the soot regenerates NO with a single pulse. There is a constant flux of NO₂ to the soot using multiple pulses resulting in a larger adsorbed fraction. More soot oxidation also occurs.
Fig. 5.9. Soot properties for a residence time of 3 s. (a) Site occupancy for a single pulse. (b) Site occupancy for multiple pulses. (c) Diameter of the soot. Almost all of the adsorbed NO$_2$ desorbs to produce NO with a single pulse. When using multiple pulses, the soot is almost completely oxidized due to the increased time for desorption between pulses.
Fig. 5.10. Circular NO and NO$_2$ chemistry. In the absence of soot particles, NO to NO$_2$ conversion by reaction with HO$_2$ produces OH, and by reactions with $\beta$HAPs leads to formation of HO$_2$. The reaction of OH with C$_3$H$_6$ starts a chain reaction which results in the formation of $\beta$HAPs. The reaction of HO$_2$ with NO therefore leads to the formation of $\beta$HAPs and those of $\beta$HAPs with NO lead to HO$_2$ formation. The products of the conversion of NO to NO$_2$ are themselves the reactions for further NO to NO$_2$ conversion. With soot, this cycle is more pronounced due to the heterogeneous conversion of NO$_2$ back to NO.
Fig. 5.11. Molecular and radical densities for cases with and without soot as a function of time. (a) $C_3H_6$ for a single pulse. (b) $C_3H_6$ for multiple pulses. (c) OH for 20$^{th}$ of 20 pulses. Due to the more pronounced circular chemistry with soot, more OH production results and so more $C_3H_6$ is consumed. There is increased overlap in time of reacting species densities with multiple pulses and so larger $C_3H_6$ consumption occurs.
Fig. 5.12. Remediation parameters as a function of energy deposition. (a) Gas phase densities of NO and NO₂, and fraction of surface sites on soot adsorbed with NO₂ for a single pulse. (b) Gas phase densities of NO and NO₂, and fraction of surface sites on soot adsorbed with NO₂ with multiple pulses. (c) $W$-value for NOₓ for single and multiple pulses. Multiple pulses are more efficient for NOₓ removal due to the increased overlap in time of densities of NO₂ and NO with consuming radical densities.
Fig. 5.13. Densities of nitrogen containing products and aldehydes as a function of time when using single and multiple pulses with soot. (a) HNO$_3$ and HNO$_2$. (b) CH$_3$ONO$_2$ and C$_2$H$_5$OONO$_2$. (c) CH$_3$CHO and HCHO. Due to the increased overlap in time of the densities of NO and NO$_2$ with the radicals produced during each pulse, multiple pulses in general lead to larger densities of aldehydes and nitrogen containing products.
Fig. 5.14. Soot removal parameters as a function of energy deposition when using single and multiple pulses. (a) Mass fraction of soot. (b) $W$-value for soot oxidation. (c) Increase in CO. In general multiple pulses are more efficient for soot oxidation because of the sustained densities of NO$_2$ compared to the single pulse case.
Fig. 5.15. NO\textsubscript{x} and HNO\textsubscript{2} densities as a function of C\textsubscript{3}H\textsubscript{6} inlet density for multiple pulses. There is increased NO\textsubscript{2} to NO conversion with soot and so larger NO and HNO\textsubscript{3} densities result. The interconversion between NO and NO\textsubscript{2} is a combined result of the heterogeneous reaction of NO\textsubscript{2} and the homogeneous conversion of NO by $\beta$HAP radicals. With increasing densities of UHCs, larger densities of $\beta$HAPs are generated and the rate of interconversion between NO and NO\textsubscript{2} increases, leading to the increased formation of HNO\textsubscript{2}, and larger NO\textsubscript{x} removal.
Fig. 5.16. NO and NO$_x$ densities as a function of soot density and diameter when using a single pulse. (a) NO. (b) NO$_x$. Increasing the soot density and diameter results in a larger surface area for heterogeneous NO$_2$ to NO conversion leading to larger exit densities of NO. Since this process only converts NO$_2$ to NO, the overall NO$_x$ density remains nearly a constant.
Fig. 5.17. NO and NO\textsubscript{x} densities as a function of soot density and diameter when using multiple pulses. (a) NO. (b) NO\textsubscript{x}. Due to the increased overlap in time of radical densities and the densities of NO and NO\textsubscript{2}, more NO\textsubscript{x} removal occurs compared to using single pulses. The interconversion between NO and NO\textsubscript{2} only leads to a change in the composition of NO\textsubscript{x} without appreciably altering its density.
5.5 References


6. CONSEQUENCES OF UNBURNED HYDROCARBONS ON THE TRANSPORT IN MICROSTREAMERS DURING THE DBD PROCESSING OF NO\textsubscript{X}

6.1 Introduction

In this chapter, we extend our study on plasma remediation of NO\textsubscript{X} to include diffusive and advective transport in microstreamers in addition to the chemical kinetics. Gentile and Kushner [1] showed that radial transport of species to and from the microstreamer region significantly influences the efficiency of NO\textsubscript{X} remediation. Localized energy deposition in these microstreamers results in spatially nonuniform temperature and species densities which initiate advective and diffusive transport leading to the movement of species into and out of the microstreamer. We saw in Chapter 3 that UHCs significantly influence the NO\textsubscript{X} chemistry during the plasma processing of NO\textsubscript{X} in diesel exhausts. In this investigation we study the combined effects of UHCs and species transport on the overall remediation of NO\textsubscript{X}.

A description of the one-dimensional radial model used to study the streamer evolution and the hydrodynamics is given in Section 2.4. Results from this model on the consequences of UHCs-NO\textsubscript{X} reactions and advective and diffusive transport on the NO\textsubscript{X} remediation are discussed in Section 6.2. Concluding remarks are given in Section 6.3.

6.2 Consequences of UHCs on the Transport in Microstreamers During DBD Processing of NO\textsubscript{X}

The base case conditions are N\textsubscript{2}/O\textsubscript{2}/H\textsubscript{2}O=86/8/6 with 500 ppm NO (1 atm, 453 K), electrode separation of 3 mm, gas residence time of $10^{-2}$ s, and a pulse repetition frequency of 300 Hz. A voltage of 10 kV is applied across the gap to produce a streamer-
volume averaged energy deposition of 170 J/L. The computational area is 1 cm × 1 cm and the initial streamer radius is 10 µm. This large disparity in the sizes is deliberately made so as to minimize edge effects (for example, reflection of acoustic waves). Since the reaction mechanisms for NOx remediation in the absence of UHCs and in the presence of C3H6 have been discussed in detail previously,[1,2] only those reactions of direct importance to this study will be addressed.

The electron density (ne) and the on axis electron temperature (Te) for the first and the last pulse are shown in Fig. 6.1. During the current pulse which lasts ≈70 ns, electron avalanche in the streamer region occurs through electron impact ionizations of N2, O2, and H2O and results in the production of N, O, and OH radicals. Peak on axis electron temperature is 3.2 eV and the peak electron density is 3.7 × 10^{13} cm^{-3}. Following the current pulse, electrons are rapidly lost to O2 and H2O by attachment and as a result their diffusion to regions far beyond the streamer is limited. Since the densities of the dominant background gases do not significantly change after any given pulse, the electron temperature and electron densities for the first and the last pulse are not significantly different.

The gas temperature, mass flux, and the total gas density during and following the current pulse are shown in Fig. 6.2. With the flow of current through the microstreamer, the gas temperature rises by ≈120 K producing a pressure gradient which initiates advection radially outward. The advection wave can be compared to a weak blast wave which pushes the hot mass out of the streamer region producing significantly increased temperatures at radii noticeably outside of the streamer region. Following the current pulse, temperature begins to decrease by expansion cooling and thermal conduction and
the peak in the mass flux moves radially outward continuing to push hot mass away from the streamer region. Once the temperature in the streamer decreases sufficiently, the pressure gradient reverses resulting in an influx of mass back into the streamer region. With time, the wave is widened and flattened as a result of opposing forces of viscosity, and pressure and thermal gradients. Advection at longer times (>1 µs) is restricted to small acoustic waves which propagate back and forth throughout the gas. Owing to their small amplitude, these waves do not contribute significantly to changes in species densities at these times.

The densities of O atoms for the first and last pulses are shown in Figs. 6.3a and 6.3b. During the current pulse, O atoms are dominantly produced in the streamer region by the electron impact dissociation of O2. Most of the O is consumed by reactions with O2 to form O3,

\[
O + O_2 + M \rightarrow O_3 + M, \quad k = 3.4 \times 10^{-34} (T / 298)^{-1.2} \text{ cm}^6 \text{s}^{-1} \quad [3]. \quad (6.1)
\]

The production of O atoms in the regions outside of the microstreamer during and slightly after the current pulse (a few hundred ns) is mainly due to the ambipolar diffusion of electrons which produce O by the dissociation of O2. Due to their high reactivity, O atoms are quickly exhausted (a few hundred µs) and hence do not accumulate pulse to pulse. Since the density of O2, its primary precursor and consumer does not change from pulse to pulse, O atom densities are not significantly different for the first and the last pulse.
To determine the effects of UHCs, 2000 ppm of C$_3$H$_6$ were added to the base case mixture. The densities of O atoms for the first and the last pulse are shown in Figs. 6.3c and 6.3d. The initial production of O atoms, primarily by the electron impact dissociation of O$_2$ is not significantly influenced by the presence of C$_3$H$_6$ and so does not differ from the case without C$_3$H$_6$. At longer times (> many µs) and in the presence of C$_3$H$_6$, O atoms are also consumed by reactions with C$_3$H$_6$ and hence their densities are smaller,

\[
\text{O} + \text{C}_3\text{H}_6 \rightarrow \text{Methyl Oxirane}, \quad k = 1.2 \times 10^{-12} \text{ cm}^3\text{s}^{-1} \quad [4], \quad (6.2)
\]

\[
\rightarrow \text{C}_2\text{H}_5\text{CHO}, \quad k = 1.2 \times 10^{-12} \text{ cm}^3\text{s}^{-1} \quad [4], \quad (6.3)
\]

\[
\rightarrow \text{CH}_2\text{CHO} + \text{CH}_3, \quad k = 0.8 \times 10^{-12} \text{ cm}^3\text{s}^{-1} \quad [4], \quad (6.4)
\]

\[
\rightarrow \text{C}_2\text{H}_5 + \text{HCO}, \quad k = 0.8 \times 10^{-12} \text{ cm}^3\text{s}^{-1} \quad [4]. \quad (6.5)
\]

Since the rates for consumption of O atoms by reactions with C$_3$H$_6$ are larger than that by the reaction with O$_2$ (Eq. 6.1), O atoms are preferentially and more rapidly consumed by reactions with C$_3$H$_6$ and as a result their diffusion to regions outside of the microstreamer is limited. Due to the decreased availability of O for reactions with O$_2$, the densities of O$_3$ are smaller compared to the case without C$_3$H$_6$, as shown in Fig. 6.4. Subsequently, diffusion of O$_3$ to regions outside of the microstreamer becomes restricted in the case with C$_3$H$_6$. In both cases, most of the O$_3$ is consumed by reactions with NO to form NO$_2$,

\[
\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2, \quad k = 4.3 \times 10^{-12} \exp(-1598/T) \text{ cm}^3\text{s}^{-1},
\]

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Since NO is abundant both within and outside the streamer region, most of the O₃ is consumed and so the density of O₃ does not accumulate pulse to pulse.

The densities of OH for the first and the last pulse for the cases with and without C₃H₆ are shown in Fig. 6.5. Initially ($t < 100$ ns), OH is produced in the streamer region primarily by the electron impact dissociation of H₂O. At times following the current pulse, OH is produced in regions outside of the streamer mainly by the dissociation of H₂O by electrons resulting from ambipolar diffusion from the streamer region. At later times and in the absence of C₃H₆, OH is depleted in the streamer region by reactions with NO to form HNO₂ and by diffusion to regions outside,

$$
OH + NO + M \rightarrow HNO₂ + M, \quad k = 8.6 \times 10^{-31} \frac{(T / 298)^{-2.5} \exp(34 / T)}{cm^6 s^{-1}},
$$

$$
k_{298} = 9.7 \times 10^{-31} \frac{cm^6 s^{-1}}{scmTk}[5]. \quad (6.7)
$$

In the presence of C₃H₆, OH is favorably and more rapidly consumed by reactions with C₃H₆ to form C₃H₆OH,

$$
OH + C₃H₆ \rightarrow C₃H₆OH, \quad k = 4.9 \times 10^{-12} \frac{\exp(504 / T)}{cm^3 s^{-1}},
$$

$$
k_{298} = 2.6 \times 10^{-11} \frac{cm^3 s^{-1}}{scmTk}[4], \quad (6.8)
$$
and as a result, diffusion of OH to regions far beyond the streamer region is not as pronounced as in the case without C₃H₆. C₃H₆OH quickly reacts with O₂ to form C₃H₆(OH)O₂ (β-hydroxy alkyl peroxy radicals or simply βHAPs),

\[
C₃H₆OH + O₂ \rightarrow βHAPs, \quad k = 1.6 \times 10^{-11} \text{ cm}^3 \text{s}^{-1} \quad [4], \quad (6.9)
\]

which further react with NO to form NO₂ and C₃H₆(OH)O (β-hydroxy alkoxy radicals or simply βHAs),

\[
NO + βHAPs \rightarrow NO₂ + βHAs, \quad k = 5.4 \times 10^{-12} \exp(360/T) \text{ cm}^3 \text{s}^{-1},
\]

\[k_{298} = 1.8 \times 10^{-11} \text{ cm}^3 \text{s}^{-1} \quad [4]. \quad (6.10)
\]

Electron impact dissociation of H₂O also produces H in addition to OH. Most of the H reacts with O₂ to form HO₂,

\[
H + O₂ + M \rightarrow HO₂ + M, \quad k = 1.8 \times 10^{-32} (T/298)^{-0.8} \text{ cm}^6 \text{s}^{-1} \quad [6]. \quad (6.11)
\]

The densities of HO₂ are shown in Fig. 6.6 for the cases with and without C₃H₆. In the presence of C₃H₆, more HO₂ is produced by the reactions of O₂ with the products of βHA radical decomposition,

\[
βHA \rightarrow β\text{-hydroxy alkyl radicals} + HCHO,
\]
\[ k = 7.9 \times 10^{13} \exp(-10517/T) \text{ s}^{-1}, \quad k_{298} = 3.7 \times 10^{-2} \text{ s}^{-1} [3], \quad (6.12) \]

\[ \text{β-hydroxy alkyl radicals + O}_2 \rightarrow \text{CH}_3\text{CHO + HO}_2, \]

\[ k = 1.9 \times 10^{-11} \text{ cm}^3 \text{s}^{-1} [7]. \quad (6.13) \]

Since these reactions occur on time scales of tens of µs, HO$_2$ densities are sustained for longer times in the presence of C$_3$H$_6$. Depletion of HO$_2$ occurs by diffusion to outer radii and by reaction with NO to produce NO$_2$,

\[ \text{NO + HO}_2 \rightarrow \text{NO}_2 + \text{OH}, \quad k = 3.5 \times 10^{-12} \exp(240/T) \text{ cm}^3 \text{s}^{-1}, \quad (6.14) \]

\[ k_{298} = 7.8 \times 10^{-12} \text{ cm}^3 \text{s}^{-1} [4]. \]

The densities of NO for the cases with and without C$_3$H$_6$ are shown in Fig. 6.7. The NO density in the streamer region initially decreases due to the rarefaction of the core resulting from advection. Peak in the NO density occurs in the region outside of the streamer corresponding to the peak in the shock wave which results from the current impulse. At later times, reversal of the pressure gradient and back diffusion refills NO in the streamer region. This refilling of core from the large reservoir of NO around the streamer region being larger than the depletion of NO by reactions, NO densities in the streamer region increase. At the end of the afterglow period, the density of NO in the streamer region is almost the same as that of the outer regions and so the densities of NO during subsequent pulses do not significantly differ. In the presence of C$_3$H$_6$, more NO is consumed by reactions with βHAPs (Eq. 6.10) and HO$_2$ (Eq. 6.14) and as a result the
density of NO at a given time and radial location is smaller compared to the case without C$_3$H$_6$. Correspondingly, it takes longer time to repopulate NO in the streamer region by diffusion from outside.

The densities of NO on the axis ($r = 0$) and slightly off the streamer edge ($r = 12 \mu m$) as a function of time are shown in Fig. 6.8. For $t < 100$ ns, rarefaction of the streamer region by radial advection depletes NO on the axis and results in a peak in the NO density slightly outside the streamer region. Reversal of the pressure gradient and back diffusion refill NO in the streamer region at later times. Due to the larger consumption of NO by βHAPs, NO densities in the presence of C$_3$H$_6$, both on the axis as well as slightly off the streamer edge are less compared to those without C$_3$H$_6$. At $t > 10^{-4}$ s, the density of NO is leveled by diffusion.

The densities of NO$_2$ with and without C$_3$H$_6$ are shown in Fig. 6.9. In general larger amount of NO$_2$ is produced in the presence of C$_3$H$_6$ by the reactions of βHAP radicals with NO (Eq. 6.10). In the absence of C$_3$H$_6$, NO$_2$ is mainly formed by the reactions of NO with O$_3$ and HO$_2$ (Eq. 6.6 and 6.14) at time scales on the order of a few to 10s of µs. The rarefaction of the core and the abundance of NO and O$_3$ outside the streamer region results in an off-axis peak in the density of NO$_2$ at $t \approx 3 \times 10^{-5}$ s. Due to the smaller reactivity of NO$_2$ compared to NO, the density of NO$_2$ accumulates from pulse to pulse, with the accumulation more pronounced in the presence of C$_3$H$_6$ due to the larger production of NO$_2$.

The on-axis densities of NO$_2$ for the cases with and without C$_3$H$_6$ are shown in Fig. 6.10. During the first pulse, the densities of NO$_2$ at the start of the current pulse are insignificant and hence are not affected by advection. With the accumulation of NO$_2$
from pulse to pulse, the initial depletion of on axis NO\textsubscript{2} by radial advection becomes increasingly evident, with the effect more pronounced in the presence of C\textsubscript{3}H\textsubscript{6}. Typically, the density of NO\textsubscript{2} increases until \(\approx\)10s of \(\mu\)s due to production from NO and at later times decreases due to the depletion by diffusion to regions outside the streamer.

The densities of C\textsubscript{3}H\textsubscript{6} and \(\beta\)HAPs are shown in Fig. 6.11. Initial radial advection depletes C\textsubscript{3}H\textsubscript{6} from the streamer region and results in a peak in its density at the crest of the shock wave. Refilling of the core at later times restores the density of C\textsubscript{3}H\textsubscript{6}. Although significant depletion of C\textsubscript{3}H\textsubscript{6} in the streamer region occurs by reactions with O and OH, diffusion from the large volume of C\textsubscript{3}H\textsubscript{6} outside the streamer region overshadows the effect. Consumption of C\textsubscript{3}H\textsubscript{6} by OH leads to the formation of \(\beta\)HAP radicals (Eqs. 6.8 and 6.9), which further react with NO to produce NO\textsubscript{2}. More \(\beta\)HAPs are consumed outside the streamer region due to the abundant NO. With time, \(\beta\)HAPs in the streamer region are exhausted by reactions with NO and by diffusion to outer radii.

Although most of the NO removed is by conversion to NO\textsubscript{2}, some amount of NO is also lost by reactions with OH to form HNO\textsubscript{2} (Eq. 6.7). The densities of HNO\textsubscript{2} with and without C\textsubscript{3}H\textsubscript{6} are shown in Fig. 6.12. In the presence of C\textsubscript{3}H\textsubscript{6}, OH is preferentially consumed by reactions with C\textsubscript{3}H\textsubscript{6} and so less is available for reactions with NO and so the initial production of HNO\textsubscript{2} is smaller compared to the case without C\textsubscript{3}H\textsubscript{6}. At later times, larger densities of HNO\textsubscript{2} are sustained in the presence of C\textsubscript{3}H\textsubscript{6} by the reaction of HO\textsubscript{2} with NO\textsubscript{2},

\[
\text{HO}_2 + \text{NO}_2 \rightarrow \text{HNO}_2 + \text{O}_2, \quad k = 1.2 \times 10^{-13} \text{ cm}^3 \text{s}^{-1} \text{ [3].} \quad (6.15)
\]
Since the densities of HO$_2$ and NO$_2$ are larger and are sustained for longer periods in the presence of C$_3$H$_6$ (see Figs. 6.6 and 6.9), more HNO$_2$ is produced at longer times.

### 6.3 Concluding Remarks

In the filamentary mode of operation of atmospheric pressure plasmas, energy is dominantly deposited in confined volumes resulting in localized temperature rise in these regions. This initiates advection leading to transport of species to and from the microstreamer. C$_3$H$_6$, representative of the UHCs typically found in diesel exhausts, reacts with the O and OH radicals produced in the streamer region and limits their convection to larger radii, and thus decreases the remediation of NO in the regions outside of the streamer. However, NO conversion increases in the streamer region in the presence of C$_3$H$_6$ due to the larger production of βHAPs and HO$_2$ which efficiently convert NO to NO$_2$. Thus, in the presence of C$_3$H$_6$, the removal of NO increases in the streamer region and decreases at outer radii.
Fig. 6.1. Electron density \( n_e \) (cm\(^{-3}\)) and on-axis electron temperature \( T_e \) for the 1\(^{\text{st}}\) and the 3\(^{\text{rd}}\) pulse. (a) \( n_e \) for the 1\(^{\text{st}}\) pulse. (b) \( n_e \) for the 3\(^{\text{rd}}\) pulse. (c) On-axis \( T_e \) for the 1\(^{\text{st}}\) pulse. (d) On-axis \( T_e \) for the 3\(^{\text{rd}}\) pulse. Conditions are N\(_2\)/O\(_2\)/H\(_2\)O=86/8/6 with 500 ppm NO (1 atm, 453 K), gas residence time of \( 10^{-2} \) s, 300 Hz, streamer-volume averaged energy deposition = 170 J/L.
Fig. 6.2. Microstreamer characteristics during the initial 100 ns. The current pulse lasts ≈70 ns. Localized energy deposition in the microstreamer results in a temperature rise which initiates radial advection leading to the movement of hot mass to regions outside the streamer. Following the current pulse, temperature decreases by cooling and thermal conduction.
Fig. 6.3. Densities of O (cm$^{-3}$). (a) Without C$_3$H$_6$, 1$^{st}$ pulse. (b) Without C$_3$H$_6$, 3$^{rd}$ pulse. (c) With C$_3$H$_6$, 1$^{st}$ pulse. (d) With C$_3$H$_6$, 3$^{rd}$ pulse. Conditions are as in Fig. 6.1. O atoms are more rapidly consumed in the presence of C$_3$H$_6$ and hence their diffusion to larger radii is limited.
Fig. 6.4. Density of O$_3$ (cm$^{-3}$). (a) Without C$_3$H$_6$. (b) With C$_3$H$_6$. Due to the preferential consumption of O by C$_3$H$_6$, O$_3$ production is limited in the presence of C$_3$H$_6$ and as a result, diffusion to larger radii at longer times becomes restricted. Conditions are as in Fig. 6.1
Fig. 6.5. Densities of OH (cm⁻³). (a) Without C₃H₆, 1st pulse. (b) Without C₃H₆, 3rd pulse. (c) With C₃H₆, 1st pulse. (d) With C₃H₆, 3rd pulse. Conditions are as in Fig. 6.1. OH radicals are more rapidly consumed in the presence of C₃H₆ and hence their diffusion to larger radii is limited.
Fig. 6.6. Density of HO$_2$ (cm$^{-3}$). (a) Without C$_3$H$_6$. (b) With C$_3$H$_6$. Due to the additional production of HO$_2$ by C$_3$H$_6$ initiated reactions, the densities of HO$_2$ are larger for the case with C$_3$H$_6$. 
Fig. 6.7. Densities of NO (cm$^{-3}$). (a) Without C$_3$H$_6$, 1$^{st}$ pulse. (b) Without C$_3$H$_6$, 3$^{rd}$ pulse. (c) With C$_3$H$_6$, 1$^{st}$ pulse. (d) With C$_3$H$_6$, 3$^{rd}$ pulse. Conditions are as in Fig. 6.1. In the presence of C$_3$H$_6$, larger amount of NO is consumed in the streamer region by reactions with βHAP radicals and as a result NO densities are smaller at any given time compared to the case without C$_3$H$_6$. 
Fig. 6.8. NO density at different locations in the gas. (a) On-axis. (b) Slightly off the streamer edge. Advection at $t \approx 70$ ns results in depletion of NO along the axis. The radial outward motion of mass results in accumulation of NO near the streamer edge. In the presence of $C_3H_6$, more NO is consumed by reactions with $\beta$HAPs and as a result, NO densities are smaller.
Due to the increased conversion of NO to NO₂ in the presence of C₃H₆, NO₂ densities are larger.
Fig. 6.10. On axis densities of NO. (a) Without C₃H₆. (b) With C₃H₆. Due to the larger production of NO₂ in the presence of C₃H₆, the initial effects of advection are more prominent.
Fig. 6.11. Species density (cm$^{-3}$). (a) C$_3$H$_6$. (b) βHAPs. Radial advection results in movement of C$_3$H$_6$ to regions outside of the streamer. C$_3$H$_6$ is consumed by reactions with O and OH.
HNO$_2$ ($100 = 9 \times 10^{12}$)

Initial streamer radius

Fig. 6.12. Densities of HNO$_2$ (cm$^{-3}$). (a) Without C$_3$H$_6$. (b) With C$_3$H$_6$. For $t<$ tens of $\mu$s, HNO$_2$ is primarily produced by the reactions of OH with NO. Due to the increased consumption of OH in the presence of C$_3$H$_6$, less HNO$_2$ is produced initially. The larger densities of HNO$_2$ at longer times in the presence of C$_3$H$_6$ are due to the increased densities of HO$_2$ and NO$_2$, which also react to produce HNO$_2$. 
6.5 References


7. PLASMA SURFACE MODIFICATION OF POLYPROPYLENE

7.1 Introduction

In this chapter, we present results from our computational investigations on the gas phase and surface kinetics during the modification of polypropylene (PP) in humid-air plasmas. A pseudo-homogeneous global kinetics model interfaced to a surface site balance model was developed and validated against experiments. The consequences of process variables which have experimentally been found to control the resulting surface properties,[1] (energy deposition, relative humidity (RH), gas temperature, and web speed) were investigated. We found that increasing energy deposition not only results in increased densities of peroxy and acid groups on the PP surface, but also increases the production of gas phase byproducts such as N\textsubscript{x}O\textsubscript{y} and O\textsubscript{3}. Increasing the RH resulted in decreased production of O\textsubscript{3} and increased concentrations of peroxy and acid groups on the surface. Increasing the gas temperature increased the surface concentration of peroxy radicals and decreased the concentrations of alcohol, carbonyl, and acid groups. For a given energy deposition, increasing the web speed resulted in decreased densities of peroxy, alcohol, carbonyl, and acid groups on the PP surface.

The modified form of GLOBAL\textsubscript{KIN} used for the study is described in Section 2.5. The gas phase reaction mechanism for humid air and the surface reaction mechanism for PP are described in Sections 7.2 and 7.3. Results for plasma surface modification of PP are presented in Section 7.4. Concluding remarks are in Section 7.5.
7.2 Gas Phase Reaction Mechanism for Humid Air

Consider humid air plasma treatment of PP having $N_2/O_2/H_2O = 79/20/1$ (1% $H_2O$ corresponds to a RH of approximately 30% at 300 K, 1 atm). The species considered in this model are listed in Appendix A and the gas phase reactions pertaining to them are in Appendix B. The reaction mechanism involves 90 species (65 in the gas phase and 25 on the polymer surface) and nearly 400 reactions.

The fractional energy deposition by electron impact processes as a function of electric field/total gas number density ($E/N$) is shown in Fig. 7.1 (At 300 K, 1 atm, $N \approx 2.4 \times 10^{19}$ cm$^{-3}$). The current pulse typically lasts a few ns during which $E/N \approx 300-600$ Td (1 Td = 1 Townsend = $1.0 \times 10^{-17}$ V-cm$^2$). For these $E/N$, energy is dissipated mainly by electronic excitation and ionization of $N_2$ and $O_2$, dissociation of $N_2$, and vibrational excitation of $N_2$.

\[
e + N_2 \rightarrow N_2^* + e, \quad (7.1)
\]
\[
e + O_2 \rightarrow O_2^* + e, \quad (7.2)
\]
\[
e + N_2 \rightarrow N_2^+ + e + e, \quad (7.3)
\]
\[
e + O_2 \rightarrow O_2^+ + e + e, \quad (7.4)
\]
\[
e + N_2 \rightarrow N + N + e, \quad (7.5)
\]
\[
e + N_2 \rightarrow N_2(v) + e. \quad (7.6)
\]

In Eqs. 7.1 and 7.2, $N_2^*$ and $O_2^*$ represent the sum of excited states of $N_2$ and $O_2$. We used $N_2(A)$ and $O_2(^1\Delta)$ for their characteristics.
Most of the $N_2^*$ relaxes to $N_2$ by collisions with $N_2$ while some collide with $O_2$ to produce $O$ atoms,

$$N_2^* + N_2 \rightarrow N_2 + N_2, \quad k = 1.9 \times 10^{-13} \text{ cm}^3 \text{s}^{-1} [2], \quad (7.7)$$

$$N_2^* + O_2 \rightarrow O + O + N_2, \quad k = 1.5 \times 10^{-12} \text{ cm}^3 \text{s}^{-1} [2], \quad (7.8)$$

where $k$ is the rate coefficient for the reaction.

Most of the $O_2^*$ is consumed by reaction with $O_3$ (ozone), while a smaller fraction is quenched by collisions with $N_2$,

$$O_2^* + O_3 \rightarrow O + O_2 + O_2, \quad k = 5.2 \times 10^{-11} \exp(-2840/T) \text{ cm}^3 \text{s}^{-1},$$

$$k_{298} = 3.8 \times 10^{-15} \text{ cm}^3 \text{s}^{-1} [3], \quad (7.9)$$

$$O_2^* + N_2 \rightarrow O_2 + N_2, \quad k = 3.0 \times 10^{-18} \exp(-200/T) \text{ cm}^3 \text{s}^{-1},$$

$$k_{298} = 1.5 \times 10^{-18} \text{ cm}^3 \text{s}^{-1} [4], \quad (7.10)$$

where $k_{298}$ is the reaction rate coefficient at 298 K.

The reaction mechanism for the charged species is given in Fig. 7.2a. The initiation reactions are the ionization of $N_2$, $O_2$, and $H_2O$ producing secondary electrons, $N_2^+$ (Eq. 7.3), $O_2^+$ (Eq. 7.4) and $H_2O^+$,

$$e + H_2O \rightarrow H_2O^+ + e + e. \quad (7.11)$$
Most of the $N_2^+$ reacts with $N_2$ to form $N_4^+$ while some $N_2^+$ undergoes charge exchange with $O_2$ and $H_2O$ to produce $O_2^+$ and $H_2O^+$,

$$N_2^+ + N_2 + M \rightarrow N_4^+ + M, \quad k = 1.1 \times 10^{-29} \text{cm}^6 \text{s}^{-1} [5]. \quad (7.12)$$

$$N_2^+ + O_2 \rightarrow O_2^+ + N_2, \quad k = 5.1 \times 10^{-11} \text{cm}^3 \text{s}^{-1} [5], \quad (7.13)$$

$$N_2^+ + H_2O \rightarrow H_2O^+ + N_2, \quad k = 2.0 \times 10^{-9} \text{cm}^3 \text{s}^{-1} [6]. \quad (7.14)$$

$O_2^+$ is also formed by the dissociative charge exchange reaction of $N_4^+$ with $O_2$,

$$N_4^+ + O_2 \rightarrow O_2^+ + N_2 + N_2, \quad k = 2.5 \times 10^{-10} \text{cm}^3 \text{s}^{-1} [5]. \quad (7.15)$$

Most of the $O_2^+$ reacts with $H_2O$ to form the cluster ion $O_2^+ \cdot H_2O$ which further reacts with $H_2O$ to form $H_3O^+$,

$$O_2^+ + H_2O + M \rightarrow O_2^+ \cdot H_2O + M, \quad k = 2.5 \times 10^{-28} \text{cm}^6 \text{s}^{-1} [5], \quad (7.16)$$

$$O_2^+ \cdot H_2O + H_2O \rightarrow H_3O^+ + OH + O_2, \quad k = 1.2 \times 10^{-9} \text{cm}^3 \text{s}^{-1} [5]. \quad (7.17)$$

$H_2O^+$ also reacts with $H_2O$ to form $H_3O^+$ and $OH$,

$$H_2O^+ + H_2O \rightarrow H_3O^+ + OH, \quad k = 1.7 \times 10^{-9} \text{cm}^3 \text{s}^{-1} [5]. \quad (7.18)$$
Most of the H$_3$O$^+$ then forms the cluster ion H$_3$O$^+$·H$_2$O by reaction with H$_2$O,

$$H_3O^+ + H_2O + M \rightarrow H_3O^+\cdot H_2O + M, \quad k = 5.0 \times 10^{-27} \, cm^6 \, s^{-1} \quad [5]. \quad (7.19)$$

Most of the electrons are lost by three-body attachment to O$_2$, while some are consumed by recombination with H$_3$O$^+\cdot$H$_2$O and O$_2^+\cdot$H$_2$O,

$$e + O_2 + M \rightarrow O_2^- + M. \quad (7.20)$$

$$e + H_3O^+\cdot H_2O \rightarrow H + H_2O + H_2O, \quad (7.21)$$

$$e + O_2^+\cdot H_2O \rightarrow O_2 + H_2O. \quad (7.22)$$

H$_3$O$^+\cdot$H$_2$O and O$_2^+\cdot$H$_2$O are also neutralized by reactions with O$_2^-$ forming O$_2$, H, and H$_2$O,

$$O_2^- + H_3O^+\cdot H_2O \rightarrow O_2 + H + H_2O + H_2O, \quad k = 2.0 \times 10^{-6} \, cm^3 \, s^{-1} \quad [5], \quad (7.23)$$

$$O_2^- + O_2^+\cdot H_2O \rightarrow O_2 + O_2 + H_2O, \quad k = 2.0 \times 10^{-6} \, cm^3 \, s^{-1} \quad [5]. \quad (7.24)$$

The reaction mechanism for free radical chemistry in the gas phase is shown in Fig. 7.2b. The initiating reactions are the electron impact dissociations of N$_2$ (Eq. 7.5), O$_2$, and H$_2$O producing N, O, OH and H,
\[ e + O_2 \rightarrow O + O + e, \]  \hspace{1cm} (7.25)

\[ e + H_2O \rightarrow OH + H + e. \]  \hspace{1cm} (7.26)

N atoms are consumed by reactions with OH, NO, and O\(_2\) forming NO and N\(_2\),

\[ N + OH \rightarrow NO + H, \quad k = 3.8 \times 10^{-11} \exp(85/T) \text{ cm}^3 \text{s}^{-1}, \]
\[ k_{298} = 7.7 \times 10^{-17} \text{ cm}^3 \text{s}^{-1} [7], \]  \hspace{1cm} (7.27)

\[ N + NO \rightarrow N_2 + O, \quad k = 3.4 \times 10^{-11} \exp(-24/T) \text{ cm}^3 \text{s}^{-1}, \]
\[ k_{298} = 3.2 \times 10^{-11} \text{ cm}^3 \text{s}^{-1} [8], \]  \hspace{1cm} (7.28)

\[ N + O_2 \rightarrow NO + O, \quad k = 4.4 \times 10^{-12} \exp(-3220/T) \text{ cm}^3 \text{s}^{-1}, \]
\[ k_{298} = 7.7 \times 10^{-17} \text{ cm}^3 \text{s}^{-1} [7]. \]  \hspace{1cm} (7.29)

Apart from the electron impact dissociation of O\(_2\), other pathways for O production include dissociation of O\(_2\) by N\(_2^*\) (Eq. 7.8), and dissociation of O\(_3\) by O\(_2^*\) (Eq. 7.9). O atoms are consumed to a large extent by reactions with O\(_2\) to form O\(_3\), and to a smaller extent by reactions with HO\(_2\), OH, and O\(_3\),

\[ O + O_2 + M \rightarrow O_3 + M, \quad k = 3.4 \times 10^{-34}(T/298)^{-1.2} \text{ cm}^6 \text{s}^{-1} [8]. \]  \hspace{1cm} (7.30)

\[ O + HO_2 \rightarrow OH + O_2, \quad k = 2.9 \times 10^{-11} \exp(-200/T) \text{ cm}^3 \text{s}^{-1}, \]
\[ k_{298} = 1.5 \times 10^{-11} \text{ cm}^3 \text{s}^{-1} [7], \]  \hspace{1cm} (7.31)
\[ O + OH \rightarrow H + O_2, \quad k = 2.3 \times 10^{-11} \exp(110/T) \text{cm}^3\text{s}^{-1}, \]
\[ k_{298} = 3.3 \times 10^{-11} \text{cm}^3\text{s}^{-1} \quad [9], \quad (7.32) \]
\[ O + O_3 \rightarrow O_2 + O_2, \quad k = 8.0 \times 10^{-12} \exp(-2060/T) \text{cm}^3\text{s}^{-1}, \]
\[ k_{298} = 8.0 \times 10^{-15} \text{cm}^3\text{s}^{-1} \quad [7]. \quad (7.33) \]

OH radicals are produced by the electron impact dissociation of H₂O (Eq. 7.26) and by the reactions of H with O₃, O₂⁺-H₂O with H₂O, and O with HO₂,

\[ H + O_3 \rightarrow OH + O_2, \quad k = 1.4 \times 10^{-10} \exp(-470/T) \text{cm}^3\text{s}^{-1}, \]
\[ k_{298} = 2.9 \times 10^{-11} \text{cm}^3\text{s}^{-1} \quad [8], \quad (7.34) \]
\[ O_2^+\cdot H₂O + H₂O \rightarrow H₃O^+ + OH + O₂, \quad k = 1.2 \times 10^{-9} \text{cm}^3\text{s}^{-1} \quad [5], \quad (7.35) \]
\[ O + HO₂ \rightarrow OH + O₂, \quad k = 2.9 \times 10^{-11} \exp(200/T) \text{cm}^3\text{s}^{-1}, \]
\[ k_{298} = 5.7 \times 10^{-11} \text{cm}^3\text{s}^{-1} \quad [8]. \quad (7.36) \]

OH is primarily consumed by reactions with N (Eq. 7.27) and HO₂ forming NO and H₂O, and secondarily by the reactions with O atoms (Eq. 7.32), O₃, and NO₂,

\[ OH + HO₂ \rightarrow H₂O + O₂, \quad k = 8.0 \times 10^{-11} \text{cm}^3\text{s}^{-1} \quad [8]. \quad (7.37) \]
\[ OH + O₃ \rightarrow HO₂ + O₂, \quad k = 1.9 \times 10^{-12} \exp(-1000/T) \text{cm}^3\text{s}^{-1}, \]
\[ k_{298} = 6.6 \times 10^{-14} \text{cm}^3\text{s}^{-1} \quad [10], \quad (7.38) \]
OH + NO₂ + M → HNO₃ + M, \( k = 2.2 \times 10^{-30} (T / 298)^{-2.9} \text{ cm}^6 \text{s}^{-1} \) [8]. (7.39)

H atoms are produced by the electron impact dissociation of H₂O (Eq. 7.26) and by the reactions of N with OH (Eq. 7.27), O with OH (Eq. 7.32), and H₃O⁺·H₂O with O₂⁻ (Eq. 7.23). H atoms are mainly consumed by reactions with O₃ to form OH (Eq. 7.34), and by reactions with O₂ to form HO₂,

\[ \text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}, \quad k = 1.8 \times 10^{-32} (T / 298)^{-0.8} \text{ cm}^6 \text{s}^{-1} \] [11]. (7.40)

HO₂ radicals mutually react to produce hydrogen peroxide (H₂O₂), which is also produced by mutual reactions of OH,

\[ \text{HO}_2 + \text{HO}_2 + \text{M} \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 + \text{M}, \quad k = 1.9 \times 10^{-33} \exp(980 / T) \text{ cm}^6 \text{s}^{-1}, \]

\[ k_{298} = 5.1 \times 10^{-32} \text{ cm}^6 \text{s}^{-1} \] [4]. (7.41)

\[ \text{OH} + \text{OH} + \text{M} \rightarrow \text{H}_2\text{O}_2 + \text{M}, \quad k = 6.9 \times 10^{-31} (T / 298)^{-0.8} \text{ cm}^6 \text{s}^{-1} \] [4]. (7.42)

H₂O₂ is consumed by reactions with OH to form H₂O and HO₂,

\[ \text{H}_2\text{O}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{HO}_2, \quad k = 2.9 \times 10^{-12} \exp(-160 / T) \text{ cm}^6 \text{s}^{-1}, \]

\[ k_{298} = 1.7 \times 10^{-12} \text{ cm}^3 \text{s}^{-1} \] [4]. (7.43)
Major N-containing products in the gas phase include NO, NO$_2$, N$_2$O, N$_2$O$_5$, HNO$_2$, and HNO$_3$. NO is produced dominantly by the reactions of N with OH (Eq. 7.27), N with O$_2$ (Eq. 7.29), and O with NO$_2$,

\[
O + NO_2 \rightarrow NO + O_2, \quad k = 6.5 \times 10^{-12} \exp(120/T) \text{ cm}^3 \text{s}^{-1},
\]

\[
k_{298} = 9.7 \times 10^{-12} \text{ cm}^3 \text{s}^{-1} \quad [7]. \tag{7.44}
\]

NO is consumed primarily by reactions with N (Eq. 7.28), O$_3$, OH, and HO$_2$, forming N$_2$, NO$_2$, HNO$_2$, and NO$_2$ respectively,

\[
NO + O_3 \rightarrow NO_2 + O_2, \quad k = 4.3 \times 10^{-12} \exp(-1598/T) \text{cm}^3 \text{s}^{-1},
\]

\[
k_{298} = 2.1 \times 10^{-14} \text{ cm}^3 \text{s}^{-1} \quad [12], \tag{7.45}
\]

\[
NO + OH + M \rightarrow HNO_2 + M, \quad k = 8.6 \times 10^{-31} (T / 298)^{-2.5} \exp(34/T) \text{ cm}^6 \text{s}^{-1},
\]

\[
k_{298} = 9.7 \times 10^{-31} \text{ cm}^6 \text{s}^{-1} \quad [13], \tag{7.46}
\]

\[
NO + HO_2 \rightarrow NO_2 + OH, \quad k = 3.5 \times 10^{-12} \exp(240/T) \text{cm}^3 \text{s}^{-1},
\]

\[
k_{298} = 7.8 \times 10^{-12} \text{ cm}^3 \text{s}^{-1} \quad [12]. \tag{7.47}
\]

NO$_2$ is produced mainly by the reactions of NO with O$_3$ and HO$_2$ (Eqs. 7.45 and 7.47), and by the reaction of OH with HNO$_2$,

\[
OH + HNO_2 \rightarrow NO_2 + H_2O, \quad k = 1.8 \times 10^{-11} \exp(-390/T) \text{cm}^3 \text{s}^{-1},
\]

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\[ k_{298} = 4.9 \times 10^{-12} \text{ cm}^3 \text{s}^{-1} \] [8]. \hspace{1cm} (7.48)

Important consumption channels for NO\textsubscript{2} include reactions with OH, O, and N forming HNO\textsubscript{3} (Eq. 7.39), NO (Eq. 44), N\textsubscript{2}O (nitrous oxide), and NO\textsubscript{3},

\[ \text{NO}_2 + \text{N} \rightarrow \text{N}_2\text{O} + \text{O}, \hspace{1cm} k = 2.4 \times 10^{-12} \text{ cm}^3 \text{s}^{-1} \] [5], \hspace{1cm} (7.49)

\[ \text{NO}_2 + \text{O} + \text{M} \rightarrow \text{NO}_3 + \text{M}, \hspace{1cm} k = 9.0 \times 10^{-32} (T/298)^{-2.0} \text{ cm}^6 \text{s}^{-1} \] [8]. \hspace{1cm} (7.50)

NO\textsubscript{3} is also produced by the reaction of OH with HNO\textsubscript{3},

\[ \text{OH} + \text{HNO}_3 \rightarrow \text{NO}_3 + \text{H}_2\text{O}, \hspace{1cm} k = 1.5 \times 10^{-14} \exp(650/T) \text{ cm}^3 \text{s}^{-1}, \hspace{1cm} \]

\[ k_{298} = 1.3 \times 10^{-13} \text{ cm}^3 \text{s}^{-1} \] [10]. \hspace{1cm} (7.51)

NO\textsubscript{3} is consumed by reactions with NO\textsubscript{2} forming N\textsubscript{2}O\textsubscript{5} (dinitrogen pentoxide),

\[ \text{NO}_3 + \text{NO}_2 + \text{M} \rightarrow \text{N}_2\text{O}_5 + \text{M}, \hspace{1cm} k = 2.7 \times 10^{-30} (T/298)^{-3.4} \text{ cm}^6 \text{s}^{-1} \] [7]. \hspace{1cm} (7.52)

N\textsubscript{2}O\textsubscript{5} decomposes to regenerate NO\textsubscript{2} and NO\textsubscript{3},

\[ \text{N}_2\text{O}_5 \rightarrow \text{NO}_3 + \text{NO}_2, \hspace{1cm} k = 9.7 \times 10^{14} (T/298)^{0.1} \exp(-11080/T) \text{ s}^{-1}, \hspace{1cm} \]

\[ k_{298} = 0.07 \text{ s}^{-1} \] [4]. \hspace{1cm} (7.53)
HNO₂ is primarily produced by the reaction of OH with NO (Eq. 7.46) and dominantly consumed by the reaction with OH to form NO₂ (Eq. 7.48). HNO₃ is produced by the reaction of OH with NO₂ (Eq. 7.39) and is consumed by reaction with OH to form NO₃ (Eq. 7.51).

7.3 Surface Reaction Mechanism For PP

PP is a saturated hydrocarbon polymer with a carbon backbone containing hydrogen and methyl (-CH₃) groups arranged in an alternating fashion. We used 10¹⁵ cm⁻² for the total density of surface sites, as reported for virgin PP.[14]

The reactivities of the hydrogen groups in PP depend on the nature of the C atom to which they are attached. There are three types of C atoms in any given monomer unit of PP, primary C, to which only one C atom is bonded; secondary C, to which two C atoms are bonded; and tertiary C, to which three C atoms are bonded (see Fig. 7.3a). In general, the reactivities of hydrogen bound to these C atoms scale as: \( H_{\text{tert}} > H_{\text{sec}} > H_{\text{pri}} \).

A monomer unit of PP consists of two secondary H atoms, a tertiary H atom, and a methyl (-CH₃) group. Assuming equal likelihood for any of these four groups to be pointing out towards the plasma, their initial surface densities are, \( N_{H,\text{sec}} = 0.5 \times 10^{15} \) cm⁻², \( N_{H,\text{tert}} = 0.25 \times 10^{15} \) cm⁻², and \( N_{\text{methyl}} = 0.25 \times 10^{15} \) cm⁻². The total number of surface sites is, however, allowed to vary with treatment time. When a “hole” is made in the PP chain, the diffusing species are allowed to react with the newly formed dangling bonds in the broken chains as well as with the exposed PP chain below, as shown in Fig. 7.3b.
The plasma surface modification of PP is primarily oxidative by reactions with free radicals in the gas phase. The reactions with gas phase ions can be neglected in comparison. The loss frequencies for ions in the gas phase are orders of magnitude larger than their loss frequencies with PP and as a result, ions are preferentially consumed in the gas phase. For example, the loss frequency for $\text{H}_3\text{O}^+\cdot\text{H}_2\text{O}$ in the gas phase is $\approx10^7 \text{ s}^{-1}$. For a unit reaction probability for the reaction with the PP surface, the loss frequency for $\text{H}_3\text{O}^+\cdot\text{H}_2\text{O}$ is $\approx10^4 \text{ s}^{-1}$. The densities of free radicals are generally both larger and are sustained for longer periods in the gas phase ($\sim \text{ms}$) and so their reactions with the PP surface are more important in comparison. The ions arriving at the PP surface are thermal due to the collisional sheath and so do not contribute to energy activated reactions with PP such as sputtering. On that basis we have little justification to differentiate ions from the free radicals with respect to their reactivities.

The surface reaction mechanism for PP is given in Table 7.1. In general, the reactions can be classified as: initiation, propagation, and termination.

### 7.3.1 Initiation

The initiating reactions are abstractions of hydrogen from the PP chain. Although cleavage of PP at the C-C bond is possible, the resulting radicals, due to their mutual proximity have been found to quickly recombine to yield back the polymer. The dominant reactive species in the gas phase are $\text{O}_2^*$, O$_3$, H, N, HO$_2$, O, and OH. Investigations have shown that $\text{O}_2^*$ reactions on saturated hydrocarbons are slow at best.[15] The rate constant for O$_3$ reactivity on PP is $1.3\times10^{-22} \text{ cm}^3 \text{ s}^{-1}$,[16] which is at least a few orders of magnitude smaller than both the rate constant for the gas phase
consumption of O₃ and the rate constant for the reaction of O or OH with PP (which is ≈ $10^{-11}$ cm$^3$ s$^{-1}$ [8]). The reactivities for H abstraction by H atoms are two to four orders of magnitude smaller than those for O or OH and hence, H atoms are less likely to be a significant source of H abstraction.[17] Similarly, the reactivities of N and HO₂ towards PP are significantly smaller compared to those of O and OH and so can be safely neglected. Oxidation by molecular oxygen is not likely since gas temperatures above 700 K are typically required for such processes to be important.

OH has been observed spectroscopically during the oxidation of hydrocarbon polymers by atomic oxygen as evidence of H-abstraction.[18] H can be abstracted from any of the primary, secondary, and tertiary sites in PP. The probability of abstraction scales as $H_{\text{tert}} > H_{\text{sec}} > H_{\text{pri}}$ and this ranking is generally independent of the nature of the attacking radical.[19] This trend is supported by the observation that oxidative attack in atactic PP (a configuration of PP in which the methyl groups are placed randomly on both sides of the chain) at tertiary sites is approximately 20 times faster than at secondary sites.[20] Another example is the abstraction of H from iso-butane (iso-C₄H₁₀) by O atoms,

$$\text{O} + \text{iso-C₄H₁₀} \rightarrow \text{OH} + \text{iso-C₄H₉}, \quad k_{\text{iso,298}} = 2.0 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1} [8], \quad (7.54)$$

$$\text{O} + \text{iso-C₄H₁₀} \rightarrow \text{OH} + \text{tert-C₄H₉}, \quad k_{\text{tert,298}} = 150.0 \times k_{\text{iso,298}} [8]. \quad (7.55)$$

The rate of tertiary H abstraction is 150 times larger than that of secondary H. Similar trends have been observed in reactions of O with n-heptane where rate constants for
abstraction of secondary hydrogen are approximately two orders of magnitude larger than those for primary hydrogen.[8]

O atoms abstract H from PP to produce a PP alkyl radical and OH,

\[
\text{O(g) + } \sim \text{CH}_2\text{-C-CH}_2\text{-CH}_3 \rightarrow \sim \text{CH}_2\text{-C-CH}_2\text{-CH}_3 + \text{OH(g)}
\]  \hspace{1cm} (7.56)

Based on the work by Gomez et al. [21], at atmospheric pressure the surface reaction probability for this reaction is < 0.01. For this work, we used \( \gamma_{\text{tert}} = 10^{-3} \), \( \gamma_{\text{sec}} = 10^{-4} \), and \( \gamma_{\text{pri}} = 10^{-5} \).

OH radicals also abstract H from PP to produce a PP alkyl radical and H2O,

\[
\text{OH(g) + } \sim \text{CH}_2\text{-C-CH}_2\text{-CH}_3 \rightarrow \sim \text{CH}_2\text{-C-CH}_2\text{-CH}_3 + \text{H}_2\text{O(g)}
\]  \hspace{1cm} (7.57)

As reaction probabilities for H-abstraction by OH are not well known, estimates were obtained based on analogies with rate constants for gas phase reactions of OH with long chain saturated hydrocarbons. The rate constant for the reaction of OH with large hydrocarbon molecules (for example, C_{16}H_{34}) is \( \approx 2.5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \).[8] A gas-kinetic rate constant is \( \approx 10^{-10} \text{ cm}^3 \text{ s}^{-1} \). Assuming that a unit surface reaction probability corresponds to a gas-kinetic rate constant, the surface reaction probability for H abstraction from PP by OH can be estimated as \( \gamma_{\text{tert}} = 0.25 \). Also, the branching ratios for H-abstractions from
the tertiary, secondary, and primary sites of long chain saturated hydrocarbons in the gas phase are such that \( k_{\text{ter}}/k_{\text{sec}} \approx 5 \) and \( k_{\text{sec}}/k_{\text{pri}} \approx 20\). Therefore we estimated that \( \gamma_{\sec} = 0.05 \) and \( \gamma_{\pri} = 0.0025 \).

This method of estimating surface reaction probabilities typically provides only a lower limit. There are other factors such as orientation of the reactant with respect to the surface, its angle of incidence, and the catalytic activity of the surface which influence the surface reaction probabilities. For a strong interaction with the surface, this approach likely provides a reasonable lower limit to the reactivity because of neglect of the catalytic effect of the surface. For a weak interaction, this method provides a better estimate.

### 7.3.2 Propagation

The PP alkyl radicals produced by H abstraction by O and OH (Eqs. 66 and 67) react with O\(_2\) to form PP peroxy radicals,

\[
O_2 (g) + \cdot \text{CH}_2 = \cdot \text{C} = \cdot \text{CH}_2 \rightarrow \cdot \text{CH}_2 = \cdot \text{C} = \cdot \text{CH}_2
\]

(7.58)

The reactivity of O\(_2\), however, depends on the nature of the alkyl radicals. Studies by Kuzuya et al. showed that mid-chain alkyl radicals are much less reactive with O\(_2\) compared to end-chain alkyl radicals.[22] The reactions with end-chain radicals are usually diffusion controlled [19] and can be taken to occur at close to the encounter frequency.[23]
The PP alkyl radicals can also react with O to form alkoxy radicals [18],

\[
\text{O}_2 (g) + \text{CH}_2=\text{CH}_2^\cdot \rightarrow \text{CH}_2=\text{CH}_2^\cdot
\]

This direct pathway to the formation of alkoxy radicals is not significant. Hydrocarbon alkyl radicals are known to react with O\textsubscript{3} in the gas phase at a rate up to five times faster than O\textsubscript{2}.\textsuperscript{[24]} The analogous process for reactions of O\textsubscript{3} with alkyl surface groups could be a possible route to alkoxy radical formation,

\[
\text{O}_3 (g) + \text{CH}_2=\text{CH}_2^\cdot \rightarrow \text{CH}_2=\text{CH}_2^\cdot + \text{O}_2 (g)
\]

The PP peroxy radicals abstract hydrogen from other polymer chains or from neighboring sites on the same chain to yield PP hydroperoxides.\textsuperscript{[19]} The ratio of intermolecular to intramolecular attack on the H sites by peroxy radicals is \(\approx 1:13.\textsuperscript{[15]}\) The intramolecular attack, being more favored, leads to sequences of neighboring hydroperoxide groups along a backbone. This series of reactions has been observed during the early stages of oxidation of PP.\textsuperscript{[15]}

\[
\text{CH}_2=\text{CH}_2^\cdot + \text{CH}_2=\text{CH}_2^\cdot \rightarrow \text{CH}_2=\text{CH}_2^\cdot + \text{CH}_2=\text{CH}_2^\cdot
\]
The mean time for the reaction of polymer peroxy radicals between propagation steps, based on their reaction with neighboring tertiary radicals, is \( \approx 5 \text{ s} \).[15]

Decomposition of the resulting hydroperoxides leads to a variety of oxidized functional groups.[19] This decomposition, is however slow compared to the formation of alkoxy or peroxy radicals. For example, Poncin-Epaillard et al. [25] exposed PP previously treated by a \( \text{N}_2 \)-plasma to \( \text{O}_2 \). Hydroperoxides were formed, with densities up to \( 10^{16} \text{ cm}^{-2} \), which then decomposed with a half life of 30 h. This long-term decomposition of the hydroperoxides is excluded from the reaction mechanism as the residence times for the conditions of interest are at best a few seconds. However, note should be made that the hydroperoxides are not necessarily the end products.

Polymer alkoxy radicals (PO\(^*\)) are the main source of the chain backbone scission that typically occurs during the oxidation of PP.[19,26] The rate coefficient for the \( \beta \)-scission of PP alkoxy radicals is \( k \approx 10^3 \text{ s}^{-1} \).[15] Such \( \beta \)-scissions on tertiary carbon atoms lead to the formation of ketones while those on secondary carbon atoms result in aldehydes,
In the β-scission of tertiary alkoxy radicals (Eq. 7.63), channel (b) is more favorable because the resulting secondary polymer hydrocarbon radical is more stable than the primary CH₃ radical formed by channel (a). β-scission is known to account for only 65% of the alkoxy degradation. The remaining alkoxy radicals react with the PP matrix to produce alcohol groups.[27]

Further reactions of the alcohol groups with O and OH radicals regenerate alkoxy radicals,
Erosion of PP to produce gas phase products is initiated by the abstraction of H in the aldehydes groups by O or OH to produce carbonyl radicals. These carbonyl radicals further react with O atoms to produce CO$_2$ and PP alkyl radicals,

$$\text{~CH}_2\text{C=O} + \text{O(g), OH(g)} \rightarrow \text{~CH}_2\text{C=O} + \text{OH(g), H}_2\text{O(g)} + \text{O(g)}$$

(7.68)

The etched product CO$_2$ exposes the site beneath for further oxidation.

7.3.3 Termination

While hydrogen atoms are less likely than O or OH to abstract H from PP, they compete with O and OH for the PP alkyl radicals,[28]
Reactions of OH with alkyl and carbonyl radicals result in the formation of alcohols and acids,

\[
\text{OH}_{(g)} + \cdot \text{CH}_2\text{C} = \text{O} \rightarrow \cdot \text{CH}_2\text{C} = \text{O} + \text{H}_2\text{O}
\]  

These reactions are considered terminal because of the stability of the end products compared to the free radicals.

### 7.4 Plasma Surface Modification of Polypropylene

To validate the surface reaction mechanism, comparisons were made to experiments conducted by O’Hare et al.[29] for humid-air plasma treatment of PP. The gas composition was N\(_2\)/O\(_2\)/H\(_2\)O = 78.9/20.0/1.1, at 1 atm and initially 300 K (1.1% H\(_2\)O corresponds to a RH of ≈30%). The downstream electrode length is 12 cm and the PP web speed is 250 cm/s producing a gas residence time of 0.05 s. The applied voltage is
sinusoidal at 9.6 kHz across a 3 mm gap providing 460 voltage pulses per site. The energy deposition was varied (0 - 1.5 J-cm\(^{-2}\)) by changing the applied voltage (0 - 20 kV). The base case uses 0.8 J-cm\(^{-2}\).

The electron density \((n_e)\) and electron temperature \((T_e)\) for the first, last, and select intermediate pulses as a function of time for the base case are shown in Fig. 7.4. The time scale is relative to the beginning of each voltage pulse. During the first voltage pulse, the potential across the gap is mainly a result of the applied voltage. The seed electrons accelerated by the electric field gain energy and ionize the background gases, \(N_2\), \(O_2\), and \(H_2O\), producing secondary electrons, \(N_2^+\), \(O_2^+\), and \(H_2O^+\) (Eqs. 7.3, 7.4, and 7.11). For the first pulse, the peak electron temperature is 3.4 eV and the peak electron density is \(7 \times 10^{12}\) cm\(^{-3}\).

With the flow of current through the discharge, the dielectric on the surface of the electrodes is charged, thereby removing voltage from the gap and terminating the discharge. During subsequent pulses, the voltage across the dielectric adds to the gap voltage, enabling a more rapid avalanche and shorter current pulses producing larger \(n_e\) \((5 \times 10^{13}\) cm\(^{-3}\)) and \(T_e\) \((6.0\) eV) compared to the first pulse. The differences in \(n_e\) after \(10^{-7}\) s for pulses later than the first are due to changes in the composition of the background gases.

The peak \(E/N\) during later discharge pulses is \(\approx400\) Td for which nearly 70% of the energy deposition is expended in the electronic excitation of \(N_2\) (Eq. 7.1) and about 10% is expended in the electron excitation of \(O_2\) (Eq. 7.2). The densities of \(N_2^*\) and \(O_2^*\) during the first, last, and select intermediate pulses as a function of time are shown in Fig. 7.4. Most of the \(N_2^*\) (> 90%) and a smaller amount of \(O_2^*\) (< 10%) are quenched by
collisions with the background gases (Eqs. 7.7 and 7.10). Other channels for $N_2^*$ consumption ($< 10\%$) include reactions with $O_2$ to produce $O$ (Eq. 7.8). The dominant channel for $O_2^*$ consumption is the reaction with $O_3$ to produce $O$ (Eq. 7.9). $O_2^*$ is less reactive compared to $N_2^*$ and hence, its density accumulates over the pulses.

Other channels for electron energy loss include ionization of $N_2$ and $O_2$ to produce $N_2^+$ and $O_2^+$ (Eqs. 7.4 and 7.5), whose densities are shown in Fig. 7.5. Due to the nearly constant density of $N_2$ and $O_2$ and similarity in loss channels, the differences in the densities of $N_2^+$ and $O_2^+$ with pulses after the first are small. $N_2^+$ is lost by association with $N_2$ to form $N_4^+$ (Eq. 7.12). $N_4^+$ charge exchanges with $O_2$ to form $O_2^+$ (Eq. 7.15), which further reacts with $H_2O$ to form the cluster ion $O_2^+\cdot H_2O$ (Eq. 7.16). $O_2^+\cdot H_2O$ reacts with $H_2O$ to form $H_3O^+$, which further reacts with $H_2O$ to produce $H_3O^+\cdot H_2O$ (Eqs. 7.17 and 7.19). The time dependence of the densities of $H_3O^+\cdot H_2O$ and the dominant negative ion, $O_2^-$, for the first, last, and select intermediate pulses are also shown in Fig. 7.5. $O_2^-$ is produced by the attachment of electrons to $O_2$ (Eq. 7.20). $H_3O^+\cdot H_2O$ and $O_2^-$ recombine to yield $O_2$, $H$, and $H_2O$ (Eqs. 7.23 and 7.24).

Electron impact dissociation of the background gases produces $N$, $O$, and $OH$ (Eqs. 7.5, 7.25, and 7.26), whose densities are shown in Fig. 7.6. $N$ atoms are consumed by reactions with $OH$ and $O_2$ (Eqs. 7.27 and 7.29) to produce $NO$; and with $NO$ to produce $N_2$ (Eq. 7.28). The contributions of the reactions with $OH$, $NO$, and $O_2$ towards $N$ consumption are 40%, 45%, and 10% respectively. $N$ being less reactive than other radicals accumulates in the discharge from pulse to pulse.

The electron impact dissociation of $O_2$ (Eq. 7.25) accounts for $\approx 25\%$ of the $O$ atom production; while dissociation of $O_2$ by $N_2^*$ (Eq. 7.8) and $O_3$ by $O_2^*$ (Eq. 7.9) each
contribute ≈30%. O atoms are primarily consumed by reactions with O2 (≈85%) to form O3 (Eq. 7.30); and with HO2 (6%), OH (4%), and O3 (2%) to produce O2 (Eqs. 7.31-7.33). After a few hundreds of pulses, the density of O reaches a periodic steady state.

Although the initial inventory of OH in a given pulse is created by electron impact dissociation of H2O (Eq. 7.26), the contribution of this process to the overall production of OH is only 2%. Dominant channels for OH production include reactions of H with O3 (Eq. 7.34), O2+·H2O with H2O (Eq. 7.35), and O with HO2 (Eq. 7.36) with their contributions being 35%, 35%, and 20% respectively. OH is primarily consumed by reactions with N (Eq. 7.27) and HO2 (Eq. 7.37) forming NO (≈30%) and H2O (≈30%) respectively; and by reactions with O (Eq. 7.32), O3 (Eq. 7.38), and NO2 (Eq. 7.39) with their contributions being 11%, 18%, and 7%. The density of OH increases with pulses due to the increase in the density of O3 (see below), which reacts with H to produce OH (Eq. 7.34). Similar to O, the density of OH reaches a periodic steady state after a few hundreds of pulses.

The densities of H, HO2, and O3 as a function of time are shown in Fig. 7.7. H atoms are mainly produced by the reactions of N with OH (Eq. 7.27), O with OH (Eq. 7.32), and H3O+·H2O with O2− (Eq. 7.23), with their contributions being 38%, 15%, and 42%. H atoms primarily react with O3 to form OH (Eq. 7.34), and with O2 to form HO2 (Eq. 7.40). The density of H reaches a periodic steady state within 10s of pulses.

HO2 (hydroperoxy) radicals are formed by the reactions of H with O2 (Eq. 7.40). The production of HO2 dominantly occurs during the first microsecond. Later, consumption of HO2 by reactions with HO2 (Eq. 7.41) and NO (Eq. 7.47) to produce
H$_2$O$_2$ and NO$_2$ dominate. As HO$_2$ is less reactive, its density also accumulates from pulse to pulse.

O$_3$ is produced by the reaction of O with O$_2$ (Eq. 7.30) and is primarily consumed by reactions with O$_2$* (66%, Eq. 7.9), H (12%, Eq. 7.34), and OH (10%, Eq. 7.38) to form O, OH, and HO$_2$. The rapid production of O$_3$ from O and O$_2$ dominates over losses and so O$_3$ accumulates from pulse to pulse.

N-containing products in the gas phase include NO and NO$_2$, whose densities are shown in Fig. 7.8. NO is produced by the reactions of N with OH (Eq. 7.27), N with O$_2$ (Eq. 7.29), and O with NO$_2$ (Eq. 7.23), with their contributions being 70%, 15%, and 10%. NO is consumed primarily by reactions with N, O$_3$, OH, and HO$_2$ to produce N$_2$ (Eq. 7.28), NO$_2$ (Eq. 7.45), HNO$_2$ (Eq. 7.46), and NO$_2$ (Eq. 7.47) respectively, with contributions of 60%, 20%, 10%, and 10%. Due to the increase in the density of N and OH with time (see Fig. 7.6), more NO is progressively generated by the reaction of N with OH (Eq. 7.27).

NO$_2$ is produced mainly by the reactions of NO with O$_3$ and HO$_2$ (Eqs. 7.45 and 7.47), and OH with HNO$_2$ (Eq. 7.48), with their contributions being 50%, 22%, and 21% respectively. NO$_2$ is primarily consumed by reactions with OH, O, N forming HNO$_3$ (Eq. 7.39), NO (Eq. 7.44), and N$_2$O (Eq. 7.49) with their contributions being 50%, 10%, and 21%. Approximately 5% of NO$_2$ is consumed by reactions with O forming NO$_3$ (Eq. 7.50). Since the densities of O$_3$ and N increase with time, the density of NO$_2$ accumulates over the pulses.

The consequences of varying energy deposition on the exit densities of O$_3$, N$_2$O$_x$, HNO$_x$, and CO$_2$ are shown in Fig. 7.9. With increasing energy deposition, larger
differences of O, N, and OH are produced. As O₃ is primarily formed by the reaction of O with O₂ (Eq. 7.30), its density increases with increasing energy deposition. Similarly, NO is dominantly produced by the reaction of N with OH (Eq. 7.27) and so the NO production increases. O₃ and NO react to produce NO₂ (Eq. 7.45) and so the density of NO₂ also increases with energy deposition. This further leads to the increased production of N₂O₅ (Eq. 7.52) and N₂O (Eq. 7.49). OH reacts with NO to produce HNO₂ (Eq. 54) and with NO₂ to form HNO₃ (Eq. 7.39), and so their densities increase. The density of CO₂ increases due to increased erosion of PP initiated by O and OH (Eq. 68).

The relative surface concentrations of alcohol, acid, peroxy, and carbonyl groups on PP as a function of energy deposition are shown in Fig. 7.10. With increasing energy deposition, the surface concentrations of the peroxy and acid groups increase and saturate with a small surface coverage, while those of the alcohol groups initially increase and then decrease. The initial increase in the densities of peroxy and acid groups is due to the increased availability of radicals. Their saturation at higher energy deposition is due to the balance between the consumption and production of alkyl radicals, their precursor. The densities of alcohols and carbonyls decrease at higher energy deposition because of consumption by O and OH to form alkoxy radicals and CO₂ (Eqs. 7.66-7.68). The computed surface densities of alcohol groups agree well with the experiments of O’Hare et al.[29] The less good agreement for the densities of peroxy and carbonyl groups at high energy deposition is due to the overestimation of the erosion of PP by the model. With larger erosion, more alkyl radicals and subsequently more peroxy radicals are generated. The agreement for the densities of acid groups is within 25%.
The surface densities of the alkyl, peroxy, and alkoxy radicals on PP as a function of time are shown in Fig. 7.11. Alkyl radicals are formed by the abstraction of H from PP by O and OH (Eqs. 7.56 and 7.57). Due to the production of O and OH in the gas phase with every discharge pulse (see Fig. 7.6), there is a constant flux of O and OH to the PP surface and so the alkyl radicals are produced with each pulse. During a given pulse, the production of alkyl radicals dominantly occurs for $t < 20 \, \mu s$. At later times, these radicals are consumed by reactions with O$_2$ and O$_3$ to form peroxy and alkoxy radicals (Eqs. 7.58 and 7.60). As the free sites on the PP surface are depleted at later pulses, the densities of the alkyl radicals decrease. There is little intra-pulse structure in the densities of alkoxy and peroxy radicals as their densities receive a small increment each pulse.

The surface densities of the alcohol and carbonyl groups on PP as a function of time are shown in Fig. 7.12. As with the alkoxy and peroxy radicals, the densities of these species have little intrapulse structure. The alkoxy radicals react with the hydrogen in the neighbouring sites to produce alcohols (Eq. 7.65). Alcohol groups are consumed by reactions with O and OH in the gas phase to regenerate alkoxy radicals (Eqs. 7.66 and 7.67). Carbonyl groups, namely aldehydes and ketones, are produced by the β-scission of alkoxy radicals (Eqs. 7.63 and 7.64).

Studies by Foulon-Belkacemi et al. [30] have shown that the surface composition of polymers subjected to humid-air coronas is sensitive to the RH. The time-averaged densities of O and OH (denoted as $<O>$ and $<OH>$) and the exit density of O$_3$ are shown in Fig. 7.13a as a function of RH. For a given energy deposition, with increasing RH, more energy is channeled into H$_2$O decomposition and so more OH is produced.
Correspondingly, the production of O is decreased. This decrease results in decreased O$_3$ densities, $\approx$30\% from RH of 1 to 100\%. The relative concentrations of peroxy, alcohol, carbonyl, and acid groups as a function of RH are shown in Fig. 7.13b. Since more OH is produced at larger RH and since OH is more reactive than O, the rate of the initial step of H abstraction from PP is increased and so more alkyl radicals are generated (Eq. 7.57). Since the density of O$_3$ decreases, PP alkyl radicals are preferentially consumed by O$_2$ and so larger densities of peroxy radicals are formed. The surface density of the alcohol groups initially increases and then decreases. The increased formation of alkyl radicals and subsequently alkoxy radicals (Eqs. 7.57 and 7.60) result in an initial increase in the surface concentration of alcohols with RH (Eq. 7.65). Due to the decreased flux of O$_3$ to the PP surface, fewer alkoxy radicals are generated and so production of alcohols and carbonyl radicals decreases (Eqs. 7.60, 7.63-7.65). The densities of alcohols also decrease with RH due to their increased consumption by OH (Eq. 7.67). Similarly, the decrease in carbonyl radicals with RH is in part due to the increased consumption by reaction with OH to form acids (Eq. 7.71).

The densities of NO, NO$_2$, N$_2$O$_5$, N$_2$O, HNO$_2$, and HNO$_3$ in the gas phase as a function of RH are shown in Figs. 7.14c and 7.14d. The densities of NO and NO$_2$ increase only slightly with RH. Due to their high reactivities, NO and NO$_2$ are mostly converted into species such as HNO$_3$ (Eq. 7.39), N$_2$O (Eq. 7.49), HNO$_2$ (Eq. 7.46), and N$_2$O$_5$ (Eq. 7.52). As NO is dominantly produced by the reaction of N with OH (Eq. 7.27), the increased production of OH with RH increases the density of NO. The density of NO$_2$ also increases since it is primarily produced from NO (Eqs. 7.45 and 7.47). As a result, the densities of HNO$_2$ and HNO$_3$ also increase (Eqs. 7.39 and 7.46). OH further
reacts with HNO₃ to produce NO₃ and H₂O (Eq. 7.51). The increasing densities of NO₃ and NO₂ then produce N₂O₅ (Eq. 7.52). N₂O is dominantly produced by the reaction of N with NO₂ (Eq. 7.49). NO₂ is preferentially consumed by reaction with OH to form HNO₃ (Eq. 7.39). Therefore, less NO₂ is available for reaction with N and so the production of N₂O decreases. CO₂ is produced as a result of the erosion of PP (Eq. 7.68). The initial increase in the density of CO₂ with RH is due to the increased production of carbonyl radicals (Eq. 7.68). However, as the density of OH increases with RH, carbonyl radicals are preferentially consumed by reaction with OH to form acids and so the density of CO₂ decreases.

The surface concentrations of alcohols, acids, carbonyl, and peroxy radicals and the densities of the dominant gas phase products as a function of gas temperature are shown in Fig. 7.14. Although the rate constant for the production of O₃ from O increases with temperature (Eq. 7.30), the rate constants for the consumption of O₃ (for example, with NO (Eq. 7.45)) also increase, resulting in a net decrease of O₃. This decrease in O₃ results in the decreased formation of alkoxy radicals on the PP surface (Eq. 7.60) and therefore a decreased production of alcohols, carbonyl, and acid groups (Eqs. 7.63-7.65, 7.71). The small decrease in the density of carbonyl groups does not significantly affect the erosion process (Eq. 7.68) and so the density of CO₂ remains almost constant. Due to the lower rate of consumption of alkyl radicals by reaction with O₃ with increasing gas temperature, more alkyl radicals are available for reaction with O₂ and so the peroxy radical concentration increases (Eq. 7.58).

The increased rate of reaction of O₃ with NO produces larger densities of NO₂ (Eq. 7.45) and so the density of HNO₃ also increases (Eq. 7.39). Due to the high
reactivities of NO and NO$_2$, their densities are relatively small compared to products such as HNO$_3$ and N$_2$O. Most of the NO is lost by reduction to N$_2$ (Eq. 7.28) and oxidation to NO$_2$ (Eqs. 7.45 and 7.47) and to a lesser degree to HNO$_2$ (Eq. 7.46). Most of the NO$_2$ is converted to HNO$_3$ (Eq. 7.39). The end result of the increased production of NO and NO$_2$ is the increased density of HNO$_3$ and N$_2$O. N$_2$O$_5$ is mainly produced by the reaction of NO$_2$ with NO$_3$ (Eq. 7.52) and so its production increases. This increase is offset by the increase in its unimolecular decomposition and so its density decreases.

The web speed and repetition rate of the discharge pulses determine the energy deposition and the time between generation of radicals. For example, as the web speed increases, the residence time of PP decreases and so the discharge frequency must be increased to keep the energy deposition constant (for a fixed voltage). Time-averaged and exit densities of gas phase species and concentrations of surface species are shown in Fig. 7.15 as a function of web speed for a constant energy deposition. As the pulse repetition frequency increases with web speed, O and OH radicals are refreshed more frequently, their time-averaged densities increase, and so their fluxes to the PP surface increase (Fig. 7.15a). Although the fluxes of O and OH increase with web speed, the surface concentrations of the alcohol, peroxy, carbonyl, and acid groups decrease (Fig. 7.15b). As the web speed increases from 150 cm/s to 350 cm/s, the residence time of the PP decreases from 0.08 s to 0.03 s. Since the reactions on the PP surface that produce these groups occur on time scales on the order of a few tens of ms, a factor of two change in the residence time noticeably affects their surface concentrations.

Although the densities of NO and NO$_2$ increase with the web speed (Fig. 7.15c), the change is not significant. Most of the NO is consumed to produce N$_2$ and NO$_2$ (Eqs.
7.28, 7.45, and 7.47) and most of the NO₂ is consumed by OH to produce HNO₃ (Eq. 7.39). Since these reactions occur on time scales of less than 1 ms, the densities of NO, NO₂ and the products they form (HNO₃, N₂O, N₂O₅) are not significantly affected by the change in the residence time (Figs. 7.15c and 7.15d). The density of O₃ slightly decreases due to the smaller time available for the reaction of O with O₂ to produce O₃ (Eq. 7.30). Due to the decrease in the density of carbonyl groups with web speed, the production of CO₂ also decreases.

7.5 Concluding Remarks

The gas phase and surface kinetics during the atmospheric pressure humid-air plasma processing of PP have been investigated. Using a pseudo-homogeneous global kinetics model, the consequences of process variables such as energy deposition, RH, web speed, and gas temperature on the surface properties of PP were investigated. Increasing energy deposition leads to an increased production of alcohol, carbonyl, acid, and peroxy radicals on the PP surface while increasing the gas phase production of O₃ and NₓOᵧ. Increasing the RH resulted in decreased production of O₃. The surface concentrations of peroxy radicals increased with RH while those of alcohol, carbonyl, and acid groups decreased. Increasing the gas temperature resulted in decreased surface concentrations of alcohol, carbonyl, and acid groups while the concentration of peroxy radicals increased. While keeping the energy deposition constant, increasing the web speed resulted in decreased concentrations of alcohols, peroxy radicals, carbonyl, and acid groups, indicating that residence time is an important process variable.
## 7.6 Tables and Figures

Table 7.1. Surface reaction mechanism for PP

<table>
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<tr>
<th>Reaction</th>
<th>a) Probabilities or reaction rate coefficient</th>
<th>b) Comments</th>
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<tr>
<td><strong>Initiation</strong></td>
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<td>(10^{-3}, 10^{-4}, 10^{-5})</td>
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<td>OH(_g) + PP-H (\rightarrow) PP(^*) + H(_2)O(_g)</td>
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<td>PP(^<em>) + O(<em>{2,g}) (\rightarrow) PP-O(</em>{2,</em>})</td>
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<td>c</td>
</tr>
<tr>
<td>PP(^<em>) + O(_{3,g}) (\rightarrow) PP-O(^</em>) + O(_{2,g})</td>
<td>(1.0, 0.5, 0.5)</td>
<td>c</td>
</tr>
<tr>
<td>PP-O(_{2,<em>}) + PP-H (\rightarrow) PP-OOH + PP(^</em>)</td>
<td>(5.5\times10^{-16} \text{ cm}^2 \text{ s}^{-1})</td>
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<tr>
<td>PP-O(^<em>) (\rightarrow) aldehydes + PP(^</em>)</td>
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<td></td>
</tr>
<tr>
<td>PP-O(^<em>) (\rightarrow) ketones + PP(^</em>)</td>
<td>(500 \text{ s}^{-1})</td>
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<td>O(_g) + PP=O (\rightarrow) OH(_g) + PP=O</td>
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<td>OH(_g) + PP=O (\rightarrow) H(_2)O(_g) + PP=O</td>
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<td>O(<em>g) + PP=O (\rightarrow) CO(</em>{2,g}) + PP-H</td>
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<td>PP-O(^<em>) + PP-H (\rightarrow) PP-OH + PP(^</em>)</td>
<td>(8.0\times10^{-14} \text{ cm}^2 \text{ s}^{-1})</td>
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</tr>
<tr>
<td>O(_g) + PP-OH (\rightarrow) PP-O + OH(_g)</td>
<td>(7.5\times10^{-4})</td>
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</tr>
<tr>
<td>OH(_g) + PP-OH (\rightarrow) PP-O + H(_2)O(_g)</td>
<td>(8.2\times10^{-3})</td>
<td></td>
</tr>
</tbody>
</table>
Termination

\[ \text{H}_g + \text{PP}^* \rightarrow \text{PP-H} \quad \begin{array}{ccc} 0.2, & 0.2, & 0.2 \end{array} \quad c \]

\[ \text{OH}_g + \text{PP}^* \rightarrow \text{PP-OH} \quad \begin{array}{ccc} 0.2, & 0.2, & 0.2 \end{array} \quad c \]

a) Subscript $g$ denotes gas phase species. PP-H denotes polypropylene.

b) Those coefficients without units are reaction probabilities.

c) Reaction probabilities for tertiary, secondary, and primary radicals respectively.
Fig. 7.1. Fractional disposition of energy deposition into electron impact processes as a function of electric field/gas number density (E/N) (1 Td = 1.0 × 10^{-17} V-cm²). Conditions are: N₂/O₂/H₂O = 78.9/20.0/1.1, 1 atm, 300 K. The E/Ns of interest are 300-600 Td. (a) Electronic and vibration excitation. (b) Dissociation and ionization.
Fig. 7.2. Reaction mechanism for gas phase chemistry in humid-air plasma. (a) Charged species chemistry. (b) Free radical chemistry.
Fig. 7.3. Surface reaction mechanism. (a) A monomer unit in PP. (b) Surface site balance model. PP is a saturated hydrocarbon polymer consisting of two secondary Hs, a tertiary H, and a methyl group attached to a carbon backbone. The total number of surface sites is allowed to vary.
Fig. 7.4. Plasma parameters and densities of excited species for the base case conditions. (a) Electron density ($n_e$). (b) Electron temperature ($T_e$). (c) $N_2^*$. (d) $O_2^*$. Conditions are $N_2/O_2/H_2O = 78.9/20.0/1.1$, 1 atm, 300 K (1.1% $H_2O$ corresponds to a relative humidity of approximately 30%). The energy deposition is 0.8 J cm$^{-2}$ and the applied voltage is 15 kV. Due to the charging of the dielectric, the $T_e$ and $n_e$ are larger for later pulses. $O_2^*$ being a relatively stable species, has a longer lifetime and its density accumulates with time.
Fig. 7.5. Time dependence of densities of charged species. (a) $N_2^+$. (b) $O_2^+$. (c) $H_3O^+\cdot H_2O$. (d) $O_2^-$. $N_2^+$ and $O_2^+$ are formed mainly by the electron impact ionization of $N_2$ and $O_2$. $N_2^+$ is mainly consumed by reactions with $N_2$ to form $N_4^+$ (Eq. 22). $O_2^+$ is primarily consumed by reactions with $H_2O$ to form the cluster ion $O_2^+\cdot H_2O$. The end result of the ion chemistry is the production of the $H_3O^+\cdot H_2O$ and $O_2^-$. 
Fig. 7.6. Densities of primary radicals as a function of time. (a) N. (b) O. (c) OH. N being less reactive than O and OH accumulates between pulses. O and OH are largely consumed in the interpulse period.
Fig. 7.7. Densities of radicals as a function of time. (a) H. (b) HO$_2$. (c) O$_3$. HO$_2$ and O$_3$ being less reactive compared to H accumulate over pulses.
Fig. 7.8. Densities of NO$_y$ as a function of time. (a) NO. (b) NO$_2$. Most of the NO and NO$_2$ are primarily converted to HNO$_3$ (Eq. 7.39) and N$_2$O (Eq. 7.49).
Fig. 7.9. Effect of energy deposition on the exit densities of gas phase species. (a) O$_3$ and NyO$_x$. (b) HNO$_x$. With increasing energy deposition, larger densities of O, OH, and N are produced thereby increasing the production of O$_3$, NO, NO$_2$, N$_2$O$_5$, N$_2$O, HNO$_2$, and HNO$_3$. 
Fig. 7.10. Experimental [29] and modeling results for percentage coverage of PP by functional groups after humid-air corona treatment. (a) Alcohol: C-OH. (b) Peroxy: C-OO. (c) Acid: HO-C=O. (d) Carbonyl: C=O. The energy deposition is varied by changing the applied voltage. With increasing energy deposition, the relative surface concentration of the acid increases, while those of the alcohol and carbonyl groups initially increase and then decrease. Conditions are as in Fig. 7.4.
Fig. 7.11. Time dependence of surface densities. (a) Alkyl radicals. (b) Peroxy radicals. (c) Alkoxy radicals. Alkyl radicals are produced by the reaction of O with PP-H (Eqs. 7.57 and 7.58) and are consumed by the reactions with O₂ and O₃ to form peroxy and alkoxy radicals (Eqs. 7.59 and 7.61).
Fig. 7.12. Surface densities as a function of time. (a) Alcohols. (b) Carbonyls. There is little intrapulse structure. Alcohol groups are produced by the abstraction of H from neighbouring sites on PP by alkoxy radicals (Eq. 7.66). Carbonyl groups are produced by the β-scission of alkoxy radicals (Eqs. 7.64 and 7.65).
Fig. 7.13. Consequences of varying RH on the exit surface composition of PP and on the time-averaged and exit densities of gas phase species. (a) Time-averaged densities of O and OH (denoted as \(<O>\) and \(<\text{OH}>\)) and exit density of O\(_3\). (b) Surface concentrations of alcohol, peroxy, carbonyl, and acid groups. (c) Exit N\(_x\)O\(_x\). (d) Exit CO\(_2\) and HNO\(_x\). Conditions are same as in Fig. 7.4.
Fig. 7.14. Effects of gas temperature on the exit surface properties of PP and the densities of important gas phase products during the humid-air corona processing of PP. (a) Surface concentrations of alcohol, peroxy, carbonyl, and acid groups. (b) Exit $O_3$ and $N_2O$. (c) Exit $CO_2$ and $HNO_x$. Conditions are same as in Fig. 7.4.
Fig. 7.15. Exit surface properties of PP and time-averaged and exit densities of gas phase species as a function of web speed. (a) Time-averaged densities of O and OH (denoted as $<\text{O}>$ and $<\text{OH}>$). (b) Exit surface concentrations of alcohol, peroxy, carbonyl, and acid groups. (c) Exit O$_3$ and N$_2$O$_5$. (d) Exit CO$_2$ and HNO$_x$. Conditions are same as in Fig. 7.4. To keep the energy deposition constant, the discharge frequency was adjusted.
7.7 References


8. CONCLUDING REMARKS

We have developed 0-D and 1-D (radially dependent) computer models for dielectric barrier discharge (DBD) processing of gases and surfaces at atmospheric pressure. In particular, we applied these models to investigate the plasma remediation of nitrogen oxides (NO\textsubscript{x}) from diesel exhausts and to study the plasma surface treatment of polypropylene (PP). The models allow for a detailed analysis of the plasma induced chemical reactions both in the gas phase and on the surface. The goals of the analyses include optimizing the energy efficiencies and minimizing the formation of harmful byproducts.

Unburned hydrocarbons (UHCs) present in diesel exhausts significantly affect the plasma remediation of NO\textsubscript{x} by oxidizing NO, the major form of NO\textsubscript{x} in the exhaust, into NO\textsubscript{2}. The efficiency of NO\textsubscript{x} removal improves when a given amount of energy is deposited in a large number of shorter duration pulses than in a single pulse. This increase in efficiency is due to the increased formation of organic nitrates resulting from the larger overlap in the densities of hydrocarbon radicals and NO\textsubscript{2}. With each pulse, radicals initiating the plasma chemistry are generated and during the interpulse period, these radicals undergo reactions thereby changing the composition of the plasma. The reaction chemistry for the follow-on pulses is different from that which would be obtained from an equivalent energy deposition in a single or smaller number of pulses due to the accumulation of these inter-pulse products.

Soot influences the chemistry of NO\textsubscript{x} plasma remediation dominantly through NO\textsubscript{2}-soot interactions and influences the ionization kinetics through electron attachment
to and ion neutralizations with the particles. The resulting changes of electron density and temperature may then affect the rates of electron-impact processes. When using a single pulse, NOx removal improves by as high as 10% in the presence of soot. With soot, higher energies were required for the removal of a given amount of NO. By regenerating the NO from NO2 and by indirectly leading to the increase in the density of OH radicals, soot increases the formation of HNO2, thereby improving NOx removal. The increase in the density of OH also results in increased UHC consumption. CO is the primary product of soot oxidation.

When using repetitive pulses in the presence of soot, the efficiency of NOx removal increases further. Single pulses with soot result in an initial gas phase oxidation of NO to NO2, followed by a heterogeneous conversion of NO2 to NO on the soot. Due to the larger gas phase density of NO2 when using repetitive pulses, there is an increased flux of NO2 to the soot surface, resulting in increased soot oxidation and larger rates of heterogeneous conversion of NO2 to NO. The combined effects of multiple pulses and heterogeneous chemistry on NOx remediation and soot oxidation are twofold. Improved NOx removal by the increased production of HNO2, HNO3, organic nitrates and nitrites due to the more favorable overlap in time of NO2 and reactive radical densities; and increased soot oxidation because of larger NO2 densities.

Spatially nonuniform energy deposition in DBDs results in spatial gradients in gas temperature and species densities which initiate advection and diffusion leading to transport of species to and from the microstreamer region. UHCs consume the primary radicals, O and OH, produced dominantly in the streamer region, and thereby their diffusion to regions outside of the streamer. As a result, the remediation of NOx at outer
radii decreases while more NO\textsubscript{x} is removed within the streamer region due to the increased production of hydrocarbon radicals.

Plasma surface treatment of polypropylene in humid air results in the formation of alcohol, peroxy, carbonyl, and acid groups on the surface. With increasing energy deposition, the surface concentrations of these groups increase. However, significant amounts of O\textsubscript{3} and N\textsubscript{3}O\textsubscript{y} are generated in the gas phase. Increasing the relative humidity decreases the production of O\textsubscript{3} and increases the concentrations of peroxy and acid groups on the surface. Increasing the gas temperature increases the surface concentration of peroxy radicals and decreases the concentrations of alcohol, carbonyl, and acid groups. For a given energy deposition, increasing the web speed results in decreased surface densities of peroxy, alcohol, carbonyl, and acid groups.

The major sources of inaccuracies in the models come from the simplifications in the streamer behavior and the inherent uncertainties in the reaction coefficients for heavy particle reactions and cross sections for electron impact reactions. In addition to addressing these sources of accuracies, future work could consider multiple streamers in the discharge, with variable spacing and formation times, as this is likely to change the spatial distribution of species and thereby the chemistry. In the context of plasma surface treatment of polymers, the present model could be used to study the surface treatment of other polymers such as polyethylene and poly-tetraflouroethylene.
# APPENDIX A. LIST OF SPECIES FOR N₂/O₂/H₂O/CO₂/CO/NOₓ/H₂/C₃H₆/C₃H₈ PLASMAS

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<thead>
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<th>Symbol</th>
<th>Species</th>
<th>Symbol</th>
<th>Species</th>
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<td>O₂⁻</td>
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</tr>
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<td>H₂O</td>
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<td>CH₃OH</td>
<td>CH₂Methyl Oxirane</td>
</tr>
<tr>
<td>CH₃NO₂</td>
<td>CH₃OCH₃</td>
<td>CH₂CHO</td>
<td>HCHO</td>
</tr>
<tr>
<td>CH₃OH</td>
<td>CH₂CCH₂</td>
<td>CH₂CH₂O</td>
<td>CH₂CO</td>
</tr>
<tr>
<td>CH₂CCCH₃</td>
<td>CH₂CHCH₂</td>
<td>CH₂OH</td>
<td>CH₂CO</td>
</tr>
<tr>
<td>CH₂CHCHO</td>
<td>C₂H₅ONO₂</td>
<td>CH₂CHCO</td>
<td>CH₂CO</td>
</tr>
</tbody>
</table>
APPENDIX B. LIST OF REACTIONS FOR
N₂/O₂/H₂O/CO₂/CO/NOₓ/H₂/C₃H₆/C₃H₈ PLASMAS

Electron impact reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Coefficient ¹</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>e + N₂ → N₂⁺ + e + e</td>
<td>b</td>
<td>1</td>
</tr>
<tr>
<td>e + N₂ → N₂(v) + e</td>
<td>b</td>
<td>1</td>
</tr>
<tr>
<td>e + N₂(v) → N₂ + e</td>
<td>b</td>
<td>1</td>
</tr>
<tr>
<td>e + N₂ → N₂(A) + e</td>
<td>b</td>
<td>1</td>
</tr>
<tr>
<td>e + N₂ → N + N + e</td>
<td>b</td>
<td>1</td>
</tr>
<tr>
<td>e + N₂(A) → N₂(v) + e</td>
<td>b</td>
<td>1</td>
</tr>
<tr>
<td>e + N₂(A) → N₂ + e</td>
<td>b</td>
<td>1</td>
</tr>
<tr>
<td>e + N₂(A) → N₂⁺ + e + e</td>
<td>b</td>
<td>1</td>
</tr>
<tr>
<td>e + O₂ → O⁻ + O</td>
<td>b</td>
<td>2</td>
</tr>
<tr>
<td>e + O₂ → O₂⁺ + e + e</td>
<td>b</td>
<td>2</td>
</tr>
<tr>
<td>e + O₂ → O₂(¹Δ) + e + e</td>
<td>b</td>
<td>2</td>
</tr>
<tr>
<td>e + O₂ → O + O + e</td>
<td>b</td>
<td>2</td>
</tr>
<tr>
<td>e + O₂ → O(¹D) + O + e</td>
<td>b</td>
<td>2</td>
</tr>
<tr>
<td>e + O → O(¹D) + e</td>
<td>b</td>
<td>3</td>
</tr>
<tr>
<td>e + O → O⁺ + e + e</td>
<td>b</td>
<td>3</td>
</tr>
<tr>
<td>e + O(¹D) → O + e</td>
<td>b</td>
<td>3</td>
</tr>
<tr>
<td>e + O(¹D) → O⁺ + e + e</td>
<td>b</td>
<td>3</td>
</tr>
<tr>
<td>e + H₂O → H₂O⁺ + e + e</td>
<td>b</td>
<td>4</td>
</tr>
<tr>
<td>e + H₂O → H + OH + e</td>
<td>b</td>
<td>4</td>
</tr>
<tr>
<td>e + H₂O → H⁻ + OH</td>
<td>b</td>
<td>4</td>
</tr>
<tr>
<td>e + N₂⁺ → N(²D) + N</td>
<td>2 × 10⁻⁷ Tₑ⁻⁰·⁵</td>
<td>5</td>
</tr>
<tr>
<td>e + N₃⁺ → N + N₂</td>
<td>2 × 10⁻⁷ Tₑ⁻⁰·⁵</td>
<td>5</td>
</tr>
<tr>
<td>e + H₃O⁺ · (H₂O)₂ → H + (H₂O)₃</td>
<td>2 × 10⁻⁷ Tₑ⁻⁰·⁵</td>
<td>5</td>
</tr>
</tbody>
</table>
e + NO2 → NO + O  
2 × 10^{-7} T_e^{-0.5}  
5

e + NO2 → NO + O(1D)  
2 × 10^{-7} T_e^{-0.5}  
5

e + H2NO → H_2O + N  
2 × 10^{-7} T_e^{-0.5}  
5

e + NO → N(2D) + O  
2 × 10^{-7} T_e^{-0.5}  
6

e + NO → N + O(1D)  
2 × 10^{-7} T_e^{-0.5}  
4

e + O_2 + M → O_2 + M  
1 × 10^{-31} cm^6 s^{-1}  
5

e + NO → NO + O(1D)  
2 × 10^{-7} T_e^{-0.5}  
5

e + NO2 → NO_2^-  
4 × 10^{-11}  
5

e + N4 → N_2 + N_2  
2 × 10^{-7} T_e^{-0.5}  
5

e + NO ·(H_2O)_2 → NO + H_2O + H_2O  
2 × 10^{-7} T_e^{-0.5}  
5

e + H2O → OH + H  
6.6 × 10^{-6} T_e^{-0.5}  
6

e + H_2O → O + H + H  
2.88 × 10^{-6} T_e^{-0.5}  
6

e + H2O → O + H_2  
2.52 × 10^{-6} T_e^{-0.5}  
6

e + H3O → H_2O + H  
2 × 10^{-7} T_e^{-0.5}  
6

e + O2 → O(1D) + O  
2 × 10^{-7} T_e^{-0.5}  
5

e + H_2 → H_2  
2 × 10^{-7} T_e^{-0.5}  
6

e + O2 ·H_2O → O_2 + H_2O  
2 × 10^{-7} T_e^{-0.5}  
6

e + H3O ·H_2O → H + H_2O + H_2O  
2 × 10^{-7} T_e^{-0.5}  
5

e + NH3 → NH_2 + H  
2 × 10^{-7} T_e^{-0.5}  
5

e + NH4 → NH_3 + H  
2 × 10^{-7} T_e^{-0.5}  
5

e + NO·H_2O → NO + H_2O  
2 × 10^{-7} T_e^{-0.5}  
5

e + NO·(H_2O)_3 → NO + H_2O  
+ H_2O + H_2O  
2 × 10^{-7} T_e^{-0.5}  
5

e + CO2 → CO + O  
2 × 10^{-7} T_e^{-0.5}  
6

e + O3 → e + O_2 + O(1D)  
5 × 10^{-10}  
6

e + CO2 → O + CO + e  
b  
7
\[ e + CO_2 \rightarrow CO_2^+ + e + e \]
\[ e + CO_2 \rightarrow O^- + CO \]

Reactions of \( N_2/O_2/H_2O/NO \)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Coefficient</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>( O + O_2 + M \rightarrow O_3 + M )</td>
<td>( 6.9 \times 10^{-34} \ (T/300)^{-1.25} )</td>
<td>8</td>
</tr>
<tr>
<td>( H + OH + M \rightarrow H_2O + M )</td>
<td>( 4.3 \times 10^{-31} \ cm^6 \ s^{-1} )</td>
<td>5</td>
</tr>
<tr>
<td>( N_2O_5 \rightarrow NO_2 + NO_3 )</td>
<td>( 5.49 \times 10^{14} T^{0.1} \ exp(-11080/T) )</td>
<td>8</td>
</tr>
<tr>
<td>( NO + O_2 + NO \rightarrow NO_2 + NO_2 )</td>
<td>( 1.4 \times 10^{-38} \ cm^6 \ s^{-1} )</td>
<td>8</td>
</tr>
<tr>
<td>( NO + HO_2 \rightarrow NO_2 + OH )</td>
<td>( 3.7 \times 10^{-12} \ exp(240/T) )</td>
<td>9</td>
</tr>
<tr>
<td>( N(2D) + N_2 \rightarrow N + N_2 )</td>
<td>( 2.4 \times 10^{-14} )</td>
<td>5</td>
</tr>
<tr>
<td>( NO + O + O_2 \rightarrow NO_2 + O_2 )</td>
<td>( 2.44 \times 10^{-27} T^{-1.8} \ cm^6 \ s^{-1} )</td>
<td>9</td>
</tr>
<tr>
<td>( N(2D) + O_2 \rightarrow NO + O )</td>
<td>( 6.8 \times 10^{-12} )</td>
<td>5</td>
</tr>
<tr>
<td>( NO + OH + M \rightarrow HNO_2 + M )</td>
<td>( 7.4 \times 10^{-31} \ (T/300)^{-2.4} \ cm^6 \ s^{-1} )</td>
<td>9</td>
</tr>
<tr>
<td>( N(2D) + NO \rightarrow N_2 + O )</td>
<td>( 6.3 \times 10^{-11} )</td>
<td>5</td>
</tr>
<tr>
<td>( NO + H + M \rightarrow HNO + M )</td>
<td>( 3.4 \times 10^{-32} \ cm^6 \ s^{-1} )</td>
<td>5</td>
</tr>
<tr>
<td>( N(2D) + N_2O \rightarrow NO + N_2 )</td>
<td>( 2.6 \times 10^{-12} )</td>
<td>5</td>
</tr>
<tr>
<td>( NO + NO_3 \rightarrow NO_2 + NO_2 )</td>
<td>( 1.6 \times 10^{-11} \ exp(150/T) )</td>
<td>9</td>
</tr>
<tr>
<td>( HO_2 + NO + M \rightarrow HNO_3 + M )</td>
<td>( 5.6 \times 10^{-33} \ cm^6 \ s^{-1} )</td>
<td>8</td>
</tr>
<tr>
<td>( HO_2 + NO \rightarrow O_2 + HNO )</td>
<td>( 9.0 \times 10^{-19} \ exp(2819/T) )</td>
<td>8</td>
</tr>
<tr>
<td>( N(2D) + NO_2 \rightarrow N_2O + O )</td>
<td>( 1.5 \times 10^{-12} )</td>
<td>5</td>
</tr>
<tr>
<td>( NO + O_3 \rightarrow NO_2 + O_2 )</td>
<td>( 2.0 \times 10^{-12} \ exp(-1400/T) )</td>
<td>8</td>
</tr>
<tr>
<td>( N(2D) + NO_2 \rightarrow NO + NO )</td>
<td>( 1.5 \times 10^{-12} )</td>
<td>5</td>
</tr>
<tr>
<td>( NO + N \rightarrow N_2 + O )</td>
<td>( 3.1 \times 10^{-11} )</td>
<td>5</td>
</tr>
<tr>
<td>( H + O_2 + M \rightarrow HO_2 + M )</td>
<td>( 5.64 \times 10^{-28} T^{-1.6} \ cm^6 \ s^{-1} )</td>
<td>5</td>
</tr>
<tr>
<td>( H + H + M \rightarrow H_2 + M )</td>
<td>( 4.8 \times 10^{-33} \ cm^6 \ s^{-1} )</td>
<td>5</td>
</tr>
<tr>
<td>( H + NO_2 \rightarrow OH + NO )</td>
<td>( 8 \times 10^{-11} )</td>
<td>5</td>
</tr>
</tbody>
</table>
H + HO₂ → OH + OH \quad 2.8 \times 10^{-10} \exp(-440/T)

N₂(A) + N₂ → N₂ + N₂ \quad 1.9 \times 10^{-13}

H + O₃ → OH + O₂ \quad 1.4 \times 10^{-10} \exp(-480/T)

N₂(A) + NO → NO + N₂ \quad 3.6 \times 10^{-10}

H + HNO → H₂ + NO \quad 1 \times 10^{-11}

N₂(A) + O₂ → O + O + N₂ \quad 1.5 \times 10^{-12}

N + NO₂ → N₂O + O \quad 2.4 \times 10^{-12}

N₂(A) + O₂ → O₂ + N₂ \quad 2.8 \times 10^{-11}

N + NO₂ → NO + NO \quad 6 \times 10^{-13}

N₂(A) + N₂O → N₂ + N₂ + O \quad 1.4 \times 10^{-11}

N₂(A) + N₂O → N₂ + N₂O \quad 1.7 \times 10^{-10}

N + N + M → N₂ + M \quad 3.9 \times 10^{-33} \text{ cm}^6 \text{ s}^{-1}

N₂(A) + NO₂ → NO + O + N₂ \quad 1.0 \times 10^{-12}

N₂(A) + H₂ → N₂ + H₂ \quad 2.6 \times 10^{-11}

N + OH → NO + H \quad 3.8 \times 10^{-11} \exp(85/T)

O(¹D) + N₂ → O + N₂ \quad 1.8 \times 10^{-11} \exp(107/T)

N + O + M → NO + M \quad 5.46 \times 10^{-33} \exp(155/T) \text{ cm}^6 \text{ s}^{-1}

O(¹D) + O₂ → O + O₂ \quad 3.8 \times 10^{-11}

N + O₂ → NO + O \quad 4.4 \times 10^{-12} \exp(-3220/T)

N + O₃ → NO + O₂ \quad 5 \times 10^{-16}

O(¹D) + H₂O → O + H₂O \quad 1.2 \times 10^{-11}

O(¹D) + H₂O → OH + OH \quad 2.2 \times 10^{-10}

O + HO₂ → OH + O₂ \quad 2.9 \times 10^{-11} \exp(200/T)

O + O₃ → O₂ + O₂ \quad 8.0 \times 10^{-12} \exp(-2060/T)

O + NO₂ + M → NO₃ + M \quad 9.0 \times 10^{-32} (T/300)^{0.2} \text{ cm}^6 \text{ s}^{-1}

NO₃ + NO₃ → NO₂ + NO₂ + O₂ \quad 1.2 \times 10^{-15}

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\[
\begin{align*}
\text{OH} + \text{OH} & \rightarrow \text{O} + \text{H}_2\text{O} & 3.5 \times 10^{-16} T^{1.4} \exp(200/T) & 12 \\
\text{N}_2\text{O}_5 + \text{H}_2\text{O} & \rightarrow & 5 \times 10^{-21} & 5 \\
\text{NH} + \text{NO} & \rightarrow \text{N}_2\text{O} + \text{H} & 1.3 \times 10^{-12} & 5 \\
\text{OH} + \text{NO}_2 + \text{N}_2 & \rightarrow & 2.2 \times 10^{-30} (T/300)^{-2.9} \text{ cm}^6 \text{s}^{-1} & 9 \\
\text{NH} + \text{O}_2 & \rightarrow \text{HNO} + \text{O} & 2.3 \times 10^{-13} & 5 \\
\text{OH} + \text{HNO}_3 & \rightarrow \text{NO}_3 + \text{H}_2\text{O} & 1.5 \times 10^{-14} \exp(650/T) & 5 \\
\text{OH} + \text{HNO} & \rightarrow \text{H}_2\text{O} + \text{NO} & 2.15 \times 10^{-17} T^{1.88} \exp(481/T) & 8 \\
\text{OH} + \text{HO}_2 & \rightarrow \text{H}_2\text{O} + \text{O}_2 & 8 \times 10^{-11} & c \\
\text{H}_2\text{O}^+ + \text{H}_2\text{O} & \rightarrow \text{H}_3\text{O}^+ + \text{OH} & 1.7 \times 10^{-9} & 5 \\
\text{OH} + \text{HNO}_2 & \rightarrow \text{NO}_2 + \text{H}_2\text{O} & 1.8 \times 10^{-11} \exp(-390/T) & 9 \\
\text{H}_2\text{O}^+ + \text{O}_2 & \rightarrow \text{O}_2^+ + \text{H}_2\text{O} & 4.3 \times 10^{-10} & 5 \\
\text{OH} + \text{O}_3 & \rightarrow \text{HO}_2 + \text{O}_2 & 1.9 \times 10^{-12} \exp(-1000/T) & 5 \\
\text{N}_3^+ + \text{O}_2 & \rightarrow \text{NO}^+ + \text{N}_2\text{O} & 3.6 \times 10^{-11} & 5 \\
\text{OH} + \text{N}_2\text{O} & \rightarrow \text{HNO} + \text{NO} & 3.8 \times 10^{-17} & 5 \\
\text{N}_3^+ + \text{O}_2 & \rightarrow \text{NO}_2^+ + \text{N}_2 & 1.5 \times 10^{-11} & 5 \\
\text{HO}_2 + \text{NO}_2 & \rightarrow & 1.5 \times 10^{-31} (T/300)^{-3.2} \text{ cm}^6 \text{s}^{-1} & 9 \\
\text{N}_3^+ + \text{NO} & \rightarrow \text{NO}^+ + \text{N} + \text{N}_2 & 1.4 \times 10^{-10} & 5 \\
\text{HO}_2 + \text{O}_3 & \rightarrow \text{OH} + \text{O}_2 + \text{O}_2 & 1.4 \times 10^{-14} \exp(-600/T) & 5 \\
\text{N}_3^+ + \text{NO}_2 & \rightarrow \text{NO}_2^+ + \text{NO} + \text{N}_2 & 7 \times 10^{-11} & 5 \\
\text{NO}_2 + \text{O}_3 & \rightarrow \text{NO}_3 + \text{O}_2 & 1.2 \times 10^{-13} \exp(-2450/T) & 9 \\
\text{N}_3^+ + \text{NO}_2 & \rightarrow \text{NO}_2^+ + \text{N} + \text{N}_2 & 7 \times 10^{-11} & 5 \\
\text{N}_3^+ + \text{N}_2\text{O} & \rightarrow \text{NO}^+ + \text{N}_2 + \text{N}_2 & 5 \times 10^{-11} & 5 \\
\text{O} + \text{NO}_2 & \rightarrow \text{NO} + \text{O}_2 & 6.5 \times 10^{-12} \exp(120/T) & 9 \\
\text{O} + \text{NO}_3 & \rightarrow \text{O}_2 + \text{NO}_2 & 1 \times 10^{-11} & 5 \\
\text{N}_3^+ + \text{NO}_2^- & \rightarrow \text{N} + \text{N}_2 + \text{NO}_2 & 2 \times 10^{-6} (T/300)^{-0.5} & 5
\end{align*}
\]
O + OH → H + O₂  
O⁺ + N₂ → NO⁺ + N  
OH + OH + O₂ → H₂O₂ + O₂  
O⁺ + NO → NO⁺ + O  
OH + H₂O₂ → H₂O + HO₂  
O⁺ + O₂ → O₂⁺ + O  
H + HO₂ → H₂ + O₂  
O⁺ + NO₂ → NO₂⁺ + O  
HO₂NO₂ + O₂ → HO₂ + NO₂ + O₂  
O⁺ + NO₂⁻ → O + NO₂  
O₂⁺ + NO → NO⁺ + O₂  
O₂⁺ + NO₂ → NO₂⁺ + O₂  
O₂⁺H₂O + H₂O → H₃O⁺ + OH + O₂  
H₃O⁺ + H₂O + M → H₃O⁺⁺H₂O + M  
O₂⁺ + NO₂⁻ → O₂ + NO₂  
H₃O⁺⁺H₂O + H₂O → H₃O⁺⁺(H₂O)₂  
NO₂⁺ + NO → NO⁺ + NO₂  
H₃O⁺⁺(H₂O)₂ + NO₂⁻ → H⁺⁺(H₂O)₃ + NO₂  
H₃O⁺⁺(H₂O)₂ + NO₃⁻ → H⁺⁺(H₂O)₃ + NO₃  
NO₂⁺ + NO₂⁻ → NO₂ + NO₂  
NO₂⁺ + NO₃⁻ → NO₂ + NO₃  
N₂⁺ + NO → NO⁺ + N₂  
N₃⁺ + H₂O → H₂NO⁺ + N₂
\[
\begin{align*}
N_2^+ + NO_2 & \rightarrow NO_2^+ + N_2 + 3.3 \times 10^{-10} \\
N_2^+ + NO_2 & \rightarrow NO^+ + N_2O + 5.0 \times 10^{-11} \\
H_2NO^+ + NO_2^- & \rightarrow H_2O + N + NO_2 + 2 \times 10^{-6} (T/300)^{-0.5} \\
H_2NO^+ + NO_3^- & \rightarrow H_2O + N + NO_3 + 2 \times 10^{-6} (T/300)^{-0.5} \\
NO_2^- + HNO_3 & \rightarrow NO_3^- + HNO_2 + 1.6 \times 10^{-9} \\
N_2^+ + NO_2^- & \rightarrow N_2 + NO_2 + 3 \times 10^{-6} (T/300)^{-0.5} \\
NO_2^- + NO_2 & \rightarrow NO_3^- + NO + 1 \times 10^{-13} \\
N_2^+ + NO_3^- & \rightarrow N_2 + NO_3 + 3 \times 10^{-6} (T/300)^{-0.5} \\
NO_2^- + N_2O & \rightarrow NO_3^- + N_2 + 5 \times 10^{-13} \\
NO_2^- + N_2O_5 & \rightarrow NO_3^- + NO_2 + NO_2 + 7 \times 10^{-10} \\
NO_2^- + O_3 & \rightarrow NO_3^- + O_2 + 1.2 \times 10^{-10} \\
NO_3^- + NO & \rightarrow NO_2^- + NO_2 + 5 \times 10^{-13} \\
NO^+ + NO_2^- & \rightarrow NO + NO_2 + 3 \times 10^{-6} (T/300)^{-0.5} \\
NO^+ + NO_3^- & \rightarrow NO + NO_3 + 3 \times 10^{-6} (T/300)^{-0.5} \\
O_2^- + NO_2 & \rightarrow NO_2^- + O_2 + 7 \times 10^{-10} \\
NO^+ + O_2 + M & \rightarrow NO^+O_2 + M + 3 \times 10^{-31} \text{ cm}^6 \text{ s}^{-1} \\
O_2^- + N_2^+ & \rightarrow N_2 + O_2 + 2 \times 10^{-6} (T/300)^{-0.5} \\
NO^+O_2 + NO_2^- & \rightarrow NO + O_2 + NO_2 + 3 \times 10^{-6} (T/300)^{-0.5} \\
N_2(D) + NH_3 & \rightarrow NH + NH_2 + 5 \times 10^{-11} \\
NO^+O_2 + NO_2^- & \rightarrow NO_3 + NO_2 + 2 \times 10^{-7} (T/300)^{-0.5} \\
NO^+O_2 + NO_3^- & \rightarrow NO + O_2 + NO_3 + 3 \times 10^{-6} (T/300)^{-0.5} \\
OH + NH_3 & \rightarrow NH_2 + H_2O + 3.5 \times 10^{-12} \exp(-925/T) \\
O_1^+(D) + NH_3 & \rightarrow NH_2 + OH + 2.5 \times 10^{-10}
\end{align*}
\]
\[
\begin{align*}
\text{NH}_2 + \text{NO} & \rightarrow \text{N}_2 + \text{H}_2\text{O} & 1.6 \times 10^{-11} \text{ (T/300)^{-1.5}} & 9 \\
\text{N}^+ + \text{N}_2 + \text{M} & \rightarrow \text{N}_3^+ + \text{M} & 5.2 \times 10^{-30} \text{ cm}^6 \text{ s}^{-1} & 5 \\
\text{NH}_2 + \text{NO}_2 & \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O} & 1.9 \times 10^{-11} \text{ (T/300)^{-2.2}} & 9 \\
\text{N}^+ + \text{O}_2 & \rightarrow \text{NO}^+ + \text{O} & 2.6 \times 10^{-10} & 5 \\
\text{O}_2 + \text{NH}_3 & \rightarrow \text{NH}_3^+ + \text{O}_2 & 1 \times 10^{-9} & 13 \\
\text{N}^+ + \text{O}_2 & \rightarrow \text{O}^+ + \text{NO} & 3.1 \times 10^{-10} & 5 \\
\text{NH}_3^+ + \text{NH}_3 & \rightarrow \text{NH}_4^+ + \text{NH}_2 & 2.2 \times 10^{-9} & 5 \\
\text{N}^+ + \text{O}_2 & \rightarrow \text{O}^+ + \text{NH}_3 & 3.6 \times 10^{-11} & 5 \\
\text{H}_3\text{O}^+ + \text{NH}_3 & \rightarrow \text{NH}_4^+ + \text{H}_2\text{O} & 2.5 \times 10^{-9} & 5 \\
\text{N}^+ + \text{NO} & \rightarrow \text{NO}^+ + \text{N} & 9 \times 10^{-10} & 5 \\
\text{N}^+ + \text{NH}_3 & \rightarrow \text{NH}_3^+ + \text{N} & 2.4 \times 10^{-9} & 5 \\
\text{N}_2^+ + \text{N}_2 + \text{M} & \rightarrow \text{N}_4^+ + \text{M} & 1.1 \times 10^{-29} & 5 \\
\text{N}_3^+ + \text{NH}_3 & \rightarrow \text{NH}_3^+ + \text{N} + \text{N}_2 & 2.1 \times 10^{-9} & 5 \\
\text{N}_2^+ + \text{O}_2 & \rightarrow \text{O}_2^+ + \text{N}_2 & 5.1 \times 10^{-11} & 5 \\
\text{N}_2^+ + \text{NH}_3 & \rightarrow \text{NH}_3^+ + \text{N}_2 & 1.9 \times 10^{-9} & 5 \\
\text{N}_4^+ + \text{NO} & \rightarrow \text{NO}^+ + \text{N}_2 + \text{N}_2 & 1.8 \times 10^{-9} & 5 \\
\text{N}_4^+ + \text{NO}_2 & \rightarrow \text{NO}_2^+ + \text{N}_2 + \text{N}_2 & 2.5 \times 10^{-10} & 5 \\
\text{NH}_3^+ + \text{NO}_3^- & \rightarrow \text{NH}_3 + \text{NO}_3 & 5 \times 10^{-6} \text{ (T/300)^{-0.5}} & c \\
\text{N}_4^+ + \text{NO}_2 & \rightarrow \text{NO}^+ + \text{N}_2\text{O} + \text{N}_2 & 5 \times 10^{-11} & 5 \\
\text{NH}_4^+ + \text{NO}_3^- & \rightarrow \text{NH}_3 + \text{H} + \text{NO}_3 & 3 \times 10^{-6} \text{ (T/300)^{-0.5}} & 5 \\
\text{N}_4^+ + \text{O}_2 & \rightarrow \text{O}_2^+ + \text{N}_2 + \text{N}_2 & 2.5 \times 10^{-10} & 5 \\
\text{NO}^+ + \text{H}_2\text{O} + \text{M} & \rightarrow \text{NO}^- + \text{H}_2\text{O} + \text{M} & 1.6 \times 10^{-28} \text{ cm}^6 \text{ s}^{-1} & 5 \\
\text{NO}^+ + \text{H}_2\text{O} + \text{M} & \rightarrow \text{NO}^- + \text{H}_2\text{O} + \text{M} & 1 \times 10^{-27} & 5 \\
\text{N}_4^+ + \text{NO}_2 & \rightarrow \text{NO}_2 + \text{N}_2 + \text{N}_2 & 3 \times 10^{-6} \text{ (T/300)^{-0.5}} & 5 \\
\text{NO}^+ + \text{H}_2\text{O} + \text{M} & \rightarrow \text{NO}^- + \text{H}_2\text{O} + \text{M} & 1.3 \times 10^{-12} & 5
\end{align*}
\]
\[
\begin{align*}
\text{NO}^+ \cdot \text{H}_2\text{O} + \text{H}_2\text{O} + \text{M} \\
\text{N}_4^+ + \text{NO}_3^- \rightarrow \text{NO}_3^- + \text{N}_2 + \text{N}_2 & \quad 3 \times 10^{-6} \ (T/300)^{-0.5} \\
\text{NO}^+ \cdot \text{(H}_2\text{O})_2 + \text{H}_2\text{O} \rightarrow \text{NO}^+ \cdot \text{(H}_2\text{O})_3 & \quad 1 \times 10^{-9} \\
\text{O}_2^+ \cdot \text{H}_2\text{O} + \text{M} \rightarrow \text{O}_2^+ \cdot \text{H}_2\text{O} + \text{M} & \quad 2.5 \times 10^{-28} \ \text{cm}^6 \text{s}^{-1} \\
\text{NO}^+ \cdot \text{(H}_2\text{O})_3 + \text{H}_2\text{O} \rightarrow & \quad 8 \times 10^{-11} \\
\text{H}_3\text{O}^+ \cdot \text{(H}_2\text{O})_2 + \text{HNO}_2 \\
\text{NH}_2 + \text{O} \rightarrow \text{NH} + \text{OH} & \quad 1.2 \times 10^{-11} \\
\text{NH}_2 + \text{O} \rightarrow \text{HNO} + \text{H} & \quad 7.6 \times 10^{-11} \\
\text{HO}_2\text{NO}_2 + \text{N}_2 \rightarrow & \quad 5 \times 10^{-6} \ \text{exp}(-10000/T) \\
\text{OH} + \text{NO}_2 + \text{O}_2 \rightarrow \text{HNO}_3 + \text{O}_2 & \quad 2.6 \times 10^{-30} \ (T/300)^{-2.9} \ \text{cm}^6 \text{s}^{-1} \\
\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H} & \quad 7.7 \times 10^{-12} \ \text{exp}(-2100/T) \\
\text{O}^1(\text{D}) + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{O}_2 & \quad 2.3 \times 10^{-12} \\
\text{O}^1(\text{D}) + \text{H}_2 \rightarrow \text{OH} + \text{H} & \quad 1.1 \times 10^{-10} \\
\text{O} + \text{H}_2\text{O}_2 \rightarrow \text{OH} + \text{HO}_2 & \quad 1.4 \times 10^{-12} \ \text{exp}(-2000/T) \\
\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H} & \quad 1.6 \times 10^{-11} \ \text{exp}(-4570/T) \\
\text{H} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O} & \quad 9.4 \times 10^{-13} \\
\text{HO}_2 + \text{HO}_2 + \text{M} \rightarrow & \quad 1.9 \times 10^{-33} \ \text{exp}(980/T) \ \text{cm}^6 \text{s}^{-1} \\
\text{O} + \text{NO} + \text{N}_2 \rightarrow \text{NO}_2 + \text{N}_2 & \quad 9.1 \times 10^{-28} \ T^{-1.6} \ \text{cm}^6 \text{s}^{-1} \\
\text{NO}_2 + \text{NO}_3^- + \text{M} \rightarrow \text{N}_2\text{O}_5 + \text{M} & \quad 2.7 \times 10^{-30} \ (T/300)^{-3.4} \ \text{cm}^6 \text{s}^{-1} \\
\text{N}^+ + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^+ + \text{N} & \quad 5.55 \times 10^{-8} \ T^{-0.52} \\
\text{H}_2\text{O}^+ + \text{NO}_2^- \rightarrow \text{H}_2\text{O} + \text{NO}_2 & \quad 2 \times 10^{-6} \ (T/300)^{-0.5} \\
\text{H}_2\text{O}^+ + \text{NO}_3^- \rightarrow \text{H}_2\text{O} + \text{NO}_3 & \quad 2 \times 10^{-6} \ (T/300)^{-0.5} \\
\text{H}_2\text{O}^+ + \text{O}_2^- \rightarrow \text{H}_2\text{O} + \text{O}_2 & \quad 2 \times 10^{-6} \ (T/300)^{-0.5} \\
\text{H}_3\text{O}^+ + \text{NO}_2^- \rightarrow \text{H}_2\text{O} + \text{H} + \text{NO}_2 & \quad 2 \times 10^{-6} \ (T/300)^{-0.5} \\
\text{H}_3\text{O}^+ + \text{NO}_3^- \rightarrow \text{H}_2\text{O} + \text{H} + \text{NO}_3 & \quad 2 \times 10^{-6} \ (T/300)^{-0.5} \\
\text{H}_3\text{O}^+ + \text{O}_2^- \rightarrow \text{H}_2\text{O} + \text{H} + \text{O}_2 & \quad 2 \times 10^{-6} \ (T/300)^{-0.5}
\end{align*}
\]
\[
\begin{align*}
\text{O}_2^+ + \text{NO}_3^- & \rightarrow \text{O}_2 + \text{NO}_3 \quad 2 \times 10^{-6} \ (T/300)^{-0.5} \quad \text{14} \\
\text{O}_2^+ + \text{O}_2^- & \rightarrow \text{O}_2 + \text{O}_2 \quad 2 \times 10^{-6} \ (T/300)^{-0.5} \quad \text{14} \\
\text{N}_3^+ + \text{NO}_3^- & \rightarrow \text{N}_2 + \text{N} + \text{NO}_3 \quad 2 \times 10^{-6} \ (T/300)^{-0.5} \quad \text{c} \\
\text{N}_3^+ + \text{O}_2^- & \rightarrow \text{N}_2 + \text{N} + \text{O}_2 \quad 2 \times 10^{-6} \ (T/300)^{-0.5} \quad \text{c} \\
\text{NO}^+ + \text{O}_2^- & \rightarrow \text{NO} + \text{O}_2 \quad 2 \times 10^{-6} \ (T/300)^{-0.5} \quad \text{14} \\
\text{NO}_2^+ + \text{O}_2^- & \rightarrow \text{NO}_2 + \text{O}_2 \quad 2 \times 10^{-6} \ (T/300)^{-0.5} \quad \text{14} \\
\text{O}^+ + \text{NO}_3^- & \rightarrow \text{O} + \text{NO}_3 \quad 2 \times 10^{-6} \ (T/300)^{-0.5} \quad \text{14} \\
\text{O}^+ + \text{O}_2^- & \rightarrow \text{O} + \text{O}_2 \quad 2 \times 10^{-6} \ (T/300)^{-0.5} \quad \text{14} \\
\text{NO}^+ \cdot \text{O}_2 + \text{O}_2^- & \rightarrow \text{NO} + \text{O}_2 + \text{O}_2 \quad 2 \times 10^{-6} \ (T/300)^{-0.5} \quad \text{c} \\
\text{N}^+ + \text{O}_2^- & \rightarrow \text{N} + \text{O}_2 \quad 2 \times 10^{-6} \ (T/300)^{-0.5} \quad \text{14} \\
\text{N}^+ + \text{NO}_2^- & \rightarrow \text{N} + \text{NO}_2 \quad 2 \times 10^{-6} \ (T/300)^{-0.5} \quad \text{14} \\
\text{N}^+ + \text{NO}_3^- & \rightarrow \text{N} + \text{NO}_3 \quad 2 \times 10^{-6} \ (T/300)^{-0.5} \quad \text{14} \\
\text{N}_4^+ + \text{O}_2^- & \rightarrow \text{N}_2 + \text{N}_2 + \text{O}_2 \quad 2 \times 10^{-6} \ (T/300)^{-0.5} \quad \text{c} \\
\text{O}_2^+ \cdot \text{H}_2\text{O} + \text{O}_2^- & \rightarrow \text{O}_2 + \text{O}_2 + \text{H}_2\text{O} \quad 2 \times 10^{-6} \ (T/300)^{-0.5} \quad \text{c} \\
\text{O}_2^+ \cdot \text{H}_2\text{O} + \text{NO}_3^- & \rightarrow \text{O}_2 + \text{NO}_3 + \text{H}_2\text{O} \quad 2 \times 10^{-6} \ (T/300)^{-0.5} \quad \text{c} \\
\text{O}_2^+ \cdot \text{H}_2\text{O} + \text{NO}_2^- & \rightarrow \text{O}_2 + \text{NO}_2 + \text{H}_2\text{O} \quad 2 \times 10^{-6} \ (T/300)^{-0.5} \quad \text{c} \\
\text{H}_3\text{O}^+ \cdot \text{H}_2\text{O} + \text{NO}_2^- & \rightarrow \text{H} + \text{H}_2\text{O} + \text{H}_2\text{O} + \text{NO}_2 \quad 2 \times 10^{-6} \ (T/300)^{-0.5} \quad \text{c} \\
\text{H}_3\text{O}^+ \cdot \text{H}_2\text{O} + \text{NO}_3^- & \rightarrow \text{H} + \text{H}_2\text{O} + \text{H}_2\text{O} + \text{NO}_3 \quad 2 \times 10^{-6} \ (T/300)^{-0.5} \quad \text{c} \\
\text{H}_3\text{O}^+ \cdot \text{H}_2\text{O} + \text{O}_2^- & \rightarrow \text{H} + \text{H}_2\text{O} + \text{H}_2\text{O} + \text{O}_2 \quad 2 \times 10^{-6} \ (T/300)^{-0.5} \quad \text{c} \\
\text{H}_2\text{NO}^+ + \text{O}_2^- & \rightarrow \text{H}_2\text{O} + \text{N} + \text{O}_2 \quad 2 \times 10^{-6} \ (T/300)^{-0.5} \quad \text{c} \\
\text{NH}_3^+ + \text{NO}_2^- & \rightarrow \text{NH}_3 + \text{NO}_2 \quad 2 \times 10^{-6} \ (T/300)^{-0.5} \quad \text{14}
\end{align*}
\]
\[
\begin{align*}
\text{NH}_3^+ + \text{O}_2^- &\rightarrow \text{NH}_3 + \text{O}_2 & 2 \times 10^{-6} \, (T/300)^{-0.5} & \text{c} \\
\text{NH}_4^+ + \text{NO}_2^- &\rightarrow \text{NH}_4 + \text{H} + \text{NO}_2 \\
\text{NH}_4^+ + \text{NO}_3^- &\rightarrow \text{NH}_4 + \text{H} + \text{NO}_3 \\
\text{NH}_4^+ + \text{O}_2^- &\rightarrow \text{NH}_3 + \text{H} + \text{O}_2 & 2 \times 10^{-6} \, (T/300)^{-0.5} & \text{c} \\
\text{NO}^+ \cdot \text{H}_2\text{O} + \text{NO}_2^- &\rightarrow \text{NO} + \text{H}_2\text{O} + \text{NO}_2 \\
\text{NO}^+ \cdot \text{H}_2\text{O} + \text{NO}_3^- &\rightarrow \text{NO} + \text{H}_2\text{O} + \text{NO}_3 \\
\text{NO}^+ \cdot (\text{H}_2\text{O})_2 + \text{NO}_2^- &\rightarrow \text{NO} + \text{H}_2\text{O} + \text{H}_2\text{O} + \text{NO}_3 \\
\text{NO}^+ \cdot (\text{H}_2\text{O})_3 + \text{NO}_3^- &\rightarrow \text{NO} + \text{H}_2\text{O} + \text{H}_2\text{O} + \text{H}_2\text{O} + \text{NO}_3 \\
\text{NO}^+ \cdot (\text{H}_2\text{O})_2 + \text{NO}_2^- &\rightarrow \text{NO} + \text{H}_2\text{O} + \text{H}_2\text{O} + \text{NO}_2 \\
\text{NO}^+ \cdot (\text{H}_2\text{O})_3 + \text{NO}_2^- &\rightarrow \text{NO} + \text{H}_2\text{O} + \text{H}_2\text{O} + \text{H}_2\text{O} + \text{NO}_2 \\
\text{NO}^+ \cdot (\text{H}_2\text{O})_2 + \text{O}_2^- &\rightarrow \text{NO} + \text{H}_2\text{O} + \text{H}_2\text{O} + \text{O}_2 \\
\text{NO}^+ \cdot (\text{H}_2\text{O})_3 + \text{O}_2^- &\rightarrow \text{NO} + \text{H}_2\text{O} + \text{H}_2\text{O} + \text{H}_2\text{O} + \text{O}_2 \\
\text{O} + \text{H} + \text{M} &\rightarrow \text{OH} + \text{M} & 1.62 \times 10^{-32} \, \text{cm}^6 \, \text{s}^{-1} & 15 \\
\text{H} + \text{H}_2\text{O}_2 &\rightarrow \text{H}_2\text{O} + \text{OH} & 4 \times 10^{-11} \, \text{exp}(-2000/T) & 12 \\
\text{NO}_2 + \text{NO}_2 + \text{N}_2 &\rightarrow \text{N}_2\text{O}_4 + \text{N}_2 & 1.4 \times 10^{-33} \, (T/300)^{-3.8} \, \text{cm}^6 \, \text{s}^{-1} & 16 \\
\text{N}_2\text{O}_4 + \text{N}_2 &\rightarrow \text{NO}_2 + \text{NO}_2 + \text{N}_2 & 1.29 \times 10^{-5} \, (T/300)^{-3.8} \, \text{exp}(-6460/T) & 16 \\
\text{NH}_2 + \text{H}_2 &\rightarrow \text{NH}_3 + \text{H} & 5.98 \times 10^{-12} \, \text{exp}(-2290/T) & 17
\end{align*}
\]
\[
\begin{align*}
\text{NH}_3 + H & \rightarrow \text{NH}_2 + H_2 & 1.35 \times 10^{-10} \exp(-3660/T) & 17 \\
\text{OH} + \text{NO}_3 & \rightarrow \text{HO}_2 + \text{NO}_2 & 2.6 \times 10^{-11} & 18 \\
\text{HO}_2 + \text{NO}_3 & \rightarrow \text{OH} + \text{NO}_2 + \text{O}_2 & 3.6 \times 10^{-12} & 18 \\
\text{HO}_2 + \text{NO}_3 & \rightarrow \text{HNO}_3 + \text{O}_2 & 9.2 \times 10^{-13} & 18 \\
\text{H} + \text{H}_2\text{O}_2 & \rightarrow \text{HO}_2 + \text{H}_2 & 8 \times 10^{-11} \exp(-4000/T) & 12 \\
\text{HNO}_3 + \text{NO} & \rightarrow \text{HNO}_2 + \text{NO}_2 & 7.37 \times 10^{-21} & 19 \\
\text{H}_2 + \text{O}_2 & \rightarrow \text{H} + \text{HO}_2 & 2.4 \times 10^{-10} \exp(-28500/T) & 12 \\
\text{H} + \text{O}_2 & \rightarrow \text{OH} + \text{O} & 2.8 \times 10^{-7} \exp(-7850/T) & 12 \\
\text{OH} + \text{M} & \rightarrow \text{O} + \text{H} + \text{M} & 4 \times 10^{-9} \exp(-50000/T) & 12 \\
\text{OH} + \text{O}_2 & \rightarrow \text{O} + \text{HO}_2 & 3.7 \times 10^{-11} \exp(-26500/T) & 12 \\
\text{OH} + \text{H} & \rightarrow \text{O} + \text{H}_2 & 1.14 \times 10^{-12} \exp(-518/T) & 6 \\
\text{HO}_2 + \text{M} & \rightarrow \text{H} + \text{O}_2 + \text{M} & 2 \times 10^{-5} \exp(-24363/T) & 12 \\
\text{HO}_2 + \text{H}_2 & \rightarrow \text{H}_2\text{O}_2 + \text{H} & 5 \times 10^{-11} \exp(-13100/T) & 12 \\
\text{H}_2\text{O}_2 + \text{O}_2 & \rightarrow \text{HO}_2 + \text{HO}_2 & 9 \times 10^{-11} \exp(-20000/T) & 12 \\
\text{H}_2\text{O} + \text{H} & \rightarrow \text{H}_2 + \text{OH} & 1.03 \times 10^{-16} \exp(-9265/T) & 12 \\
\text{H}_2\text{O} + \text{O} & \rightarrow \text{OH} + \text{OH} & 7.6 \times 10^{-15} \exp(-8605/T) & 12 \\
\text{H}^+ + \text{N}_2^+ & \rightarrow \text{H} + \text{N}_2 & 3 \times 10^{-6} (T/300)^{-0.5} & c \\
\text{O}^+ + \text{N}_2^+ & \rightarrow \text{O} + \text{N}_2 & 3 \times 10^{-6} (T/300)^{-0.5} & c \\
\text{O}^+ + \text{H}_2^+ & \rightarrow \text{O} + \text{H}_2 & 3 \times 10^{-6} (T/300)^{-0.5} & 14 \\
\text{O}_2^- + \text{H}_2^+ & \rightarrow \text{O}_2 + \text{H}_2 & 3 \times 10^{-6} (T/300)^{-0.5} & 14 \\
\text{H}^+ + \text{H}_2^+ & \rightarrow \text{H} + \text{H}_2 & 3 \times 10^{-6} (T/300)^{-0.5} & 14 \\
\text{H}^+ + \text{H}_2\text{O}^+ & \rightarrow \text{H} + \text{H}_2\text{O} & 3 \times 10^{-6} (T/300)^{-0.5} & 14 \\
\text{O}^- + \text{H}_2\text{O}^+ & \rightarrow \text{O} + \text{H}_2\text{O} & 3 \times 10^{-6} (T/300)^{-0.5} & 14 \\
\text{H}^- + \text{H}_3\text{O}^+ & \rightarrow \text{H}_2 + \text{H}_2\text{O} & 3 \times 10^{-6} (T/300)^{-0.5} & c \\
\text{O}^- + \text{H}_3\text{O}^+ & \rightarrow \text{OH} + \text{H}_2\text{O} & 3 \times 10^{-6} (T/300)^{-0.5} & c \\
\text{H}^- + \text{O}_2^+ + \text{M} & \rightarrow \text{H}_2\text{O} + \text{M} & 1.2 \times 10^{-25} & c \\
\text{O}^- + \text{O}_2^+ & \rightarrow \text{O} + \text{O}_2 & 3 \times 10^{-6} (T/300)^{-0.5} & 14
\end{align*}
\]
\[
\begin{align*}
H^+ + N_3^+ & \rightarrow NH + N_2 & 3 \times 10^{-6} \ (T/300)^{-0.5} \\
O^- + N_3^+ & \rightarrow NO + N_2 & 3 \times 10^{-6} \ (T/300)^{-0.5} \\
H^+ + NO^+ + M & \rightarrow HNO + M & 1.2 \times 10^{-25} \, cm^6 \, s^{-1} \\
O^- + NO^+ & \rightarrow NO + O & 3 \times 10^{-6} \ (T/300)^{-0.5} \\
H^+ + NO_2^+ + M & \rightarrow HNO_2 + M & 1.2 \times 10^{-25} \, cm^6 \, s^{-1} \\
O^- + NO_2^+ & \rightarrow NO_2 + O & 3 \times 10^{-6} \ (T/300)^{-0.5} \\
H^+ + O^+ + M & \rightarrow OH + M & 1.2 \times 10^{-25} \, cm^6 \, s^{-1} \\
O^- + O^+ + M & \rightarrow O_2 + M & 1.2 \times 10^{-25} \, cm^6 \, s^{-1} \\
H^+ + NO_2^- : O_2 & \rightarrow HNO + O_2 & 3 \times 10^{-6} \ (T/300)^{-0.5} \\
O^- + NO_2^- : O_2 & \rightarrow NO_2 + O_2 & 3 \times 10^{-6} \ (T/300)^{-0.5} \\
H^+ + N^+ + M & \rightarrow NH + M & 1.2 \times 10^{-25} \, cm^6 \, s^{-1} \\
O^- + N^+ + M & \rightarrow NO + M & 1.2 \times 10^{-25} \, cm^6 \, s^{-1} \\
H^+ + N_2^+ & \rightarrow H + N_2 + N_2 & 3 \times 10^{-6} \ (T/300)^{-0.5} \\
O^- + N_4^+ & \rightarrow O + N_2 + N_2 & 3 \times 10^{-6} \ (T/300)^{-0.5} \\
H^+ + O_2^- : H_2O & \rightarrow HO_2 + H_2O & 3 \times 10^{-6} \ (T/300)^{-0.5} \\
O^- + O_2^- : H_2O & \rightarrow O + O_2 + H_2O & 3 \times 10^{-6} \ (T/300)^{-0.5} \\
H^+ + H_3O^- : H_2O & \rightarrow H + HNO & 3 \times 10^{-6} \ (T/300)^{-0.5} \\
O^- + H_3O^- : H_2O & \rightarrow OH + HNO & 3 \times 10^{-6} \ (T/300)^{-0.5} \\
H^+ + NH_3^+ & \rightarrow H + NH_3 & 3 \times 10^{-6} \ (T/300)^{-0.5} \\
O^- + NH_3^+ & \rightarrow O + NH_3 & 3 \times 10^{-6} \ (T/300)^{-0.5} \\
H^+ + NH_4^+ & \rightarrow H_2 + NH_3 & 3 \times 10^{-6} \ (T/300)^{-0.5} \\
\end{align*}
\]
\[ \text{O}^- + \text{NH}_4^+ \rightarrow \text{OH} + \text{NH}_3 \quad 3 \times 10^{-6} \left(\frac{T}{300}\right)^{-0.5} \quad \text{c} \]

\[ \text{H}^+ + \text{NO}_2^+ \cdot \text{H}_2\text{O} \rightarrow \text{H} + \text{NO} + \text{H}_2\text{O} \quad 3 \times 10^{-6} \left(\frac{T}{300}\right)^{-0.5} \quad \text{c} \]

\[ \text{O}^- + \text{NO}_2^+ \cdot \text{H}_2\text{O} \rightarrow \text{O} + \text{NO} + \text{H}_2\text{O} \quad 3 \times 10^{-6} \left(\frac{T}{300}\right)^{-0.5} \quad \text{c} \]

\[ \text{H}^+ + \text{NO}_2^+ \cdot (\text{H}_2\text{O})_2 \rightarrow \text{HNO} + \text{H}_2\text{O} + \text{H}_2\text{O} \quad 3 \times 10^{-6} \left(\frac{T}{300}\right)^{-0.5} \quad \text{c} \]

\[ \text{O}^- + \text{NO}_2^+ \cdot (\text{H}_2\text{O})_3 \rightarrow \text{NO}_2 + \text{H}_2\text{O} + \text{H}_2\text{O} + \text{H}_2\text{O} \quad 3 \times 10^{-6} \left(\frac{T}{300}\right)^{-0.5} \quad \text{c} \]

\[ \text{OH} + \text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_3 + \text{H}_2\text{O} \quad 2.2 \times 10^{-30} \left(\frac{T}{300}\right)^{-2.9} \quad 8 \]

\[ \text{N}_2^+ + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^+ + \text{N}_2 \quad 2 \times 10^{-9} \quad \text{c} \]

\[ \text{O} + \text{OH} + \text{M} \rightarrow \text{HO}_2 + \text{M} \quad 2.76 \times 10^{-31} \text{ cm}^6 \text{ s}^{-1} \quad 8 \]

\[ \text{O}(^1\text{D}) + \text{O}_3 \rightarrow \text{O}_2 + \text{O} + \text{O} \quad 1.2 \times 10^{-10} \quad 8 \]

\[ \text{O}(^1\text{D}) + \text{NO} \rightarrow \text{O}_2 + \text{N} \quad 8.5 \times 10^{-11} \quad 8 \]

\[ \text{NH} + \text{NO} \rightarrow \text{N}_2 + \text{OH} \quad 4.5 \times 10^{-11} \quad 8 \]

\[ \text{N}_3 + \text{NO} \rightarrow \text{N}_2\text{O} + \text{N}_2 \quad 1.19 \times 10^{-12} \quad 8 \]

\[ \text{NH}_2 + \text{O} \rightarrow \text{H}_2 + \text{NO} \quad 8.3 \times 10^{-12} \quad 8 \]

\[ \text{OH} + \text{NO}_2 \rightarrow \text{HO}_2 + \text{NO} \quad 3.03 \times 10^{-11} \exp(-3360/T) \quad 8 \]

\[ \text{NO}_3 + \text{NO}_2 \rightarrow \text{NO} + \text{NO}_2 + \text{O}_2 \quad 8.21 \times 10^{-14} \exp(-1480/T) \quad 8 \]

\[ \text{O}(^1\text{D}) + \text{NO}_2 \rightarrow \text{O}_2 + \text{NO} \quad 2.5 \times 10^{-10} \quad 8 \]

\[ \text{O}(^1\text{D}) + \text{N}_2\text{O} \rightarrow \text{NO} + \text{NO} \quad 6.7 \times 10^{-11} \quad 8 \]

\[ \text{NO}_2 + \text{O}_3 \rightarrow \text{O}_2 + \text{O}_2 + \text{NO} \quad 1.0 \times 10^{-18} \quad 8 \]

\[ \text{O} + \text{N}_3 \rightarrow \text{NO} + \text{N}_2 \quad 1.12 \times 10^{-11} \quad 8 \]

\[ \text{O} + \text{HNO} \rightarrow \text{OH} + \text{NO} \quad 1.82 \times 10^{-11} \quad 8 \]

\[ \text{HNO} + \text{O}_2 \rightarrow \text{NO} + \text{HO}_2 \quad 5.25 \times 10^{-12} \exp(-1510/T) \quad 8 \]

\[ \text{O} + \text{O} + \text{M} \rightarrow \text{O}_2 + \text{M} \quad 5.21 \times 10^{-35} \exp(900/T) \text{ cm}^6 \text{ s}^{-1} \quad 8 \]
### Additional reactions for CO₂

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Coefficient</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{N}_2(\text{A}) + \text{CO}_2 \rightarrow \text{N}_2 + \text{CO}_2 )</td>
<td>( 2.5 \times 10^{-11} )</td>
<td>10</td>
</tr>
<tr>
<td>( \text{N}_2(\text{A}) + \text{CO} \rightarrow \text{N}_2 + \text{CO} )</td>
<td>( 1.1 \times 10^{-10} )</td>
<td>10</td>
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<tr>
<td>( \text{O}^\cdot (\text{D}) + \text{CO}_2 \rightarrow \text{O} + \text{CO}_2 )</td>
<td>( 7.4 \times 10^{-11} )</td>
<td>c</td>
</tr>
<tr>
<td>( \text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{H} )</td>
<td>( 1.12 \times 10^{-13} \exp(-91000/T) )</td>
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<tr>
<td>( \text{CO}_2^+ + \text{NO} \rightarrow \text{NO}^+ + \text{CO}_2 )</td>
<td>( 1.2 \times 10^{-10} )</td>
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<tr>
<td>( \text{CO}_2^+ + \text{O}_2 \rightarrow \text{O}_2^+ + \text{CO}_2 )</td>
<td>( 5.6 \times 10^{-11} )</td>
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<tr>
<td>( \text{CO}_2^+ + \text{NO}_2^- \rightarrow \text{CO}_2 + \text{NO}_2 )</td>
<td>( 2 \times 10^{-6} \left( \frac{T}{300} \right)^{-0.5} )</td>
<td>14</td>
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<tr>
<td>( \text{CO}_2^+ + \text{NO}_3^- \rightarrow \text{CO}_2 + \text{NO}_3 )</td>
<td>( 2 \times 10^{-6} \left( \frac{T}{300} \right)^{-0.5} )</td>
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<tr>
<td>( \text{CO}_2^+ + \text{O}_2^- \rightarrow \text{CO}_2 + \text{O}_2 )</td>
<td>( 2 \times 10^{-6} \left( \frac{T}{300} \right)^{-0.5} )</td>
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<tr>
<td>( \text{CO}_2^+ + \text{O} \rightarrow \text{CO} + \text{OH} )</td>
<td>( 2.5 \times 10^{-10} \exp(-13300/T) )</td>
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<tr>
<td>( \text{CO}_2 + \text{O} \rightarrow \text{CO} + \text{O}_2 )</td>
<td>( 2.8 \times 10^{-11} \exp(-26500/T) )</td>
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<tr>
<td>( \text{CO} + \text{O}_2 \rightarrow \text{CO}_2 + \text{O} )</td>
<td>( 4.2 \times 10^{-12} \exp(-24000/T) )</td>
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<tr>
<td>( \text{CO} + \text{O} + \text{M} \rightarrow \text{CO}_2 + \text{M} )</td>
<td>( 1.7 \times 10^{-33} \exp(-1510/T) \text{ cm}^6 \text{ s}^{-1} )</td>
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<tr>
<td>( \text{CO} + \text{HO}_2 \rightarrow \text{OH} + \text{CO}_2 )</td>
<td>( 2.5 \times 10^{-10} \exp(-11900/T) )</td>
<td>12</td>
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<tr>
<td>( \text{HCO} + \text{M} \rightarrow \text{H} + \text{CO} + \text{M} )</td>
<td>( 8.5 \times 10^{-3} T^{-2.14} \exp(-10278/T) )</td>
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<tr>
<td>( \text{HCO} + \text{H}_2 \rightarrow \text{CH}_2\text{O} + \text{H} )</td>
<td>( 3 \times 10^{-18} T^2 \exp(-8972/T) )</td>
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<tr>
<td>( \text{HCO} + \text{O}_2 \rightarrow \text{HO}_2 + \text{CO} )</td>
<td>( 8.5 \times 10^{-11} \exp(-850/T) )</td>
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<tr>
<td>( \text{HCO} + \text{H} \rightarrow \text{H}_2 + \text{CO} )</td>
<td>( 2 \times 10^{-10} )</td>
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<tr>
<td>( \text{HCO} + \text{O} \rightarrow \text{H} + \text{CO}_2 )</td>
<td>( 5 \times 10^{-11} )</td>
<td>12</td>
</tr>
<tr>
<td>( \text{HCO} + \text{O} \rightarrow \text{OH} + \text{CO} )</td>
<td>( 5 \times 10^{-11} )</td>
<td>12</td>
</tr>
<tr>
<td>( \text{HCO} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{CO} )</td>
<td>( 5 \times 10^{-11} )</td>
<td>12</td>
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<tr>
<td>( \text{HCO} + \text{HO}_2 \rightarrow \text{OH} + \text{H} + \text{CO}_2 )</td>
<td>( 5 \times 10^{-11} )</td>
<td>12</td>
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<tr>
<td>( \text{HCO} + \text{H}_2\text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{HO}_2 )</td>
<td>( 1.7 \times 10^{-13} \exp(-3486/T) )</td>
<td>12</td>
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<tr>
<td>( \text{HCO} + \text{H}_2\text{O} \rightarrow \text{CH}_2\text{O} + \text{OH} )</td>
<td>( 3.9 \times 10^{-16} T^{1.35} \exp(-13146/T) )</td>
<td>12</td>
</tr>
</tbody>
</table>
\begin{align*}
\text{HCO} + \text{HCO} & \to \text{CH}_2\text{O} + \text{CO} \quad 3 \times 10^{-11} \\
\text{HCO} + \text{HCO} & \to \text{H}_2 + \text{CO} + \text{CO} \quad 5 \times 10^{-12} \\
\text{H}^- + \text{CO}_2^+ & \to \text{H} + \text{CO}_2 \quad 3 \times 10^{-6} (T/300)^{-0.5} \\
\text{O}^- + \text{CO}_2^+ & \to \text{O} + \text{CO}_2 \quad 3 \times 10^{-6} (T/300)^{-0.5} \\
\text{CH}_2\text{O} + \text{OH} & \to \text{H} + \text{HCOOH} \quad 2 \times 10^{-13} \\
\text{HCOOH} + \text{OH} & \to \text{H}_2\text{O} + \text{CO}_2 + \text{H} \quad 4.8 \times 10^{-13} \\
\text{CN} + \text{O} & \to \text{CO} + \text{N} \quad 1.7 \times 10^{-11} \\
\text{CN} + \text{N} & \to \text{N}_2 + \text{C} \quad 3 \times 10^{-10} \\
\text{CN} + \text{N} + \text{M} & \to \text{CNN} + \text{M} \quad 2.76 \times 10^{-32} \text{ cm}^6 \text{ s}^{-1} \\
\text{CN} + \text{NO} & \to \text{N}_2 + \text{CO} \quad 1.2 \times 10^{-13} \\
\text{CN} + \text{H}_2 \to \text{HCN} + \text{H} \quad 1.13 \times 10^{-10} \exp(-2700/T) \\
\text{CN} + \text{O}_2 & \to \text{NCO} + \text{O} \quad 9.0 \times 10^{-16} T^{1.21} \exp(-3824/T) \\
\text{CN} + \text{CO}_2 & \to \text{NCO} + \text{CO} \quad 2 \times 10^{-15} \\
\text{HCN} + \text{O} & \to \text{OH} + \text{CN} \quad 4.5 \times 10^{-15} T^{1.58} \exp(-13386/T) \\
\text{HCN} + \text{O} & \to \text{H} + \text{NCO} \quad 3.3 \times 10^{-16} T^{1.47} \exp(-3774/T) \\
\text{HCN} + \text{O} & \to \text{CO} + \text{NH} \quad 9.0 \times 10^{-16} T^{1.21} \exp(-3824/T) \\
\text{HCN} + \text{OH} & \to \text{H}_2\text{O} + \text{CN} \quad 1.28 \times 10^{-11} \exp(-4161/T) \\
\text{HCN} + \text{OH} & \to \text{HOCN} + \text{H} \quad 2.01 \times 10^{-11} \exp(-8516/T) \\
\text{HCN} + \text{OH} & \to \text{HNCO} + \text{H} \quad 2.84 \times 10^{-13} \exp(-4397/T) \\
\text{HCN} + \text{OH} & \to \text{NH}_2 + \text{CO} \quad 1.07 \times 10^{-13} \exp(-5892/T) \\
\text{HCN} + \text{H} & \to \text{CN} + \text{H}_2 \quad 6.31 \times 10^{-10} \exp(-12400/T) \\
\text{NCO} + \text{H}_2 & \to \text{H} + \text{HNCO} \quad 1.26 \times 10^{-21} T^3 \exp(-2012/T) \\
\text{NCO} + \text{O} & \to \text{NO} + \text{CO} \quad 1.48 \times 10^{-11}
\end{align*}
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>NCO + O₂ → NO + CO₂</td>
<td>(1.32 \times 10^{-12})</td>
<td></td>
</tr>
<tr>
<td>NCO + NO → CO + N₂ + O</td>
<td>(7.61 \times 10^{-12})</td>
<td></td>
</tr>
<tr>
<td>NCO + NO → CO₂ + N₂</td>
<td>(1.45 \times 10^{-11})</td>
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</tr>
<tr>
<td>NCO + NO → N₂O + CO</td>
<td>(1.09 \times 10^{-11})</td>
<td></td>
</tr>
<tr>
<td>NCCN + O → CN + NCO</td>
<td>(4.15 \times 10^{-11}) exp(-5500/T)</td>
<td>8</td>
</tr>
<tr>
<td>NCCN + H → NCN + CN</td>
<td>(8.59 \times 10^{-16})</td>
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<tr>
<td>CO + H + M → HCO + M</td>
<td>(1.99 \times 10^{-33}) exp(-842/T) cm(^6) \text{s}^{-1}</td>
<td>8</td>
</tr>
<tr>
<td>CO + NO₂ → CO₂ + NO</td>
<td>(1.48 \times 10^{-10}) exp(-17009/T)</td>
<td>8</td>
</tr>
<tr>
<td>CO + O₃ → O₂ + CO₂</td>
<td>(4 \times 10^{-25})</td>
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</tr>
<tr>
<td>C + CO + M → C₂O + M</td>
<td>(6.3 \times 10^{-32}) cm(^6) \text{s}^{-1}</td>
<td>8</td>
</tr>
<tr>
<td>C₂O + O → CO + CO</td>
<td>(9.51 \times 10^{-11})</td>
<td></td>
</tr>
<tr>
<td>C₂O + O₂ → C₂O + CO</td>
<td>(3.3 \times 10^{-13})</td>
<td></td>
</tr>
<tr>
<td>C₂O + N → CO + CN</td>
<td>(5.5 \times 10^{-10})</td>
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<tr>
<td>C + N + M → CN + M</td>
<td>(9.41 \times 10^{-33}) cm(^6) \text{s}^{-1}</td>
<td>8</td>
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<tr>
<td>C + NCCN → CN + CCN</td>
<td>(3 \times 10^{-11})</td>
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<tr>
<td>C + NO → CN + O</td>
<td>(4.8 \times 10^{-11})</td>
<td></td>
</tr>
<tr>
<td>C + N₂ + M → CNN + M</td>
<td>(3.1 \times 10^{-33}) cm(^6) \text{s}^{-1}</td>
<td>8</td>
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<tr>
<td>C + N₃ → CN + N₂</td>
<td>(1.10 \times 10^{-10})</td>
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</tr>
<tr>
<td>C + O₂ → CO + O</td>
<td>(2.6 \times 10^{-11})</td>
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<tr>
<td>CCN+ O → CO + CN</td>
<td>(6 \times 10^{-12})</td>
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</tr>
<tr>
<td>CCN+ N → CN + CN</td>
<td>(1 \times 10^{-10})</td>
<td></td>
</tr>
<tr>
<td>CO₂ + N → CO + NO</td>
<td>(3.2 \times 10^{-13}) exp(-1710/T)</td>
<td>8</td>
</tr>
<tr>
<td>C⁺ + H⁻ → C + H</td>
<td>(5 \times 10^{-8}) ((T/300)^{-0.5})</td>
<td>14</td>
</tr>
<tr>
<td>C⁺ + O⁻ → C + O</td>
<td>(5 \times 10^{-8}) ((T/300)^{-0.5})</td>
<td>14</td>
</tr>
<tr>
<td>C⁺ + O₂⁻ → C + O₂</td>
<td>(5 \times 10^{-8}) ((T/300)^{-0.5})</td>
<td>14</td>
</tr>
</tbody>
</table>
## Additional reactions for C₃H₆ and C₃H₈

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Coefficient $^d$</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₃H₈ + H → n-C₃H₇ + H₂</td>
<td>$4.31 \times 10^{-12} (T/300)^{2.54} \exp(-3400/T)$</td>
<td>20</td>
</tr>
<tr>
<td>C₃H₈ + H → i-C₃H₇ + H₂</td>
<td>$1.90 \times 10^{-12} (T/300)^{2.4} \exp(-2250/T)$</td>
<td>20</td>
</tr>
<tr>
<td>C₃H₈ + O → n-C₃H₇ + OH</td>
<td>$1.39 \times 10^{-12} (T/300)^{2.68} \exp(-1870/T)$</td>
<td>20</td>
</tr>
<tr>
<td>C₃H₈ + O → i-C₃H₇ + OH</td>
<td>$4.08 \times 10^{-13} (T/300)^{2.71} \exp(-1060/T)$</td>
<td>20</td>
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<tr>
<td>C₃H₈ + C₂H₅ → n-C₃H₇ + C₂H₆</td>
<td>$1.65 \times 10^{-15} (T/300)^{3.65} \exp(-4600/T)$</td>
<td>20</td>
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<tr>
<td>C₃H₈ + C₂H₅ → i-C₃H₇ + C₂H₆</td>
<td>$9.31 \times 10^{-16} (T/300)^{3.46} \exp(-3760/T)$</td>
<td>20</td>
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<tr>
<td>C₃H₈ + CH₃ → n-C₃H₇ + CH₄</td>
<td>$1.65 \times 10^{-15} (T/300)^{3.65} \exp(-3600/T)$</td>
<td>20</td>
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<tr>
<td>C₃H₈ + CH₃ → i-C₃H₇ + CH₄</td>
<td>$9.31 \times 10^{-16} (T/300)^{3.46} \exp(-2760/T)$</td>
<td>20</td>
</tr>
<tr>
<td>C₃H₈ + OH → n-C₃H₇ + H₂O</td>
<td>$7.95 \times 10^{-13} (T/300)^{2} \exp(-2270/T)$</td>
<td>20</td>
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<tr>
<td>C₃H₈ + OH → i-C₃H₇ + H₂O</td>
<td>$1.44 \times 10^{-12} (T/300)^{1} \exp(-130/T)$</td>
<td>20</td>
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<tr>
<td>n-C₃H₇ + O₂ → n-C₃H₇O₂</td>
<td>$5.64 \times 10^{-12} (T/300)^{-2.7}$</td>
<td>20</td>
</tr>
<tr>
<td>i-C₃H₇ + O₂ → (CH₃)₂CHO₂</td>
<td>$1.50 \times 10^{-11}$</td>
<td>20</td>
</tr>
<tr>
<td>n-C₃H₇O₂ + NO → n-C₃H₇O + NO₂</td>
<td>$8.69 \times 10^{-12}$</td>
<td>21</td>
</tr>
<tr>
<td>n-C₃H₇O₂ + NO → n-C₃H₇ONO₂</td>
<td>$1.80 \times 10^{-13}$</td>
<td>21</td>
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<tr>
<td>(CH₃)₂CHO₂ + NO → (CH₃)₂CHO + NO₂</td>
<td>$2.70 \times 10^{-12} \exp(-360/T)$</td>
<td>21</td>
</tr>
<tr>
<td>(CH₃)₂CHO₂ + NO → (CH₃)₂CHONO₂</td>
<td>$3.80 \times 10^{-13}$</td>
<td>21</td>
</tr>
<tr>
<td>n-C₃H₇O₂ + HO₂ → n-C₃H₇OOH + O₂</td>
<td>$1.90 \times 10^{-13} \exp(-130/T)$</td>
<td>21</td>
</tr>
<tr>
<td>(CH₃)₂CHO₂ + HO₂ → (CH₃)₂CHOOH + O₂</td>
<td>$1.90 \times 10^{-13} \exp(-130/T)$</td>
<td>23</td>
</tr>
<tr>
<td>n-C₃H₇O + O₂ → C₂H₅CHO + HO₂</td>
<td>$6.00 \times 10^{-14} \exp(-550/T)$</td>
<td>21</td>
</tr>
<tr>
<td>(CH₃)₂CHO + O₂ → CH₃COCH₃ + HO₂</td>
<td>$1.50 \times 10^{-14} \exp(-200/T)$</td>
<td>21</td>
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<tr>
<td>n-C₃H₇ → C₂H₄ + CH₃</td>
<td>$1.20 \times 10^{13} \exp(-15300/T)$ s⁻¹</td>
<td>20</td>
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<tr>
<td>n-C₃H₇ → C₃H₆ + H</td>
<td>$1.09 \times 10^{13} \exp(-17800/T)$ s⁻¹</td>
<td>20</td>
</tr>
<tr>
<td>n-C₃H₇ + H₂ → C₃H₈ + H</td>
<td>$3.25 \times 10^{14} (T/300)^{2.84} \exp(-4600/T)$</td>
<td>20</td>
</tr>
</tbody>
</table>
n-C₃H₇ + H → C₃H₆ + H₂  \quad 3.00 \times 10^{-12}  

n-C₃H₇ + OH → C₃H₆ + H₂O \quad 4.00 \times 10^{-11}  

n-C₃H₇ + OH → n-C₃H₇OH \quad 4.00 \times 10^{-11}  

n-C₃H₇ + HO₂ → C₂H₅ + OH + HCHO \quad 4.00 \times 10^{-11}  

n-C₃H₇ + H₂O₂ → HO₂ + C₃H₈ \quad 5.23 \times 10^{-15} (T/300)^{2.11} \exp(-1290/T)  

n-C₃H₇ + CH₄ → C₃H₈ + CH₃ \quad 3.63 \times 10^{-16} (T/300)^{4.2} \exp(-5470/T)  

n-C₃H₇ + C₂H₆ → C₃H₈ + C₂H₅ \quad 1.22 \times 10^{-15} (T/300)^{3.82} \exp(-4550/T)  

n-C₃H₇ + HCHO → C₃H₈ + HCO \quad 7.63 \times 10^{-14} (T/300)^{2.9} \exp(-2950/T)  

n-C₃H₇ + HCO → C₃H₈ + CO \quad 1.00 \times 10^{-10}  

n-C₃H₇ + HCO → C₃H₇CHO \quad 2.00 \times 10^{-11}  

n-C₃H₇ + CH₃ → CH₄ + C₃H₆ \quad 3.06 \times 10^{-12} (T/300)^{-0.32}  

n-C₃H₇ + C₂H₅ → C₃H₈ + C₂H₄ \quad 1.90 \times 10^{-12}  

n-C₃H₇ + C₃H₈ → C₃H₈ + i-C₃H₇ \quad 1.13 \times 10^{-17} (T/300)^{4} \exp(-2380/T)  

n-C₃H₇ + n-C₃H₇ → C₃H₆ + C₃H₈ \quad 2.80 \times 10^{-12}  

n-C₃H₂O → C₂H₅ + HCHO \quad 5.01 \times 10^{13} \exp(-785/T) \text{s}^{-1}  

i-C₃H₇ → C₃H₆ + H \quad 1.60 \times 10^{13} \exp(-18000/T) \text{s}^{-1}  

i-C₃H₇ + H₂ → C₃H₈ + H \quad 7.73 \times 10^{-14} (T/300)^{3.28} \exp(-4360/T)  

i-C₃H₇ + H → C₃H₆ + H₂ \quad 6.00 \times 10^{-12}  

i-C₃H₇ + OH → C₃H₆ + H₂O \quad 4.00 \times 10^{-11}  

i-C₃H₇ + HO₂ → CH₃CHO + CH₃ + OH \quad 4.00 \times 10^{-11}  

i-C₃H₇ + H₂O₂ → C₃H₈ + HO₂ \quad 4.92 \times 10^{-15} (T/300)^{2.83} \exp(-2040/T)  

i-C₃H₇ + C₂H₆ → C₃H₈ + C₂H₅ \quad 3.55 \times 10^{-16} (T/300)^{4.2} \exp(-4390/T)  

i-C₃H₇ + HCHO → C₃H₈ + HCO \quad 1.80 \times 10^{-13} \exp(-3500/T)  

i-C₃H₇ + HCO → C₃H₈ + CO \quad 2.00 \times 10^{-10}  

i-C₃H₇ + HCO → C₃H₇CHO \quad 3.00 \times 10^{-11}  

i-C₃H₇ + CH₃ → CH₄ + C₃H₆ \quad 7.52 \times 10^{-12} (T/300)^{-0.68}  

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<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
<th>Temperature Exponent</th>
</tr>
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<tbody>
<tr>
<td>$i$-$C_3H_7 + C_2H_5 \rightarrow C_3H_8 + C_2H_4$</td>
<td>$4.16 \times 10^{-12}$</td>
<td>$(T/300)^{-0.35}$</td>
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<tr>
<td>$i$-$C_3H_7 + C_2H_5 \rightarrow C_3H_6 + C_2H_6$</td>
<td>$5.20 \times 10^{-12}$</td>
<td>$(T/300)^{-0.35}$</td>
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<tr>
<td>$i$-$C_3H_7 + C_2H_4 \rightarrow C_3H_6 + C_2H_5$</td>
<td>$4.40 \times 10^{-14}$</td>
<td>$\exp(-3320/T)$</td>
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<tr>
<td>$i$-$C_3H_7 + C_3H_8 \rightarrow C_3H_8 + n$-$C_3H_7$</td>
<td>$3.55 \times 10^{-16}$</td>
<td>$(T/300)^{4.2} \exp(-4390/T)$</td>
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<tr>
<td>$i$-$C_3H_7 + n$-$C_3H_7 \rightarrow C_3H_6 + C_3H_8$</td>
<td>$1.16 \times 10^{-11}$</td>
<td>$(T/300)^{-0.35}$</td>
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<td>$i$-$C_3H_7 + i$-$C_3H_7 \rightarrow C_3H_6 + C_3H_8$</td>
<td>$6.50 \times 10^{-12}$</td>
<td>$(T/300)^{-0.7}$</td>
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<tr>
<td>$CH_4 + H \rightarrow CH_3 + H_2$</td>
<td>$1.01 \times 10^{-12}$</td>
<td>$(T/300)^3 \exp(-4410/T)$</td>
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<td>$CH_4 + HO_2 \rightarrow CH_3 + H_2O_2$</td>
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<td>$\exp(-9350/T)$</td>
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<tr>
<td>$C_2H_6 + H \rightarrow C_2H_5 + H_2$</td>
<td>$4.03 \times 10^{-12}$</td>
<td>$(T/300)^{-2.1} \exp(-3510/T)$</td>
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<tr>
<td>$C_2H_6 + O \rightarrow C_2H_5 + OH$</td>
<td>$2.91 \times 10^{-12}$</td>
<td>$(T/300)^{2.25} \exp(-2520/T)$</td>
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<tr>
<td>$C_2H_6 + OH \rightarrow C_2H_5 + H_2O$</td>
<td>$1.62 \times 10^{-12}$</td>
<td>$(T/300)^{1.81} \exp(-533/T)$</td>
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<tr>
<td>$CH_3 + H_2 \rightarrow CH_4 + H$</td>
<td>$2.61 \times 10^{-14}$</td>
<td>$(T/300)^{-2.77} \exp(-3990/T)$</td>
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<tr>
<td>$CH_3 + O_2 \rightarrow HCHO + OH$</td>
<td>$1.60 \times 10^{-15}$</td>
<td>$(T/300)^{-2.5} \exp(-1110/T)$</td>
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<tr>
<td>$CH_3 + OH \rightarrow CH_3OH$</td>
<td>$1.15 \times 10^{-08}$</td>
<td>$(T/300)^{-4.4} \exp(-1260/T)$</td>
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<tr>
<td>$CH_3 + OH \rightarrow CH_2OH + H$</td>
<td>$1.25 \times 10^{-5}$</td>
<td>$(T/300)^{-5.0} \exp(-8260/T)$</td>
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<tr>
<td>$CH_3 + H_2O_2 \rightarrow CH_4 + HO_2$</td>
<td>$2.00 \times 10^{-14}$</td>
<td>$\exp(-300/T)$</td>
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<tr>
<td>$CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5$</td>
<td>$9.79 \times 10^{-17}$</td>
<td>$(T/300)^{5.64} \exp(-2830/T)$</td>
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<tr>
<td>$CH_3 + HCHO \rightarrow CH_4 + HCO$</td>
<td>$1.87 \times 10^{-15}$</td>
<td>$(T/300)^{4.85} \exp(-1750/T)$</td>
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<tr>
<td>$CH_3 + CO \rightarrow CH_3CO$</td>
<td>$1.98 \times 10^{-10}$</td>
<td>$(T/300)^{-8.3} \exp(-5270/T)$</td>
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<tr>
<td>$CH_3 + HCO \rightarrow CH_4 + CO$</td>
<td>$2.00 \times 10^{-10}$</td>
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<tr>
<td>$CH_3 + HCO \rightarrow CH_3CHO$</td>
<td>$3.00 \times 10^{-11}$</td>
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</tr>
<tr>
<td>$CH_3 + N \rightarrow H + H + HCN$</td>
<td>$3.32 \times 10^{-13}$</td>
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</table>
\[ \text{CH}_3 + \text{N} \rightarrow \text{HCN} + \text{H}_2 \quad 8.59 \times 10^{-12} \quad 21 \]
\[ \text{CH}_3 + \text{NO}_2 \rightarrow \text{CH}_3\text{NO}_2 \quad 3.44 \times 10^{-11} \left(\frac{T}{300}\right)^{-0.6} \quad 21 \]
\[ \text{CH}_3 + \text{NO}_2 \rightarrow \text{HCHO} + \text{HNO} \quad 5.39 \times 10^{-12} \quad 21 \]
\[ \text{CH}_3 + \text{NO}_2 \rightarrow \text{CH}_3\text{ONO} \quad 1.16 \times 10^{-13} \quad 21 \]
\[ \text{CH}_3 + \text{NO}_2 \rightarrow \text{CH}_3\text{O} + \text{NO} \quad 2.50 \times 10^{-11} \quad 21 \]
\[ \text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_4 + \text{H} \quad 4.44 \times 10^{12} \left(\frac{T}{300}\right)^{1.2} \exp(-18700/T) \quad 12 \]
\[ \text{C}_2\text{H}_5 + \text{H}_2 \rightarrow \text{C}_2\text{H}_6 + \text{H} \quad 4.22 \times 10^{-15} \left(\frac{T}{300}\right)^{3.6} \exp(-4250/T) \quad 12 \]
\[ \text{C}_2\text{H}_5 + \text{O}_2 \rightarrow \text{C}_2\text{H}_4 + \text{HO}_2 \quad 1.40 \times 10^{-12} \exp(-1950/T) \quad 12 \]
\[ \text{C}_2\text{H}_5 + \text{O}_2 \rightarrow \text{C}_2\text{H}_5\text{O}_2 \quad 7.66 \times 10^{-10} \left(\frac{T}{300}\right)^{5.12} \exp(-1490/T) \quad 12 \]
\[ \text{C}_2\text{H}_5 + \text{O}_2 \rightarrow \text{CH}_3\text{CHO} + \text{OH} \quad 1.14 \times 10^{-13} \left(\frac{T}{300}\right)^{-0.12} \exp(-4280/T) \quad 12 \]
\[ \text{C}_2\text{H}_5 + \text{H} \rightarrow \text{C}_2\text{H}_6 \quad 1.66 \times 10^{-10} \quad 12 \]
\[ \text{C}_2\text{H}_5 + \text{H} \rightarrow \text{CH}_3 + \text{CH}_3 \quad 6.05 \times 10^{-10} \left(\frac{T}{300}\right)^{-1.4} \exp(-659/T) \quad 12 \]
\[ \text{C}_2\text{H}_5 + \text{H} \rightarrow \text{C}_2\text{H}_4 + \text{H}_2 \quad 3.00 \times 10^{-12} \quad 12 \]
\[ \text{C}_2\text{H}_5 + \text{O} \rightarrow \text{CH}_3\text{CHO} + \text{H} \quad 1.33 \times 10^{-10} \quad 12 \]
\[ \text{C}_2\text{H}_5 + \text{O} \rightarrow \text{HCHO} + \text{CH}_3 \quad 2.67 \times 10^{-11} \quad 12 \]
\[ \text{C}_2\text{H}_5 + \text{OH} \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O} \quad 4.00 \times 10^{-11} \quad 12 \]
\[ \text{C}_2\text{H}_5 + \text{OH} \rightarrow \text{CH}_3 + \text{H} + \text{HCHO} \quad 4.00 \times 10^{-11} \quad 12 \]
\[ \text{C}_2\text{H}_5 + \text{HO}_2 \rightarrow \text{CH}_3 + \text{HCHO} + \text{OH} \quad 4.00 \times 10^{-11} \quad 12 \]
\[ \text{C}_2\text{H}_5 + \text{HO}_2 \rightarrow \text{C}_2\text{H}_6 + \text{O}_2 \quad 5.00 \times 10^{-13} \quad 12 \]
\[ \text{C}_2\text{H}_5 + \text{HO}_2 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O}_2 \quad 5.00 \times 10^{-13} \quad 12 \]
\[ \text{C}_2\text{H}_5 + \text{H}_2\text{O}_2 \rightarrow \text{C}_2\text{H}_6 + \text{HO}_2 \quad 1.45 \times 10^{-14} \exp(-490/T) \quad 12 \]
\[ \text{C}_2\text{H}_5 + \text{HCHO} \rightarrow \text{C}_2\text{H}_6 + \text{HCHO} \quad 8.33 \times 10^{-14} \left(\frac{T}{300}\right)^{2.81} \exp(-2950/T) \quad 12 \]
\[ \text{C}_2\text{H}_5 + \text{HCO} \rightarrow \text{C}_2\text{H}_6 + \text{CO} \quad 2.00 \times 10^{-10} \quad 12 \]
\[ \text{C}_2\text{H}_5 + \text{HCO} \rightarrow \text{C}_2\text{H}_5\text{CHO} \quad 3.00 \times 10^{-11} \quad 12 \]
\[ \text{C}_2\text{H}_5 + \text{CH}_3 \rightarrow \text{C}_3\text{H}_8 \quad 4.70 \times 10^{-11} \left(\frac{T}{300}\right)^{-0.5} \quad 12 \]
\[ \text{C}_2\text{H}_5 + \text{CH}_3 \rightarrow \text{CH}_4 + \text{C}_2\text{H}_4 \quad 1.88 \times 10^{-12} \left(\frac{T}{300}\right)^{-0.5} \quad 12 \]
\[ \text{C}_2\text{H}_5 + \text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_4 + \text{C}_2\text{H}_6 \quad 2.30 \times 10^{-12} \quad 12 \]
\begin{align*}
C_2H_4 + H & \rightarrow C_2H_5 & 6.87 \times 10^{-12} \left(\frac{T}{300}\right)^{1.49} \exp(-499/T) & 12 \\
C_2H_4 + H & \rightarrow C_2H_3 + H_2 & 4.07 \times 10^{-12} \left(\frac{T}{300}\right)^{2.53} \exp(-6160/T) & 12 \\
C_2H_4 + O & \rightarrow CH_3 + HCO & 1.52 \times 10^{-12} \left(\frac{T}{300}\right)^{1.55} \exp(-215/T) & 12 \\
C_2H_4 + O & \rightarrow CH_2CHO + H & 6.24 \times 10^{-13} & 12 \\
C_2H_4 + O & \rightarrow CH_2CO + H_2 & 3.81 \times 10^{-14} & 12 \\
C_2H_4 + O & \rightarrow C_2H_3 + OH & 1.33 \times 10^{-12} \left(\frac{T}{300}\right)^{1.91} \exp(-1880/T) & 12 \\
C_2H_4 + OH & \rightarrow C_2H_3 + H_2O & 1.69 \times 10^{-13} \left(\frac{T}{300}\right)^{2.75} \exp(-2100/T) & 12 \\
C_2H_4 + OH & \rightarrow C_2H_4OH & 9.00 \times 10^{-12} & 12 \\
C_2H_4 + HO_2 & \rightarrow CH_3CHO + OH & 1.00 \times 10^{-14} \exp(-4000/T) & 12 \\
C_2H_3 + H_2 & \rightarrow C_2H_4 + H & 1.64 \times 10^{-13} \left(\frac{T}{300}\right)^{2.63} \exp(-4300/T) & 12 \\
C_2H_3 + O_2 & \rightarrow C_2H_2 + HO_2 & 2.00 \times 10^{-13} & 12 \\
C_2H_3 + H & \rightarrow C_2H_2 + H_2 & 1.60 \times 10^{-10} & 12 \\
C_2H_3 + O & \rightarrow CH_2CO + H & 1.60 \times 10^{-10} & 12 \\
C_2H_3 + OH & \rightarrow H_2O + C_2H_2 & 5.00 \times 10^{-11} & 12 \\
C_2H_3 + OH & \rightarrow CH_3CHO & 5.00 \times 10^{-11} & 12 \\
C_2H_3 + HO_2 & \rightarrow OH + CH_3 + CO & 5.00 \times 10^{-11} & 12 \\
C_2H_3 + H_2O_2 & \rightarrow C_2H_4 + HO_2 & 2.00 \times 10^{-14} \exp(-300/T) & 12 \\
C_2H_3 + CH_4 & \rightarrow C_2H_4 + CH_3 & 2.18 \times 10^{-14} \left(\frac{T}{300}\right)^{4.02} \exp(-2750/T) & 12 \\
C_2H_3 + C_2H_6 & \rightarrow C_2H_4 + C_2H_5 & 1.50 \times 10^{-13} \left(\frac{T}{300}\right)^{3.3} \exp(-5290/T) & 12 \\
C_2H_3 + HCHO & \rightarrow C_2H_4 + HCO & 8.22 \times 10^{-14} \left(\frac{T}{300}\right)^{2.81} \exp(-2950/T) & 12 \\
C_2H_3 + CO & \rightarrow C_2H_3CO & 2.50 \times 10^{-13} \exp(-2420/T) & 12 \\
C_2H_3 + HCO & \rightarrow C_2H_4 + CO & 1.50 \times 10^{-10} & 12 \\
C_2H_3 + HCO & \rightarrow C_2H_3CHO & 3.00 \times 10^{-11} & 12 \\
C_2H_3 + CH_3 & \rightarrow C_2H_2 + CH_4 & 3.40 \times 10^{-11} & 12 \\
C_2H_3 + CH_3 & \rightarrow C_3H_6 & 1.20 \times 10^{-10} & 12 \\
C_2H_3 + C_2H_5 & \rightarrow C_2H_4 + C_2H_4 & 8.00 \times 10^{-13} & 12 \\
C_2H_3 + C_2H_5 & \rightarrow C_2H_2 + C_2H_6 & 8.00 \times 10^{-13} & 12
\end{align*}
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
<th>Notes</th>
</tr>
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<tbody>
<tr>
<td>( \text{C}_2\text{H}_3 + \text{C}_2\text{H}_3 \rightarrow \text{C}_2\text{H}_4 + \text{C}_2\text{H}_2 )</td>
<td>( 1.60 \times 10^{-12} )</td>
<td>12</td>
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<tr>
<td>( \text{C}_2\text{H}_2 + \text{O} \rightarrow \text{CH}_2 + \text{CO} )</td>
<td>( 5.15 \times 10^{-12} )</td>
<td>( (T/300)^{1.17} \exp(-1070/T) ) 12</td>
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<td>( \text{C}_2\text{H}_2 + \text{O} \rightarrow \text{C}_2\text{H}_4 + \text{H} )</td>
<td>( 1.50 \times 10^{-11} )</td>
<td>( \exp(-2290/T) ) 12</td>
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<td>( \text{C}_2\text{H}_2 + \text{OH} \rightarrow \text{C}_2\text{H} + \text{H}_2\text{O} )</td>
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<td>( (T/300)^{2.68} \exp(-6060/T) ) 12</td>
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<td>( \text{C}_2\text{H}_2 + \text{HO}_2 \rightarrow \text{CH}_2\text{CO} + \text{OH} )</td>
<td>( 1.00 \times 10^{-14} )</td>
<td>( \exp(-4000/T) ) 12</td>
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<td>( \text{C}_2\text{H}_2 + \text{CH}_3 \rightarrow \text{C}_3\text{H}_5 )</td>
<td>( 1.00 \times 10^{-12} )</td>
<td>( \exp(-3880/T) ) 12</td>
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<td>( \text{C}_2\text{H}_2 + \text{OH} \rightarrow \text{C}_2\text{H}_2\text{OH} )</td>
<td>( 8.50 \times 10^{-12} )</td>
<td>( \exp(-705/T) ) 12</td>
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<td>( 1.90 \times 10^{-11} )</td>
<td>( \exp(-1450/T) ) 12</td>
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<td>( \text{C}_2\text{H} + \text{O}_2 \rightarrow \text{CO} + \text{HCO} )</td>
<td>( 4.00 \times 10^{-12} )</td>
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<td>( \text{C}_2\text{H} + \text{O}_2 \rightarrow \text{C}_2\text{HO} + \text{O} )</td>
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<td>( 3.00 \times 10^{-10} )</td>
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<td>( \text{C}_2\text{H} + \text{O} \rightarrow \text{CH} + \text{CO} )</td>
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<td>( \text{C}_2\text{H} + \text{OH} \rightarrow \text{C}_2\text{H}_2 + \text{O} )</td>
<td>( 3.00 \times 10^{-11} )</td>
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<td>( \text{C}_2\text{H} + \text{OH} \rightarrow \text{CH}_2 + \text{CO} )</td>
<td>( 3.00 \times 10^{-11} )</td>
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<td>( \text{C}_2\text{H} + \text{HO}_2 \rightarrow \text{C}_2\text{H}_2 + \text{O}_2 )</td>
<td>( 3.00 \times 10^{-11} )</td>
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<td>( \text{C}_2\text{H} + \text{HO}_2 \rightarrow \text{C}_2\text{HO} + \text{OH} )</td>
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<td>( \text{C}_2\text{H} + \text{CH}_4 \rightarrow \text{C}_2\text{H}_2 + \text{CH}_3 )</td>
<td>( 3.00 \times 10^{-12} )</td>
<td>( \exp(-250/T) ) 12</td>
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<td>( \text{C}_2\text{H} + \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_2 + \text{C}_2\text{H}_5 )</td>
<td>( 6.00 \times 10^{-12} )</td>
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<tr>
<td>( \text{C}_2\text{H} + \text{CO} \rightarrow \text{C}_2\text{HCO} )</td>
<td>( 2.50 \times 10^{-13} )</td>
<td>( \exp(-2420/T) ) 12</td>
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<tr>
<td>( \text{C}_2\text{H} + \text{HCO} \rightarrow \text{C}_2\text{H}_2 + \text{CO} )</td>
<td>( 1.00 \times 10^{-10} )</td>
<td>12</td>
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<tr>
<td>( \text{C}_2\text{H} + \text{CH}_3 \rightarrow \text{C}_3\text{H}_3 + \text{H} )</td>
<td>( 4.00 \times 10^{-11} )</td>
<td>12</td>
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<tr>
<td>( \text{C}_2\text{H} + \text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_2 + \text{C}_2\text{H}_4 )</td>
<td>( 3.00 \times 10^{-12} )</td>
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<tr>
<td>( \text{C}_2\text{H} + \text{C}_2\text{H}_5 \rightarrow \text{C}_3\text{H}_3 + \text{CH}_3 )</td>
<td>( 3.00 \times 10^{-11} )</td>
<td>12</td>
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<td>( \text{C}_2\text{H} + \text{C}_2\text{H}_3 \rightarrow \text{C}_2\text{H}_2 + \text{C}_2\text{H}_2 )</td>
<td>( 1.60 \times 10^{-12} )</td>
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<tr>
<td>( \text{C}_2\text{H} + \text{C}_2\text{H} \rightarrow \text{C}_2\text{H}_2 + \text{C}_2 )</td>
<td>( 3.00 \times 10^{-12} )</td>
<td>12</td>
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<tr>
<td>( \text{CH}_3\text{CO} + \text{M} \rightarrow \text{CH}_3 + \text{CO} + \text{M} )</td>
<td>( 6.44 \times 10^{-3} )</td>
<td>( (T/300)^{8.62} \exp(-11300/T) ) 12</td>
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<tr>
<td>( \text{CH}_3\text{CO} + \text{O}_2 \rightarrow \text{CH}_3\text{COO}_2 )</td>
<td>( 3.00 \times 10^{-12} )</td>
<td>12</td>
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</table>
\begin{align*}
\text{CH}_3\text{CO} + H & \rightarrow \text{CH}_3 + \text{HCO} \quad 1.60 \times 10^{-10} \quad 12 \\
\text{CH}_3\text{CO} + O & \rightarrow \text{CH}_3 + \text{CO}_2 \quad 1.60 \times 10^{-11} \quad 12 \\
\text{CH}_3\text{CO} + \text{OH} & \rightarrow \text{CH}_2\text{CO} + \text{H}_2\text{O} \quad 2.00 \times 10^{-11} \quad 12 \\
\text{CH}_3\text{CO} + \text{OH} & \rightarrow \text{CH}_3 + \text{CO} + \text{OH} \quad 5.00 \times 10^{-11} \quad 12 \\
\text{CH}_3\text{CO} + \text{HO}_2 & \rightarrow \text{CH}_3 + \text{CO}_2 + \text{OH} \quad 5.00 \times 10^{-11} \quad 12 \\
\text{CH}_3\text{CO} + \text{H}_2\text{O}_2 & \rightarrow \text{CH}_3\text{CHO} + \text{HO}_2 \quad 3.00 \times 10^{-11} \quad 12 \\
\text{CH}_3\text{CO} + \text{HCO} & \rightarrow \text{CH}_3\text{CHO} + \text{CO} \quad 1.50 \times 10^{-11} \quad 12 \\
\text{CH}_3\text{CO} + \text{HCO} & \rightarrow \text{CH}_3\text{COCHO} \quad 3.00 \times 10^{-11} \quad 12 \\
\text{CH}_3\text{CO} + \text{CH}_3 & \rightarrow \text{CH}_3\text{COCH}_3 \quad 6.70 \times 10^{-9} \quad (T/300)^{-0.8} \quad 12 \\
\text{CH}_3\text{CO} + \text{C}_2\text{H}_5 & \rightarrow \text{C}_2\text{H}_5\text{COCH}_3 \quad 5.19 \times 10^{-10} \quad 12 \\
\text{CH}_3\text{CO} + \text{C}_2\text{H}_3 & \rightarrow \text{CH}_3 + \text{CH}_2\text{CHCO} \quad 3.00 \times 10^{-11} \quad 12 \\
\text{CH}_3\text{CO} + \text{C}_2\text{H} & \rightarrow \text{C}_2\text{HCO} + \text{CH}_3 \quad 3.00 \times 10^{-11} \quad 12 \\
\text{CH}_3\text{O}_2 + \text{H} & \rightarrow \text{CH}_3\text{O} + \text{OH} \quad 1.60 \times 10^{-10} \quad 12 \\
\text{CH}_3\text{O}_2 + \text{O} & \rightarrow \text{CH}_3\text{O} + \text{O}_2 \quad 6.00 \times 10^{-11} \quad 12 \\
\text{CH}_3\text{O}_2 + \text{OH} & \rightarrow \text{CH}_3\text{OH} + \text{O}_2 \quad 1.00 \times 10^{-10} \quad 12 \\
\text{CH}_3\text{O}_2 + \text{HO}_2 & \rightarrow \text{CH}_3\text{OOH} + \text{OH} \quad 7.70 \times 10^{-14} \quad \exp(-1300/T) \quad 12 \\
\text{CH}_3\text{O}_2 + \text{H}_2\text{O}_2 & \rightarrow \text{CH}_3\text{OOH} + \text{HO}_2 \quad 4.00 \times 10^{-12} \quad \exp(-5000/T) \quad 12 \\
\text{CH}_3\text{O}_2 + \text{HCO} & \rightarrow \text{CH}_3\text{O} + \text{H} + \text{CO}_2 \quad 5.00 \times 10^{-11} \quad 12 \\
\text{CH}_3\text{O}_2 + \text{CH}_3 & \rightarrow \text{CH}_3\text{O} + \text{CH}_3\text{O} \quad 4.00 \times 10^{-11} \quad 12 \\
\text{CH}_3\text{O}_2 + \text{C}_2\text{H}_5 & \rightarrow \text{CH}_3\text{O} + \text{C}_2\text{H}_5\text{O} \quad 4.00 \times 10^{-11} \quad 12 \\
\text{CH}_3\text{O}_2 + \text{C}_2\text{H}_3 & \rightarrow \text{CH}_3\text{O} + \text{C}_2\text{H}_3\text{O} \quad 4.00 \times 10^{-11} \quad 12 \\
\text{CH}_3\text{O}_2 + \text{C}_2\text{H} & \rightarrow \text{CH}_3\text{O} + \text{C}_2\text{HO} \quad 4.00 \times 10^{-11} \quad 12 \\
\text{CH}_3\text{O}_2 + \text{CH}_3\text{CO} & \rightarrow \text{CH}_3 + \text{CO}_2 + \text{CH}_3\text{O} \quad 4.00 \times 10^{-11} \quad 12 \\
\text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2 & \rightarrow \text{CH}_3\text{O} + \text{CH}_3\text{O} + \text{O}_2 \quad 1.30 \times 10^{-13} \quad 12 \\
\text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2 & \rightarrow \text{CH}_3\text{OH} + \text{HCHO} + \text{O}_2 \quad 2.10 \times 10^{-13} \quad 12 \\
\text{CH}_3\text{O}_2 + \text{NO} & \rightarrow \text{CH}_3\text{O} + \text{NO}_2 \quad 4.20 \times 10^{-12} \quad \exp(-180/T) \quad 12 \\
\text{CH}_3\text{O} + \text{O}_2 & \rightarrow \text{HCHO} + \text{HO}_2 \quad 1.10 \times 10^{-13} \quad \exp(-1310/T) \quad 12
\end{align*}
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
<th>Temperature Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CH}_3\text{O} + \text{H} \rightarrow \text{HCHO} + \text{H}_2$</td>
<td>$3.30 \times 10^{-11}$</td>
<td>12</td>
</tr>
<tr>
<td>$\text{CH}_3\text{O} + \text{O} \rightarrow \text{HCHO} + \text{OH}$</td>
<td>$1.00 \times 10^{-11}$</td>
<td>12</td>
</tr>
<tr>
<td>$\text{CH}_3\text{O} + \text{OH} \rightarrow \text{HCHO} + \text{OH}$</td>
<td>$3.00 \times 10^{-11}$</td>
<td>12</td>
</tr>
<tr>
<td>$\text{CH}_3\text{O} + \text{HO}_2 \rightarrow \text{HCHO} + \text{H}_2\text{O}_2$</td>
<td>$5.00 \times 10^{-13}$</td>
<td>12</td>
</tr>
<tr>
<td>$\text{CH}_3\text{O} + \text{CH}_4 \rightarrow \text{CH}_3\text{OH} + \text{CH}_3$</td>
<td>$2.60 \times 10^{-13} \exp(-4450/T)$</td>
<td>12</td>
</tr>
<tr>
<td>$\text{CH}_3\text{O} + \text{C}_2\text{H}_6 \rightarrow \text{CH}_3\text{OH} + \text{C}_2\text{H}_5$</td>
<td>$4.00 \times 10^{-13} \exp(-3570/T)$</td>
<td>12</td>
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<tr>
<td>$\text{CH}_3\text{O} + \text{HCHO} \rightarrow \text{CH}_3\text{OH} + \text{HCO}$</td>
<td>$1.70 \times 10^{-13} \exp(-1500/T)$</td>
<td>12</td>
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<tr>
<td>$\text{CH}_3\text{O} + \text{CO} \rightarrow \text{CH}_3 + \text{CO}_2$</td>
<td>$2.60 \times 10^{-11} \exp(-5940/T)$</td>
<td>12</td>
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<tr>
<td>$\text{CH}_3\text{O} + \text{HCO} \rightarrow \text{CH}_3\text{OH} + \text{CO}$</td>
<td>$1.50 \times 10^{-10}$</td>
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</tr>
<tr>
<td>$\text{CH}_3\text{O} + \text{CH}_3 \rightarrow \text{HCHO} + \text{CH}_4$</td>
<td>$4.00 \times 10^{-11}$</td>
<td>12</td>
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<tr>
<td>$\text{CH}_3\text{O} + \text{CH}_3 \rightarrow \text{CH}_3\text{OCH}_3$</td>
<td>$2.00 \times 10^{-11}$</td>
<td>12</td>
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<tr>
<td>$\text{CH}_3\text{O} + \text{C}_2\text{H}_5 \rightarrow \text{HCHO} + \text{C}_2\text{H}_6$</td>
<td>$4.00 \times 10^{-11}$</td>
<td>12</td>
</tr>
<tr>
<td>$\text{CH}_3\text{O} + \text{C}_2\text{H}_3 \rightarrow \text{HCHO} + \text{C}_2\text{H}_4$</td>
<td>$4.00 \times 10^{-11}$</td>
<td>12</td>
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<tr>
<td>$\text{CH}_3\text{O} + \text{C}_2\text{H} \rightarrow \text{HCHO} + \text{C}_2\text{H}_2$</td>
<td>$4.00 \times 10^{-11}$</td>
<td>12</td>
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<tr>
<td>$\text{CH}_3\text{O} + \text{CH}_3\text{CO} \rightarrow \text{CH}_3\text{OH} + \text{CH}_2\text{CO}$</td>
<td>$1.00 \times 10^{-11}$</td>
<td>12</td>
</tr>
<tr>
<td>$\text{CH}_3\text{O} + \text{CH}_3\text{O} \rightarrow \text{HCHO} + \text{CH}_3\text{CHO}$</td>
<td>$1.00 \times 10^{-11}$</td>
<td>12</td>
</tr>
<tr>
<td>$\text{CH}_3\text{O} + \text{CH}_3\text{O}_2 \rightarrow \text{HCHO} + \text{CH}_3\text{OOH}$</td>
<td>$5.00 \times 10^{-13}$</td>
<td>12</td>
</tr>
<tr>
<td>$\text{CH}_3\text{O} + \text{CH}_3\text{O} \rightarrow \text{CH}_3\text{OH} + \text{HCHO}$</td>
<td>$1.00 \times 10^{-10}$</td>
<td>12</td>
</tr>
<tr>
<td>$\text{CH}_3\text{O} + \text{NO}_2 \rightarrow \text{CH}_3\text{ONO}_2$</td>
<td>$1.50 \times 10^{-11}$</td>
<td>21</td>
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<tr>
<td>$\text{CH}_3\text{O} + \text{NO}_2 \rightarrow \text{HCHO} + \text{HNO}_2$</td>
<td>$3.00 \times 10^{-13}$</td>
<td>21</td>
</tr>
<tr>
<td>$\text{CH}_3\text{O} + \text{NO} \rightarrow \text{CH}_3\text{ONO}$</td>
<td>$2.00 \times 10^{-11}$</td>
<td>21</td>
</tr>
<tr>
<td>$\text{CH}_3\text{O} + \text{NO} \rightarrow \text{HCHO} + \text{HNO}$</td>
<td>$4.00 \times 10^{-12} \left(T/300\right)^{-0.7}$</td>
<td>21</td>
</tr>
<tr>
<td>$\text{CH}_3\text{OH} + \text{O} \rightarrow \text{CH}_2\text{OH} + \text{OH}$</td>
<td>$4.63 \times 10^{-14} \left(T/300\right)^{3.77} \exp(-340/T)$</td>
<td>22</td>
</tr>
<tr>
<td>$\text{CH}_3\text{OH} + \text{O} \rightarrow \text{CH}_3\text{O} + \text{OH}$</td>
<td>$7.08 \times 10^{-13} \left(T/300\right)^{1.54} \exp(-1000/T)$</td>
<td>22</td>
</tr>
<tr>
<td>$\text{CH}_3\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{CH}_2\text{OH}$</td>
<td>$8.79 \times 10^{-13}$</td>
<td>22</td>
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<tr>
<td>$\text{CH}_3\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{CH}_3\text{O}$</td>
<td>$1.66 \times 10^{11} \exp(-854/T)$</td>
<td>22</td>
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<tr>
<td>$\text{CH}_3\text{OH} + \text{H} \rightarrow \text{CH}_2\text{OH} + \text{H}_2$</td>
<td>$1.39 \times 10^{11}$</td>
<td>22</td>
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<tr>
<td>Chemical Reaction</td>
<td>Rate Constant</td>
<td>Comments</td>
</tr>
<tr>
<td>--------------------------------------------------------</td>
<td>---------------</td>
<td>-----------------------------------</td>
</tr>
<tr>
<td>$\text{CH}_3\text{OH} + \text{H} \rightarrow \text{CH}_3\text{O} + \text{H}_2$</td>
<td>$6.64 \times 10^{-11} \exp(-3070/T)$</td>
<td>22</td>
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<tr>
<td>$\text{C}_2\text{H}_5 + \text{NO} \rightarrow \text{C}_2\text{H}_5\text{NO}$</td>
<td>$6.49 \times 10^{-11} \left(\frac{T}{300}\right)^{-3.37} \exp(-1740/T)$</td>
<td>21</td>
</tr>
<tr>
<td>$\text{C}_3\text{H}_6 + \text{O} \rightarrow \text{Methyl Oxirane}$</td>
<td>$9.05 \times 10^{-12} \exp(-610/T)$</td>
<td>23</td>
</tr>
<tr>
<td>$\text{C}_3\text{H}_6 + \text{O} \rightarrow \text{C}_2\text{H}_5\text{CHO}$</td>
<td>$9.05 \times 10^{-12} \exp(-610/T)$</td>
<td>23</td>
</tr>
<tr>
<td>$\text{C}_3\text{H}_6 + \text{O} \rightarrow \text{CH}_2\text{CHO} + \text{CH}_3$</td>
<td>$6.03 \times 10^{-12} \exp(-610/T)$</td>
<td>23</td>
</tr>
<tr>
<td>$\text{C}_3\text{H}_6 + \text{O} \rightarrow \text{C}_2\text{H}_5 + \text{HCO}$</td>
<td>$6.03 \times 10^{-12} \exp(-610/T)$</td>
<td>23</td>
</tr>
<tr>
<td>$\text{C}_3\text{H}_6 + \text{OH} \rightarrow \text{CH}_3\text{CHCH}_2\text{OH}$</td>
<td>$6.56 \times 10^{-11} \left(\frac{T}{300}\right)^{-1.48} \exp(-361/T)$</td>
<td>23</td>
</tr>
<tr>
<td>$\text{C}_3\text{H}_6 + \text{OH} \rightarrow \text{CH}_3\text{CHOHCH}_2$</td>
<td>$3.53 \times 10^{-11} \left(\frac{T}{300}\right)^{-1.48} \exp(-361/T)$</td>
<td>23</td>
</tr>
<tr>
<td>$\text{C}_3\text{H}_6 + \text{H} \rightarrow \text{CH}_3 + \text{C}_2\text{H}_4$</td>
<td>$1.20 \times 10^{-11} \exp(-655/T)$</td>
<td>8</td>
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<tr>
<td>$\text{C}_3\text{H}_6 + \text{H} \rightarrow \text{i-C}_3\text{H}_7$</td>
<td>$1.00 \times 10^{-11} \left(\frac{T}{300}\right)^{0.25} \exp(-593/T)$</td>
<td>8</td>
</tr>
<tr>
<td>$\text{CH}_3\text{CH(OH)CH}_2 + \text{O}_2 \rightarrow \text{CH}_3\text{CH(OH)CH}_2\text{OO}$</td>
<td>$3.90 \times 10^{-12}$</td>
<td>23</td>
</tr>
<tr>
<td>$\text{CH}_3\text{CH(OH)CH}_2\text{OH} + \text{O}_2 \rightarrow \text{CH}_3\text{CH(O)CH}_2\text{OH}$</td>
<td>$1.16 \times 10^{-11}$</td>
<td>23</td>
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<tr>
<td>$\text{CH}_2\text{OCH(OH)CH}_2\text{OH}$</td>
<td>$1.00 \times 10^{-14}$</td>
<td>23</td>
</tr>
<tr>
<td>$\text{CH}_3\text{CH(OH)CH}_2\text{OO} + \text{NO} \rightarrow \text{NO}_2 + \text{CH}_2\text{O}$</td>
<td>$3.90 \times 10^{-12}$</td>
<td>23</td>
</tr>
<tr>
<td>$\text{CH}_3\text{CH(OO)CH}_2\text{OH} + \text{NO} \rightarrow \text{NO}_2 + \text{CH}_2\text{OH}$</td>
<td>$1.00 \times 10^{-14}$</td>
<td>23</td>
</tr>
<tr>
<td>$\text{CH}_3\text{CH(OH)CH}_2\text{O} \rightarrow \text{HCHO} + \text{CH}_3\text{CHOH}$</td>
<td>$7.94 \times 10^{13} \exp(-10500/T)$ s$^{-1}$</td>
<td>23</td>
</tr>
<tr>
<td>$\text{CH}_3\text{CH(O)CH}_2\text{OH} + \text{M} \rightarrow \text{CH}_3\text{CHO} + \text{CH}_2\text{OH} + \text{M}$</td>
<td>$1.00 \times 10^{-11}$</td>
<td>23</td>
</tr>
<tr>
<td>$\text{CH}_2\text{OH} + \text{M} \rightarrow \text{CH}_3\text{CHO} + \text{HO}_2$</td>
<td>$1.00 \times 10^{-11}$</td>
<td>23</td>
</tr>
<tr>
<td>$\text{CH}_2\text{OH} + \text{O}_2 \rightarrow \text{HCHO} + \text{HO}_2$</td>
<td>$1.06 \times 10^{-10} \left(\frac{T}{300}\right)^{-1.58} \exp(-801/T)$</td>
<td>23</td>
</tr>
<tr>
<td>$\text{CH}_2\text{CHO} + \text{NO} \rightarrow \text{ONCH}_2\text{CHO}$</td>
<td>$2.51 \times 10^{-11}$</td>
<td>24</td>
</tr>
<tr>
<td>$\text{CH}_2\text{CHO} + \text{O}_2 \rightarrow \text{CHOCHO} + \text{OH}$</td>
<td>$2.20 \times 10^{-13}$</td>
<td>24</td>
</tr>
<tr>
<td>$\text{CH}_2\text{CHO} + \text{O}_2 \rightarrow \text{HCHO} + \text{CO} + \text{OH}$</td>
<td>$3.00 \times 10^{-14}$</td>
<td>24</td>
</tr>
<tr>
<td>$\text{CH}_2\text{CHO} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{CH}_2\text{CHO}$</td>
<td>$2.66 \times 10^{-11}$</td>
<td>24</td>
</tr>
</tbody>
</table>
Methyl Oxirane + OH → H₂O + Products  \(4.95 \times 10^{-13}\)  21
C₂H₆ + N → CH₃NCH₃  \(4.00 \times 10^{-16}\)  21
C₂H₅O₂ + NO → C₂H₂O + NO₂  \(8.90 \times 10^{-12}\)  21
C₂H₅O₂ + NO → C₂H₃ONO₂  \(1.30 \times 10^{-13}\)  21
C₂H₅O₂ + NO₂ → C₂H₅OONO₂  \(2.59 \times 10^{-10} (T/300)^{-3.74} \exp(-1030/T)\)  21
C₂H₅O₂ → C₂H₄ + HO₂  \(1.87 \times 10^{-13} (T/300)^{-0.6} \exp(15890/T) \text{ s}^{-1}\)  21
C₂H₅O + NO → C₂H₅ONO  \(2.63 \times 10^{-11}\)  21
C₂H₅O + NO → CH₃CHO + HNO  \(1.30 \times 10^{-11}\)  21
C₂H₅O + NO₂ → C₂H₃ONO₂  \(2.80 \times 10^{-11}\)  21
C₂H₅O + NO₂ → CH₃CHO + HNO₂  \(6.61 \times 10^{-12}\)  21
C₂H₄ + N → HCN + CH₃  \(2.46 \times 10^{-12} (T/300)^{-3.28} \exp(-1360/T)\)  21
CH₄ + N → HCN + H₂ + H  \(2.50 \times 10^{-14}\)  21
CH₃CHO + N → HCN + H₂ + HCO  \(1.99 \times 10^{-14}\)  21
CH₃CHO + NO₃ → HNO₃ + CH₃CO  \(2.73 \times 10^{-15}\)  21
CH₃COO₂ + NO → CH₃ + CO₂ + NO₂  \(2.00 \times 10^{-11}\)  21
CH₃COO₂ + NO → CH₃COO + NO₂  \(1.40 \times 10^{-11}\)  21
CH₃COO₂ + NO₂ → CH₃CO₃NO₂  \(1.75 \times 10^{-12} \exp(-393/T)\)  21
CH₃CO + NO → CH₃CONO  \(3.32 \times 10^{-13}\)  21
CH₃CO + NO₂ → CH₃ + CO₂ + NO  \(1.66 \times 10^{-12}\)  21
CH₃CO + NO₂ → CH₃COO + NO  \(2.50 \times 10^{-11}\)  21
CH₂OH + NO → CH₂OHNO  \(2.50 \times 10^{-11}\)  21
CH₂OH + NO₂ → HOCH₂NO₂  \(2.30 \times 10^{-11}\)  21
CH₂OH + O → HCHO + OH  \(1.50 \times 10^{-10}\)  21
CH₂OH + CH₃ → CH₄ + HCHO  \(4.00 \times 10^{-12}\)  22
CH₂OH + CH₃ → C₂H₅OH  \(2.00 \times 10^{-11}\)  22
CH₂CHO + NO₂ → CH₂CO + HNO₂  \(1.48 \times 10^{-11} \exp(-80/T)\)  21
CH₂ + NO → CONH₂  \(5.76 \times 10^{-12} \exp(-190/T)\)  21
\[
\begin{align*}
\text{CH}_2\text{CO} + \text{OH} & \rightarrow \text{CH}_2\text{OH} + \text{CO} & 1.08 \times 10^{-11} & \text{21} \\
\text{CH}_2\text{CO} + \text{OH} & \rightarrow \text{HCO} + \text{HCHO} & 4.65 \times 10^{-11} & \text{21} \\
\text{CH}_2\text{CO} + \text{H} & \rightarrow \text{CH}_3 + \text{CO} & 1.88 \times 10^{-11} \exp(-1730/T) & \text{21} \\
\text{CH} + \text{NO} & \rightarrow \text{CO} + \text{NH} & 2.50 \times 10^{-10} & \text{21} \\
\text{HCO} + \text{NO} & \rightarrow \text{CO} + \text{HNO} & 1.20 \times 10^{-11} & \text{21} \\
\text{HCO} + \text{NO}_2 & \rightarrow \text{H} + \text{CO}_2 + \text{NO} & 1.95 \times 10^{-10} (T/300)^{-0.75} \exp(-970/T) & \text{21} \\
\text{HCO} + \text{NO}_2 & \rightarrow \text{HCOO} + \text{NO} & 2.71 \times 10^{-11} & \text{21} \\
\text{HCO} + \text{NO}_2 & \rightarrow \text{CO} + \text{HNO}_2 & 8.73 \times 10^{-11} \exp(-319/T) & \text{21} \\
\text{CH}_3\text{ONO} & \rightarrow \text{HCHO} + \text{HNO} & 3.98 \times 10^{-13} \exp(-19400/T) & \text{21} \\
\text{HO}_2 + \text{NO}_2 & \rightarrow \text{HNO}_2 + \text{O}_2 & 1.20 \times 10^{-13} & \text{21} \\
\text{O} + \text{HNO}_2 & \rightarrow \text{NO}_2 + \text{OH} & 2.00 \times 10^{-11} \exp(-3000/T) & \text{21}
\end{align*}
\]

\(a\) Rate coefficients have units of cm\(^3\) s\(^{-1}\) unless stated otherwise. \(T_e\) is the electron temperature in eV.

\(b\) Computed using the electron energy distribution and electron impact cross section from cited reference.

\(c\) Estimated.

\(d\) Rate coefficients have units of cm\(^3\) s\(^{-1}\) unless stated otherwise. \(T\) is the gas temperature in K and activation energies have equivalent units of K.
B.1 References


VITA

Rajesh Dorai was born in Madras, India. He received his B. Tech. degree in Chemical Engineering from the Indian Institute of Technology, Madras, India, and his M.S. degree in Chemical Engineering from the University of Illinois at Urbana-Champaign. Under the direction of Professor Mark J. Kushner, he has studied atmospheric pressure plasma processing of gases and surfaces since January 1999. His work has resulted in 5 refereed journal publications and 10 conference presentations.