MODELING OF PLASMA REMEDIATION OF NO\textsubscript{x} USING GLOBAL KINETIC MODELS ACCOUNTING FOR HYDROCARBONS

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Increasing awareness of pollution and its harmful effects has led to the development of energy efficient methods for remediation. In this study, we have numerically quantified the feasibility of Dielectric Barrier Discharges (DBD) for the remediation of NO\textsubscript{x}. Reaction mechanisms for the hydrocarbon (propane and propene) and NO\textsubscript{x} system were formulated for diesel exhausts. Parameterizations were performed to determine the optimum operating conditions for NO\textsubscript{x} removal.

Remediation of NO\textsubscript{x} for automotive emissions should ideally produce N\textsubscript{2} and O\textsubscript{2} through reduction reactions. Most of the NO in DBDs is oxidized to NO\textsubscript{2}. In the presence of hydrocarbons, propene and propane, this conversion is increased. Some extra remediation of NO\textsubscript{x} is also observed with hydrocarbons through the formation of organic nitrates and nitrites. Increased energy deposition through the application of higher applied voltages, resulted in improved NO\textsubscript{x} remediation. Multiple pulse formats have been found to produce different end products. New reactions occur in latter pulses due to the reaction products from previous pulses. Simulation of multiple discharge formats yielded better agreement of the final product concentrations with the experimental data.
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1. INTRODUCTION

The continual release of toxic gases into the atmosphere from a variety of sources has resulted in the gradual degradation of the environment and this, in turn, has motivated investigations into new methods of reducing and, if possible, preventing these harmful emissions. Increasing awareness of these emissions has resulted in legislation requiring stringent enforcement of new regulations having the goal of improving the quality of environment.

Since 1970, Environment Protection Agency (EPA) has tracked emissions of six major air pollutants – CO, lead, nitrogen oxides (NO\textsubscript{x}), particulate matter, sulfur dioxide and volatile organic compounds\cite{1}. Emissions of these pollutants have significantly decreased except for NO\textsubscript{x} which has increased approximately 10% over this period. Reducing emissions of NO\textsubscript{x} is therefore critical for improving the quality of air in urban regions. Sources of NO\textsubscript{x} are shown in Fig. 1.1 and include non-utility boilers, reciprocating internal combustion engines, gas turbines, residential fuel combustion, cement manufacturing industries, ferrous metal processing, wood, pulp and paper manufacturing and agricultural chemical manufacturing industries. NO\textsubscript{x} in air is one of the main constituents in the formation of ground-level ozone, which can cause respiratory problems. NO\textsubscript{x} also reacts to form nitrate particles, acid aerosols, as well as NO\textsubscript{2}, which also cause respiratory problems. NO\textsubscript{x} also contributes to the formation of acid rain. Apart from being a greenhouse gas, NO\textsubscript{x} also acts as a precursor for the formation of atmospheric particles that cause reduced visibility. NO\textsubscript{x} also contributes to nutrient overload that deteriorates water quality.
These economic and health implications have motivated research into abatement techniques for NO\textsubscript{x} pollution. One of the methods which are being developed for the control of NO\textsubscript{x} is plasma processing. Plasma remediation of toxic gases is a major area of research both in industry and in academia. Plasma remediation of nitrogen oxides (NO and NO\textsubscript{2}), in particular, has been the object of many studies in the past decade [2-8].

Non-thermal plasma remediation of NO\textsubscript{x} is a highly efficient method in that the operation of the reactor is such that the input energy mostly goes into heating the electrons as opposed to increasing the gas temperature. The remediation technique is also feasible for operating a reactor at atmospheric pressure. Several types of reactors are used for the non-thermal plasma processing, including electron beam (e-beam) or electrical discharges.

In e-beam processing [2-3], electrons are accelerated down a high voltage gradient in vacuum before being injected through a thin foil window that serves as a vacuum seal. The high-energy electrons then collide with neutrals in an atmospheric-pressure chamber producing ions and radicals that trigger the process chemistry. Electrical discharge reactors are typically pulsed corona discharges and dielectric barrier discharges. Pulsed corona discharge reactors, shown schematically in Fig. 1.2, employ short pulses (10s-100s of ns) of high voltage (up to 30 kV) with kilohertz repetition rates, thereby creating short-lived discharges which produce the radicals responsible for the decomposition of the undesired molecules. The reactor consists of a point to plane or wire coaxial electrode configuration. These reactors are characterized by low gas temperatures (300 K) and high electron temperatures (3-6 eV). Several studies have been performed to evaluate these reactors for the plasma remediation of pollutant gases. [3-7].
Dielectric barrier discharge reactors (DBD’s), shown schematically in Fig. 1.3, 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. DBDs are known for their high-energy efficiency, reliability, and, more importantly, their low cost [8]. DBDs also have the added advantage of operating at high pressure (atmospheric and above) resulting in higher reaction rates and larger reactor throughputs.

Many studies have been performed to analyze the importance of reactor design, choice of packing material, voltage, frequency and gas composition on the removal of NO\textsubscript{x} from automotive exhausts [9-10]. The results indicate that voltage and frequency do not affect the overall energy efficiency in certain ranges of operation. However, gas composition and choice of packing material have been found to significantly change the process outputs. The possibility of using downstream or an upstream catalytic converters with plasma remediation has been investigated. The results indicate that with the plasma reactor upstream of the catalytic converter, more NO\textsubscript{x} conversion was achieved [11-12].

Computer modeling and simulation of the plasma remediation of toxic gases have been extensively performed and all studies point towards the positive role played by plasma process [13-16].

The present study applies a global kinetics model to the study of the plasma remediation of NO\textsubscript{x} with the goal of quantifying the effects of hydrocarbons in the gas stream. Hydrocarbons are unavoidably present in the emissions and have been found to play an important role in the reaction pathways [12,15,16]. With the improvement in the knowledge base for the underlying reactions that are responsible for the NO\textsubscript{x} chemistry, simulations have been able to more closely predict the actual process outputs and thus
have been very much useful in process design. Comparisons have been made to available experimental data wherever applicable. Several hydrocarbon species have been investigated to determine their role in the NO\textsubscript{x} remediation process. The global kinetics model is described in Chapter 2. The effects of energy deposition and initial gas temperature have been parameterized. The effect of varying the hydrocarbon concentration in the inlet gas stream on the remediation of NO\textsubscript{x} is discussed in Chapter 3. The results of the simulations with the inclusion of propane in the system are discussed in Chapter 4. Multiple pulsing of the plasma has been found to yield significantly different results which are discussed in Chapter 5. The list of species considered in simulations is included in Appendix A and their corresponding reactions are in Appendix B.

In general, it was found that with increasing energy deposition into the system, NO\textsubscript{x} remediation improved but the energy efficiency decreased. Increasing the amount of hydrocarbons in the inlet stream significantly affected the NO decomposition but the NO\textsubscript{x} conversion remained almost unaffected. Variation of the temperature of the reactor resulted in an initial improvement in NO\textsubscript{x} reduction but for temperatures greater than 400 K, the NO\textsubscript{x} conversion remained at an almost constant level. Comparison to experimental data has been performed wherever possible and the overall results indicate good agreement between modeling and experiments.
Fig 1.1 : Sources of NO\textsubscript{x} emissions [1]

Fig 1.2 : Schematic of the pulsed corona discharge reactor.
Fig. 1.3. Schematic of a typical Dielectric Barrier Discharge reactor
1.1 References


2. Frank, N.W., et al. (1986), “Integrated SO\textsubscript{x} and NO\textsubscript{x} removal process”, Integrated Environmental Control Symposium, Pittsburgh, Pa.

3. Fuch, P., et al. (1987), “Removal of SO\textsubscript{2} and NO\textsubscript{x} by electron beam process”, presented at the 6\textsuperscript{th} International Meeting on Radiation Processing, Ontario, Canada.


2. DESCRIPTION OF THE MODEL

2.1 Overview

The model used to study the volumetric plasma kinetics of NO$_x$ plasma remediation is a zero-dimensional, plug flow simulation where the spatial variations are not considered and the reactor is assumed to be completely mixed and homogenous. The generalized representation of the reaction mechanism is discussed in Section 2.2. Descriptions of the 0-D model, called GLOBAL_KIN, used to investigate NO$_x$ chemistry in propene and propane mixtures are in Section 2.3.

2.2 Reaction Network Equations

When dealing with a large number of reactions, it is beneficial to have a generalized reaction network equation that represents all the reactions. The generalized reaction network equation can be written as

$$\frac{dN_i}{dt} = \sum_{j=1}^{R} a_{ji} k_j \prod_{l=1}^{s} (N_l)^{b_{jl}},$$

where,

$\frac{dN_i}{dt}$ represents the rate of change of species density $N_i$ with respect to time,

$N_i$ represents the number density of species $i$ at any given time $t$,

$j$ spans reactions in the network,

$l$ spans the species in the system,

$k_j$ is the reaction rate coefficient of reaction $j$,

$R$ is the total number of reactions occurring in the system.
S is the total number of species participating in the reactions

\[ b_{jl} = 1 \text{ if species } l \text{ appears on the L.H.S of reaction } j \]
\[ = 0 \text{ otherwise} \]

\[ a_{jl} = 0 \text{ if species } l \text{ does not appear on the L.H.S of reaction } j, \]
\[ = -1 \text{ if species } l \text{ appears on the L.H.S of reaction } j, \]
\[ = +1 \text{ if species } l \text{ appears on the R.H.S of reaction } j. \]

2.3 Description of the Zero-Dimensional Model

GLOBAL_KIN consists of an offline Boltzmann solver module for the electron energy distribution, a circuit module and a plasma chemistry module. A schematic of the modules used in GLOBAL_KIN is in Fig. 2.1 and that for the device modeled is in Fig. 2.2.

In the 0-D model, a uniform concentration of species is assumed in the reactor. Since the quantities of interest, temperature, species densities, electric field/number density (E/N) in the plasma, are continually changing in the system with time, the rate equations representing these quantities have to be constantly updated. The plasma chemistry module performs the operations of setting up the differential equations for the time evolution of the various species in the reactor at different points in time. The circuit module provides the E/N in the plasma which is further used to obtain the rate coefficients of electron impact reactions based on the electron temperature. In order to do this, an offline lookup table is initially generated using the Boltzmann solver module for the representative gas composition and temperature. The entire set of differential equations for species densities along with the circuit equations are integrated over time to
obtain the temporal evolution of the species present in the reactor. This integration in
time is accomplished by using the LSODE/ODE solver [1]. The time steps chosen for
integration are such that they are much less compared to the dynamics of the system in
that time period and are allowed to vary with time. The magnitudes of the initial time
steps for recording results are chosen to be of the order of ns in order to capture the rapid
dynamics of the system in the initial phase. With time, the time-step at which results are
recorded is increased by a fixed multiplication factor.

For validation purposes, the initial conditions for the reactor were chosen to
closely match those for the experiments conducted at Ford Research Laboratories [2].
The following procedure was adopted in choosing reactions for the simulation. First, all
the reactions of species initially present in the reactor with the products of the electron
impact reactions are considered. Of these, only those reactions that occur at appreciable
rates at the conditions of operation are considered. Then, all the appreciable reactions of
the products of these reactions with all other species present in the system are considered
and this process is repeated until the products along every given pathway are found to be
stable. For the study of NO\textsubscript{x} processing in the absence of hydrocarbons, 76 electron
impact reactions and 360 heavy particle reactions are considered. With propene included,
the total number of reactions was 752 with the electron impact reactions remaining the
same. Including propane in the model added another 54 heavy particle reactions. The
reaction mechanism is given in Appendix B.
Temperature dependent reaction rate coefficients

Look-up Table of $k$ vs. $T_e$

Plasma Chemistry Module

Circuit Module

$N(t+\Delta t), V, I$

Offline Boltzmann Solver

Fig. 2.1  Block diagram of the model

Fig. 2.2  Schematic of the DBD modeled
2.4 References


3. EFFECT OF PROPENE ON THE CONVERSION OF NO\textsubscript{x}

3.1 Overview

Most of the previous studies of NO\textsubscript{x} remediation were performed with gas mixtures predominantly containing N\textsubscript{2}, O\textsubscript{2}, NO and one or more of NO\textsubscript{2} and H\textsubscript{2}O. In real exhausts, hydrocarbons are inevitably part of the emissions. The effect of ethene on the conversion of NO\textsubscript{x} in a dielectric barrier discharge reactor has been modeled by Niessen et. al. and the results indicate a significant role played by hydrocarbons in the overall reaction chemistry \cite{1}. Their findings showed that the energy requirement for NO remediation reduced from 60 eV/NO molecule to 10 eV/molecule when 2000 ppmv of C\textsubscript{2}H\textsubscript{4} (ethene) was added to the inlet gas. However, most of the NO that was converted went into forming NO\textsubscript{2}. Hence, it is important to consider the effect of hydrocarbons on the plasma remediation of NO\textsubscript{x}. In this chapter, results from GLOBAL_KIN with and without the inclusion of propene as a model hydrocarbon will be discussed. The reaction mechanisms for NO\textsubscript{x} in the absence of hydrocarbon are discussed in Section 3.2 and the effects of energy deposition are described in Section 3.3. The reaction mechanisms for NO\textsubscript{x} in the presence of propene are discussed in Section 3.4. The results of the parameterizations of energy density, inlet hydrocarbon concentration and reaction temperature are discussed in Section 3.5, Section 3.6 and Section 3.7 respectively. The conclusions are given in Section 3.8.

3.2 Reaction Mechanisms in NO\textsubscript{x} Remediation in the Absence of C\textsubscript{3}H\textsubscript{6}

It is beneficial to study NO\textsubscript{x} processing in the absence of hydrocarbons to provide a base-case for comparison. Hence, simulations were initially performed with gas mixtures
containing N₂, NO, H₂O, O₂, CO and CO₂ (See Table 3.1). In the absence of propene, the reaction mechanism for NOₓ remediation is given in Fig. 3.1. The initial compounds and major end products are in bold. The reactor is operated at atmospheric pressure and at a temperature of 453 K (180 °C). The gas gap is 2.5 mm unless otherwise indicated. All the results presented in this chapter are for a single discharge pulse. In order to validate model against experimental data, simulations were performed with the initial conditions of the experiments conducted at Ford Research Laboratories. It is known that, for the typical operating conditions of dielectric barrier discharge reactors, radical reactions dominate over ionic reactions for remediation. However, the ion reactions have been included for completeness. During the initial current pulse period [0-100 ns], electron impact reactions produce radicals. Important electron impact reactions include,

$$e + O₂ \rightarrow O + O + e \quad [\text{3.1}]$$

$$e + N₂ \rightarrow N + N + e \quad [\text{3.2}]$$

$$e + H₂O \rightarrow OH + H + e \quad [\text{3.3}]$$

As regards NO, there are two main pathways for effective removal,

$$\text{NO} + \text{N} \rightarrow \text{N}_2 + \text{O}, \quad k = 3.41 \times 10^{-11} \exp\left(-\frac{24}{T}\right) \text{cm}^3 \text{s}^{-1} \quad [\text{3.4}]$$

$$\text{NO} + \text{O} + \text{M} \rightarrow \text{NO}_2 + \text{M}, \quad k = 1.03 \times 10^{-30} \left(\frac{T}{300}\right)^{-2.87} \exp\left(-\frac{781}{T}\right) \text{cm}^6 \text{s}^{-1} \quad [\text{3.5a}]$$

$$\text{NO}_2 + \text{OH} + \text{M} \rightarrow \text{HNO}_3 + \text{M}, \quad k = 4.62 \times 10^{-29} \left(\frac{T}{300}\right)^{-5.49} \exp\left(-\frac{1183}{T}\right) \text{cm}^6 \text{s}^{-1} \quad [\text{3.5b}]$$

Reaction 3.4 is a reduction and 3.5(a) and 3.5(b) are oxidation channels. Though reaction 3.4 is the most preferred of the three with respect to plasma remediation of automotive emissions, it is the one that occurs with the lowest probability because the concentration
of O atoms are at least an order of magnitude higher than N atoms. This is because the bond energy in O$_2$ is smaller to that in N$_2$. O$_2$ has a double bond and N$_2$ has a triple bond, which is stronger. For example, the concentrations of O and N atoms in a typical DBD are shown in Fig. 3.2. The concentrations of O atoms are at least an order of magnitude greater in comparison with N atoms at the conditions of interest. Hence reaction 3.5(a) occurs with a higher rate as compared to reaction 3.4. Reaction 3.5(b) cannot be avoided since OH radicals are produced due to electron impact dissociation of H$_2$O. Depending on the nature of the NO$_x$ source, different channels may be preferred for plasma remediation. For stationary sources such as coal-fired power plants, production of HNO$_3$ could be an acceptable option, since the effluent can then be treated with base solutions to produce salts and water which then can be easily removed. For mobile sources, Reaction 3.4 is more favorable as the harmful gas is converted into pure N$_2$. The products of the reduction reaction would result in the generation of ozone (O$_3$) through the reaction with O$_2$.

\[
O + O_2 + M \rightarrow O_3 + M, \quad k = 6.90\times10^{-34} \left( \frac{T}{300} \right)^{-1.25} \text{cm}^3\text{s}^{-1} \quad [3.6]
\]

Ozone by itself participates in the NO remediation through the reaction,

\[
O_3 + NO \rightarrow NO_2 + O_2, \quad k = 4.3\times10^{-12} \exp\left( -\frac{1598}{T} \right) \text{cm}^3\text{s}^{-1} \quad [3.7]
\]

Since NO$_x$ includes NO and NO$_2$, conversion of NO to NO$_2$ does not result in its remediation. Hence, NO$_2$ is also an unwanted byproduct of this processing.

The time evolution of electrons, ions and certain radicals are shown for a typical current pulse in Fig. 3.3. Electron densities peak at around 100 ns wherein the circuit is switched off. Near around the point where the electron densities peak, one also sees a
rise in the concentration of the radicals, O and OH in the system. These radicals then react with other species in the system to initiate the plasma chemistry.

3.3 Effect of Input Energy Density on the Remediation of NO\textsubscript{x} in the Absence of C\textsubscript{3}H\textsubscript{6}

The energy input to the system is typically varied by the voltage applied to the DBD reactor. The variation in the NO, NO\textsubscript{2} and NO\textsubscript{x} levels after 0.2 seconds is shown in Fig. 3.4 for a single discharge pulse in the absence of propene for various input energies. At the highest energy deposition (60 J/L), only about 20 ppm of NO\textsubscript{x} is removed while 130 ppm of NO is remediated. The remaining NO removed is mostly converted into NO\textsubscript{2}. Acids such as HNO\textsubscript{2} and HNO\textsubscript{3} are also produced, though in smaller quantities (=15 ppm) compared to NO\textsubscript{2} or NO\textsubscript{x}. In the absence of propene, about 10% of NO\textsubscript{x} is remediated at 60 J/L whereas the NO conversion is around 50%. As will be discussed in later chapters, the effect of multiple discharges pulse could significantly alter the product distribution by changing the composition of the gas during the inter pulse-period. The presence of CO\textsubscript{2} in the system, through e-impact dissociation, produces CO.

\[
e + \text{CO}_2 \rightarrow \text{CO} + \text{O}^- \quad [3.8]
\]

\[
e + \text{CO}_2 \rightarrow \text{CO} + \text{O} + \text{e} \quad [3.9]
\]

The production levels of CO as a function of energy input are shown in Fig. 3.5. In the absence of propene, as much as 60 ppm of CO is produced with the maximum energy input of 60 J/L.

The energy efficiency of the process is measured in terms of W-values [eV/molecule NO\textsubscript{x} remediated]. Higher W-values indicate lesser efficient processes. The W-values for
the NO\textsubscript{x} remediation in the absence of propene are shown in Fig. 3.6. At lower values of energy deposition, the W-value for NO\textsubscript{x} is 520 eV/molecule and for NO is 80 eV/molecule. Although higher energy deposition results in increased NO\textsubscript{x} remediation, the processes become less efficient. At high energy inputs \([60 \text{ J/L}]\), W-values are as high as 770 eV/molecule NO\textsubscript{x} and 190 eV/molecule NO.

3.4 Reaction Mechanisms for NO\textsubscript{x} in the Presence of Propene

In presence of a hydrocarbon (propene), the reaction mechanism has additional pathways as shown in Fig. 3.7. The channel that has a major influence on NO remediation is initiated by the reaction of propene with OH. OH is dominantly produced either by electron impact of \(H_2O\) or by the reaction of \(O(^1D)\) with \(H_2O\).

\[
O(^1D) + H_2O \rightarrow OH + OH \quad k = 2.2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \quad [3.10]
\]

The reaction of OH with propene results in the formation of \(\beta\)-hydroxyalkyl radicals (\(CH_3CHCH_2OH, CH_3CH(OH)CH_2\)) which then react rapidly with \(O_2\) to form the \(\beta\)-hydroxylalkyl peroxy radicals (\(CH_3CH(OO)CH_2OH, CH_3CH(OH)CH_2OO\)). The peroxy radicals are the major reactants as they react with NO to form NO\textsubscript{2}. The resulting alkoxy radicals (\(CH_3CH(O)CH_2OH, CH_3CH(OH)CH_2O\)) can then undergo reaction with \(O_2\), decompose or isomerize. It has been experimentally observed that decomposition of alkoxy radicals is the dominant process of the three channels \([2,3]\). The decomposition of alkoxy radicals results in the production of \(\alpha\)-hydroxyl alkyl radicals and aldehydes namely, formaldehyde (HCHO) and acetaldehyde (CH\textsubscript{3}CHO). The \(\alpha\)-hydroxy alkyl radicals react with \(O_2\) to again produce aldehydes and HO\textsubscript{2} radical. Propene is also subject to attack by \(O(^3P)\). Products of this reaction include methyl oxirane,
propionaldehyde (C₂H₅CHO), ethyl radical (C₂H₅), methyl (CH₃) and vinoxy (CH₂CHO) radical. Inclusion of these species initiate other reactions such as,

\[ \text{CH}_3 + \text{O}_2 + \text{M} \rightarrow \text{CH}_3\text{O}_2 + \text{M}, \quad k = 7.56 \times 10^{-31} \left( \frac{T}{300} \right)^{3.64} \text{cm}^6 \text{s}^{-1} \quad [3.11] \]

\[ \text{CH}_2\text{CHO} + \text{O}_2 \rightarrow \text{CHO-CHO} + \text{OH} \quad k = 2.2 \times 10^{-13} \text{cm}^3 \text{s}^{-1} \quad [3.12] \]

\[ \text{CH}_2\text{CHO} + \text{O}_2 \rightarrow \text{HCHO} + \text{CO} + \text{OH} \quad k = 3.0 \times 10^{-14} \text{cm}^3 \text{s}^{-1} \quad [3.13] \]

3.5 Effect of Varying Input Energy Density on the Conversion of NO\textsubscript{x} in the Presence of Propene

The effect of input energy in the presence of propene was investigated. The same gas composition given in Table 3.1 was used with 500 ppm of propene. Species densities after 0.2 s as a function of input energy are shown in Fig. 3.8(a) and the results indicate a significant change in the final NO\textsubscript{x} conversion. NO conversion is almost 100% at higher energy inputs [60 J/L]. However, a major portion of the converted NO goes into forming NO\textsubscript{2} thereby limiting the total NO\textsubscript{x} conversion. As much as 60 ppm of NO\textsubscript{x} is remediated at an energy input of 60 J/L. The removed NO\textsubscript{x} is mainly converted to nitrous acid (HNO₂), nitric acid (HNO₃) and 2-nitroso ethanal (ONCH₂CHO) and to some smaller extent, nitrogen. The final NO and NO\textsubscript{x} conversions with and without propene are summarized in Fig. 3.8(b). NO\textsubscript{x} remediation is nearly tripled [6.4% to 18.6%] with propene as compared to the case with no propene at an energy deposition of 30 J/L. There is a larger difference in the NO conversion levels. At 60 J/L, NO conversion is 99.6% with propene as compared to 50% without propene, primarily due to the reaction of NO with the peroxy radical to form NO\textsubscript{2}. The efficiency of the
remediation process is shown in terms of W-values in Fig. 3.9. The W-value for NO\textsubscript{x} remediation decreases from 770 eV/molecule NO\textsubscript{x} without propene to 325 eV/molecule NO\textsubscript{x} with propene, and for NO remediation, the reduction is from 190 eV/molecule NO to 90 eV/molecule.

The time integrated contributions from each of the reactions for the production and consumption of NO are shown in Fig. 3.10. NO is mainly remediated through the reactions,

\begin{align*}
\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH} & \quad k = 3.7 \times 10^{-12} \exp\left( \frac{240}{T} \right) \text{cm}^3 \text{s}^{-1} \quad [3.14] \\
\text{CH}_3\text{CH(OH)CH}_2\text{OO} + \text{NO} \rightarrow \text{CH}_3\text{CH(OH)CH}_2\text{O} + \text{NO}_2 & \quad [3.15] \\
& \quad k_{3.15} = 2.7 \times 10^{-12} \exp\left( \frac{360}{T} \right) \text{cm}^3 \text{s}^{-1} \quad [3.15a] \\
\text{CH}_3\text{CH(OO)CH}_2\text{OH} + \text{NO} \rightarrow \text{CH}_3\text{CH(O)CH}_2\text{OH} + \text{NO}_2 & \quad [3.16] \\
& \quad k_{3.16} = 2.7 \times 10^{-12} \exp\left( \frac{360}{T} \right) \text{cm}^3 \text{s}^{-1} \quad [3.16a]
\end{align*}

The inclusion of propene increases the generation of CO. This is expected since CO is the end product of many hydrocarbon induced reactions such as,

\begin{align*}
\text{HCO} + \text{O}_2 \rightarrow \text{CO} + \text{HO}_2, & \quad k = 8.5 \times 10^{-11} \exp\left( -\frac{850}{T} \right) \text{cm}^3 \text{s}^{-1} \quad [3.17] \\
\text{CH}_2\text{CHO} + \text{O}_2 \rightarrow \text{HCHO} + \text{CO} + \text{OH}, & \quad k = 3.0 \times 10^{-14} \text{cm}^3 \text{s}^{-1} \quad [3.18]
\end{align*}

The individual contributions of the major CO producing and consuming reactions are shown in Fig. 3.11. The majority of CO is produced by reactions 3.9 and 3.17.

The end product concentrations as a function of input energy density are shown in Fig. 3.12. The density of formaldehyde [HCHO] saturates at higher energy inputs ( > 40
In the initial stages of the process [0-200 ns], HCHO is primarily produced by the reaction of O atoms with methyl (CH$_3$) and ethyl radicals (C$_2$H$_5$).

CH$_3$ + O → HCHO + H, \hspace{1cm} k = 1.4 \times 10^{-10} \text{ cm}^3 \text{s}^{-1} \hspace{1cm} [3.19]

C$_2$H$_5$ + O → HCHO + CH$_3$, \hspace{1cm} k = 2.67 \times 10^{-10} \text{ cm}^3 \text{s}^{-1} \hspace{1cm} [3.20]

The production of radicals such as CH$_3$O and CH$_2$CHO induce new channels for the formation of HCHO.

CH$_3$O + O → HCHO + OH, \hspace{1cm} k = 1.0 \times 10^{-11} \left( \frac{T}{300} \right)^{0.5} \text{ cm}^3 \text{s}^{-1} \hspace{1cm} [3.21]

CH$_3$O + O$_2$ → HCHO + HO$_2$, \hspace{1cm} k = 1.1 \times 10^{-13} \exp \left( -\frac{1310}{T} \right) \text{ cm}^3 \text{s}^{-1} \hspace{1cm} [3.22]

CH$_3$O + OH → HCHO + H$_2$O, \hspace{1cm} k = 3.0 \times 10^{-11} \left( \frac{T}{300} \right)^{0.5} \text{ cm}^3 \text{s}^{-1} \hspace{1cm} [3.23]

CH$_3$O + CH$_3$O → CH$_3$OH + HCHO, \hspace{1cm} k = 1.0 \times 10^{-10} \left( \frac{T}{300} \right)^{0.7} \text{ cm}^3 \text{s}^{-1} \hspace{1cm} [3.24]

CH$_3$O + NO → HCHO + HNO, \hspace{1cm} k = 4.0 \times 10^{-12} \left( \frac{T}{300} \right)^{0.7} \text{ cm}^3 \text{s}^{-1} \hspace{1cm} [3.25]

CH$_2$CHO + O$_2$ → HCHO + CO + OH, \hspace{1cm} k = 3.0 \times 10^{-14} \text{ cm}^3 \text{s}^{-1} \hspace{1cm} [3.26]

With the formation of CH$_2$OH and CH$_3$CH(OH)CH$_2$O, new pathways for the production of HCHO are introduced.

CH$_2$OH + O$_2$ → HCHO + HO$_2$, \hspace{1cm} k = 1.06 \times 10^{-10} \left( \frac{T}{300} \right)^{-1.58} \exp \left( -\frac{801.2}{T} \right) \text{ cm}^3 \text{s}^{-1} \hspace{1cm} [3.27]

CH$_3$CH(OH)CH$_2$O → CH$_3$CHOH + HCHO, \hspace{1cm} k = 7.94 \times 10^{13} \exp \left( -\frac{10520}{T} \right) \text{s}^{-1} \hspace{1cm} [3.28]

The main pathway for the consumption of HCHO is the reaction of HCHO with OH.
HCHO + OH $\rightarrow$ HCO + H2O,  \( k = 4.74 \times 10^{-12} \left( \frac{T}{300} \right)^{1.18} \exp \left( \frac{225}{T} \right) \text{cm}^3 \text{s}^{-1} \) \[3.29\]

HCHO removal also occurs by the reaction of HCHO with O.

HCHO + O $\rightarrow$ HCO + OH,  \( k = 2.99 \times 10^{-11} \exp \left( -\frac{1543}{T} \right) \text{cm}^3 \text{s}^{-1} \) \[3.30\]

This reaction accounts for about 12% of the overall consumption of HCHO, whereas the reaction with OH contributes to around 87% of the total removal. The contributions from the various reactions towards the production and consumption of HCHO are shown in Fig. 3.13.

With increasing energy deposition, more OH and HO\(_2\) are produced. The reaction of NO with HO\(_2\) accounts for a major portion of the NO remediated.

\[
\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}
\] \[3.31\]

Hence, as more energy is deposited, the amount of NO available for reaction with the peroxy radicals decreases and so, CH\(_2\)OH, CH\(_3\)CH(OH)CH\(_2\)O and CH\(_3\)CHO, which are the products of the peroxy-initiated reactions, are generated in smaller quantities.

\[
\text{CH}_3\text{CH(OH)CH}_2\text{OO} + \text{NO} \rightarrow \text{CH}_3\text{CH(CH(OH)CH}_2\text{O} + \text{NO}_2
\] \[3.15\]

\[
\text{CH}_3\text{CH(O)CH}_2\text{OH} + \text{M} \rightarrow \text{CH}_2\text{OH} + \text{CH}_3\text{CHO} + \text{M}, \quad k_{3,32} = 1.0 \times 10^{-11} \text{cm}^3 \text{s}^{-1}
\] \[3.32\]

Hence, one sees a reduction in the production level of acetaldehyde in the system. However, the same is not the case with HCHO, since the channels for the formation of HCHO are more numerous compared to CH\(_3\)CHO. With increasing energy deposition, the reactions of O radicals with the first generation products (CH\(_3\), CH\(_3\)O) are accelerated due to the increased production of these radicals. This increase in the formation of HCHO keeps the final production almost a constant at higher energy inputs in spite of the...
decrease in its formation from CH$_2$OH. As a result one sees a saturation in the production of HCHO. With increase in energy deposition, more HCHO is produced by channels B, C, D and F. However, the contributions from the major reactions channels, E and G, decrease with increasing energy deposition, this decrease being more than the increase due to the channels B, C, D and F.

3.6 Effect of Varying Inlet Hydrocarbon Concentration on the Conversion of NO$_x$

One of the key factors that determine the NO conversion to NO$_2$ is the quantity of the peroxy radical. This is in turn dependent on the amount of propene. Simulations were performed with the same base gas composition shown in Table 3.2 and the base case operating conditions while varying the propene concentration with the input energy fixed at 18.7 J/L.

The variation in NO, NO$_2$, NO$_x$, HNO$_2$, HNO$_3$ concentrations following 0.2 seconds as a function of inlet propene concentration are shown in Fig. 3.14(a). Increasing the inlet hydrocarbon has little effect on the NO$_x$ conversion though the effects on NO conversion and NO$_2$ production are noticeable. Increasing the inlet hydrocarbon results in increased production of the peroxy radicals which then convert more NO to NO$_2$ while keeping the NO$_x$ unchanged. Increasing the inlet hydrocarbon also produces more rapid reactions of O and OH with the hydrocarbons as compared to the reactions with other competing species. Therefore, the availability of the radicals for reactions with non-hydrocarbon species becomes more limited. This is shown in the concentrations of HNO$_2$ and HNO$_3$ that result from the reaction of OH with NO$_x$. The decrease in concentration of acids is due to the depletion of OH. The fractional remediation of NO$_x$
and conversion of \( \text{C}_3\text{H}_6 \) are shown in Fig. 3.14(b) as a function of inlet \( \text{C}_3\text{H}_6 \). The radicals that are involved in the initial reactions with propene are produced in fixed amounts with fixed energy deposition and hence these are the rate-limiting species. Therefore, higher concentrations of propene in feed result in lower percentages of conversion. NO remediation increases due to the increased production of peroxy radicals. CO production almost remains the same. CO is produced mainly by the electron impact dissociation of \( \text{CO}_2 \) and by the reactions with hydrocarbons [Reactions 3.9 and 3.13].

Although the hydrocarbons are present in higher quantities, the rate limiting reactions are constrained by the radicals. The end-product concentrations as a function of inlet hydrocarbon concentration are shown in Fig. 3.15. As anticipated, increases in the inlet hydrocarbon results in increased production of the final products. Major end products include acetaldehyde (\( \text{CH}_3\text{CHO} \)), methyl oxirane and formaldehyde. Acetaldehyde and methyl oxirane are produced mainly by,

\[
\text{C}_3\text{H}_6 + \text{O} \rightarrow \text{Methyl Oxirane} \quad [3.33]
\]

\[
\text{CH}_3\text{CHOH} + \text{O}_2 \rightarrow \text{CH}_3\text{CHO} + \text{HO}_2 
\quad [3.34]
\]

\( W \)-values are shown as a function of inlet propene concentration in Fig. 3.16. With more propene in the inlet, the efficiency of the process decreases since more NO is converted to \( \text{NO}_2 \) by the hydrocarbon. However, the efficiency for NO remediation increases. At 1100 ppm of propene, the \( W \)-value for \( \text{NO}_x \) is 240 eV/molecule and that for NO is 30 eV/molecule.
3.7 Effect of Reactor Temperature on the Conversion of NO\textsubscript{x} in the Presence of Propene

The gas temperature has an important effect on the reaction characteristics through the Arrhenius dependence of reaction rate coefficients.

\[
k = A \left( \frac{T}{300} \right)^n \exp \left( -\frac{E_a}{T} \right)
\]

where,

\(k\) = reaction rate constant,

\(A\) = frequency factor,

\(T\) = temperature of the gas,

\(E_a\) = activation energy in K.

Simulations were performed to quantify the effect of temperature on NO\textsubscript{x} remediation. All the results discussed in this section are for the inlet gas mixture in Table 3.1 with 500 ppm of propene and an energy deposition of 30.9 J/L. Product concentrations are shown in Fig 3.17 as a function of initial temperature. Increasing temperature has little effect on total NO\textsubscript{x} conversion, although the effect on NO and NO\textsubscript{2} is quite significant. This is because the rate coefficients for the reaction of the peroxy radicals with NO increases with temperature. Therefore, at higher temperatures more NO gets converted into NO\textsubscript{2}. The maxima in the concentrations of HNO\textsubscript{2} and HNO\textsubscript{3} are a result of the inherent complex non-linear kinetics associated with the temperature dependence of the reaction rate coefficients. The main reactions responsible for the production of HNO\textsubscript{2} are,

\[
\text{NO} + \text{OH} + \text{M} \rightarrow \text{HNO}_2 + \text{M}, \quad k = 7.4 \times 10^{-31} \left( \frac{T}{300} \right)^{2.4} \text{cm}^3 \text{s}^{-1}
\]
\[
\text{HO}_2 + \text{NO}_2 \rightarrow \text{HNO}_2 + \text{O}_2, \quad k = 1.2 \times 10^{-13} \left( \frac{T}{300} \right)^{0.5} \text{cm}^3 \text{s}^{-1} \quad [3.37]
\]

Consumption of HNO\textsubscript{2} mainly occurs by the reaction with OH,

\[
\text{OH} + \text{HNO}_2 \rightarrow \text{NO}_2 + \text{H}_2\text{O}, \quad k = 1.8 \times 10^{-11} \exp \left( -\frac{390}{T} \right) \text{cm}^3 \text{s}^{-1} \quad [3.38]
\]

On the whole, increasing temperature reduces the production of HNO\textsubscript{2} and HNO\textsubscript{3}. The conversion levels of NO, propene and NO\textsubscript{x} are shown in Fig. 3.18. At higher temperatures, a larger proportion of propene is converted due to the overall positive temperature dependence of the propene-initiated reactions.

\[
\text{C}_3\text{H}_6 + \text{OH} \rightarrow \text{Products}, \quad k = 4.86 \times 10^{-12} \left( \frac{T}{300} \right)^{0.5} \exp \left( +\frac{504}{T} \right) \text{cm}^3 \text{s}^{-1} \quad [3.39]
\]

\[
\text{C}_3\text{H}_6 + \text{O} \rightarrow \text{Products}, \quad k = 1.25 \times 10^{-12} \left( \frac{T}{300} \right)^{2.15} \exp \left( +\frac{400}{T} \right) \text{cm}^3 \text{s}^{-1} \quad [3.40]
\]

Of the two reactions 3.39 and 3.40, \( k_{3.39} \) decreases with increasing temperature and \( k_{3.40} \) increases with increasing temperature. Also, at the temperatures of interest, \( k_{3.40} > k_{3.39} \). Since the concentration of O radicals is greater than [OH], the rate of reaction 3.40 is greater than the rate of the reaction 3.39. Hence, with an increase in temperature, there is an increased consumption of propene. Increasing amounts of CO are also produced, again due to the increased production of the radicals at higher temperatures.

\[
\text{CH}_2\text{CHO} + \text{O}_2 \rightarrow \text{HCHO} + \text{CO} + \text{OH}, \quad k = 3.0 \times 10^{-14} \left( \frac{T}{300} \right)^{0.5} \text{cm}^3 \text{s}^{-1} \quad [3.41]
\]

NO conversion increases at higher temperatures due to the increased production of the peroxies, though the NO converted mostly goes into forming NO\textsubscript{2}, keeping the level of NO\textsubscript{x} unaltered. The effect of temperature on the concentration of end products is
summarized in Fig. 3.19. In general, more aldehydes are produced. The increased rate of the initiator reaction with propene by O increases the production of oxirane and ONCH₂CHO. In general, higher temperatures result in the formation of a conducive environment for the breakdown of NO, but this breakdown unfortunately results in the production of NO₂ rather than in the conversion to N₂, nitric or nitrous acids.

3.8 Concluding Remarks

Hydrocarbons play a significant role in modifying the overall reaction chemistry of NOₓ. There is a significant change in NOₓ conversion when including the effects of hydrocarbons. Increasing energy deposition with gas mixtures containing hydrocarbons showed increased conversion levels of NOₓ. Typical products with propene include formaldehyde, acetaldehyde, propionaldehyde, methyl oxirane, glyoxal and CO. Increasing the hydrocarbon concentration resulted in decreased conversion levels of hydrocarbons for the same input energy density. However, NOₓ conversion remained the same when the inlet propene concentration was varied. With increasing reactor temperatures, NOₓ conversion remained at an almost constant level. However, NO conversion and NO₂ production levels increased with increase in temperature. End products generally showed an increase in concentration with increasing reactor temperature.
### Table 3.1  Inlet concentration of species for the DBD reactor

<table>
<thead>
<tr>
<th>Species</th>
<th>Inlet Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
<td>8%</td>
</tr>
<tr>
<td>CO₂</td>
<td>7%</td>
</tr>
<tr>
<td>H₂O</td>
<td>6%</td>
</tr>
<tr>
<td>CO</td>
<td>400 ppm</td>
</tr>
<tr>
<td>NO</td>
<td>260 ppm</td>
</tr>
<tr>
<td>H₂</td>
<td>133 ppm</td>
</tr>
<tr>
<td>N₂</td>
<td>Balance</td>
</tr>
</tbody>
</table>

### Table 3.2  Inlet concentration of species for the DBD reactor with hydrocarbons added

<table>
<thead>
<tr>
<th>Species</th>
<th>Inlet Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
<td>8%</td>
</tr>
<tr>
<td>CO₂</td>
<td>7%</td>
</tr>
<tr>
<td>H₂O</td>
<td>6%</td>
</tr>
<tr>
<td>CO</td>
<td>400 ppm</td>
</tr>
<tr>
<td>NO</td>
<td>260 ppm</td>
</tr>
<tr>
<td>H₂</td>
<td>133 ppm</td>
</tr>
<tr>
<td>C₃H₆</td>
<td>0-1100 ppm</td>
</tr>
<tr>
<td>N₂</td>
<td>Balance</td>
</tr>
</tbody>
</table>
Fig. 3.1  Simplified reaction mechanism for NO$_x$ in the absence of propene

Fig. 3.2  Time evolution of O, OH and N during the DBD processing of NO$_x$
Fig. 3.3 Time evolution of $e$, $N_2^+$, O and OH radicals during the DBD processing of NO$_x$.

Fig. 3.4 NO, NO$_2$, NO$_x$, HNO$_3$, HNO$_2$ as a function of input energy density following 0.2 seconds.
Fig. 3.5 CO production with and without propene as a function of input energy.

Fig. 3.6 W-Values for NO\textsubscript{x} and NO removal in the absence of propene as a function of input energy density
Fig. 3.7 Reaction mechanisms for NO$_x$ in the presence of propene
Fig. 3.8(a) Effect of varying energy deposition on NO, NO$_2$, NO$_x$ and propene in the plasma processing of NO$_x$.

Fig. 3.8(b) Comparison of NO and NO$_x$ conversion levels with and without the introduction of propene in the inlet gas stream.
Fig. 3.9 Variation of W-Values for NO$_x$ and NO as a function of input energy for the plasma remediation of NO$_x$ in the presence of propene
Fig. 3.10 Time integrated contribution of reactions for the generation and consumption of NO

A  NO + HO₂ → NO₂ + OH
B  NO + OH + M → HNO₂ + M
C  NO + O₃ → NO₂ + O₂
D  NO + N → N₂ + O
E  O + NO + N₂ → NO₂ + N₂
F  CH₃O₂ + NO → CH₃O + NO₂
G  CH₃O + NO → CH₃ONO
H  CH₃CH(OH)CH₂OO + NO → CH₃CH(OH)CH₂O + NO₂
I  CH₃CH(OO)CH₂OH + NO → CH₃CH(O)CH₂OH + NO₂
J  CH₂CHO + NO → ONCH₂CHO
K  O + NO₂ → NO + O₂
Fig. 3.11 Time integrated contributions from various reaction channels for the generation and consumption of CO

A  OH + CO → CO₂ + H
B  E + CO₂ → CO + O + E
C  HCO + O₂ → HO₂ + CO
D  CO₂ + N → CO + NO
E  CH₂CHO + O₂ → HCHO + CO + OH
Fig. 3.12 End product profiles of the system with propene as a function of input energy deposition following 0.2 s
Energy Deposition = 55 J/L
Energy Deposition = 38 J/L

Fig. 3.13 Time integrated contribution from various reaction channels for the generation and consumption of HCHO.

A  HCHO + OH → HCO + H₂O
B  CH₃ + O → HCHO + H
C  CH₂O + O → HCHO + OH
D  CH₂O + NO → HCHO + HNO
E  CH₂OH + O₂ → HCHO + HO₂
F  CH₂CHO + O₂ → HCHO + CO + OH
G  CH₃CH(OH)CH₂O → CH₃CHOH + HCHO
Fig. 3.14(a) Effect of propene variation on NO, NO$_2$, NO$_x$ and HNO$_x$. All values correspond to an energy deposition of 18.7 J/L.

Fig. 3.14(b) Remediation percentages and CO production levels as a function of inlet propene concentration. All values correspond to an input energy of 18.7 J/L.
Fig. 3.15 Variation of end products with inlet propene for an energy deposition of 18.7 J/L. All concentrations correspond to values following 0.2 secs.

Fig. 3.16 Variation of W-Values for NO\(_x\) and NO as a function of inlet propene. All values are for an input energy of 18.7 J/L
Fig. 3.17 Effect of reactor gas temperature on NO, NO\textsubscript{x}, NO\textsubscript{2} and HNO\textsubscript{x} production
Energy deposition = 30.86 J/L

Fig. 3.18 Variation of NO\textsubscript{x}, NO and propene conversion levels and production of CO as a function of gas temperature. Values correspond to E\textsubscript{dep} of 30.86 J/L
Fig. 3.19 Effect of temperature on the production levels of the end-products of the system with propene effects included. Input energy deposition = 30.86 J/L
3.9 References


4. EFFECT OF ADDITION OF PROPANE ON THE CONVERSION OF NO$_x$

4.1 Introduction

In the experiments that were conducted at Ford Research Labs, the gas stream also included propane (C$_3$H$_8$). In order to compare the results from GLOBAL_KIN with available data from experiments, propane was added to the reaction mechanism. This chapter contains results from GLOBAL_KIN, performed for the plasma processing of NO$_x$ with the feed containing both propane and propene. The additional reaction mechanisms when adding propane are addressed in Section 4.2. The effects of input energy and reaction temperature are discussed in Section 4.3 and 4.4 respectively. Conclusions are provided in Section 4.5.

4.2 Reaction Mechanisms in NO$_x$ Remediation in the Presence of C$_3$H$_6$ and C$_3$H$_8$

Propane adds to the reaction mechanism in almost the same way as propene does. There is, however, a significant difference in the values of the reaction rate coefficients of the underlying reactions. In contrast to propene, the initiating reactions with C$_3$H$_8$ are H-abstraction instead of addition reactions. The resulting alkyl radicals (i-C$_3$H$_7$ and n-C$_3$H$_7$) then quickly react with O$_2$ to form the peroxy radicals ((CH$_3$)$_2$CHO$_2$, nC$_3$H$_7$O$_2$) which further react with NO to form NO$_2$. The rate of reaction of OH with propene is higher than that with propane by at least two orders of magnitude at the temperatures, concentrations and pressures of interest. Hence, in a system with propane and propene, most of the initial OH reacts with propene instead of propane. Propene has higher reactivity compared to propane due to the presence of a double bond. The $\pi$ electrons
present in the double bond are more mobile compared to the $\sigma$ bond and hence, the reactivity of propene is higher. This results in effectively reducing the participation of propane in the overall reaction chemistry.

The by-product of the reaction of the peroxy radicals with NO, the alkoxy radicals $((\text{CH}_3)_2\text{CHO}, \text{C}_3\text{H}_7\text{O})$, then react with $\text{O}_2$ to generate propionaldehyde ($\text{C}_2\text{H}_5\text{CHO}$) and acetone ($\text{CH}_3\text{C(O)CH}_3$). The peroxy radicals could also produce nitrates in the reactions with NO. The reaction mechanism for propane-$\text{NO}_x$ system is summarized in Fig. 4.1.

To quantify these trends, simulations were performed under various initial conditions and input energy densities with added propane.

4.3 Effect of Input Energy Density on the Remediation of $\text{NO}_x$ in the Presence of Propane and Propene

To investigate the effect of input energy density with propane, 175 ppm of propane with 500 ppm of $\text{C}_3\text{H}_6$ was added to the gas mixture in Table 3.1. The effect of increasing energy density on NO and $\text{NO}_2$ conversion is shown in Fig. 4.2(a). As a baseline for isolating the effect of addition of propane, the case with propene alone has been included. The addition of propane has a small, though not a negligible effect. Comparison of the modeling results with experiments shows close agreement with respect to $[\text{NO}]$, but a noticeable deviation in $[\text{NO}_2]$ and hence $[\text{NO}_x]$. The model prediction of $\text{NO}_2$ deviates from the experimental values by about 35 ppm. The conversion percentages for propene in the presence and absence of propane are shown in Fig. 4.2(b). With propane, the radicals that were previously available to propene are now competed for by propane and hence one sees a decrease in the conversion levels for
propene. However, since the reactivity of propane compared with propene is small, the effect is not pronounced. The conversion levels for propane reach a high of 6% at the higher energy levels [60 J/L]. The conversion of propene in the presence of propane agrees reasonably well with the experiments.

At higher energy inputs, propane does have a noticeable effect on the CO production levels as is shown in Fig. 4.3(a). The variation of the end product concentrations with energy deposition is shown in Fig. 4.3(b). Typical end products include formaldehyde (HCHO), methyl oxirane, propionaldehyde (C\textsubscript{2}H\textsubscript{5}CHO), glyoxal (CHO-CHO), methyl nitrite (CH\textsubscript{3}ONO) and 2-nitroso ethanal (ONCH\textsubscript{2}CHO). Glyoxal is produced by the reaction of O\textsubscript{2} with vinoxy radical (CH\textsubscript{2}CHO).

\[
\text{CH}_2\text{CHO} + \text{O}_2 \rightarrow \text{CHO-CHO} + \text{OH} \quad [4.1]
\]

Experimental data was available only for HCHO and at 30 J/L. The model and the experiment agree well for that energy deposition.

### 4.4 Effect of Reactor Temperature on NO\textsubscript{x} Conversion with Inlet Gas containing Propane and Propene

As described in the last chapter, temperature plays the important role of altering the reaction rate coefficients and thus the overall process output. The effect of temperature on NO\textsubscript{x} remediation was analyzed with 500 ppm of propene and 175 ppm of propane. The results of the analysis are shown in Figs. 4.4(a) and 4.4(b). Propene, propane, CO and NO conversion increased with increasing temperature, though the NO\textsubscript{x} conversion remained at an almost fixed level. The increase in the conversion levels for
propene, CO and NO can be explained along the same lines as described in Chapter 3. The degradation of propane occurs mainly by the following mechanisms.

\[
C_3H_8 + OH \rightarrow i-C_3H_7 + H_2O, \quad k = 7.95 \times 10^{-13} \left( \frac{T}{300} \right)^{2.0} \exp \left( -\frac{227}{T} \right) \text{cm}^3\text{s}^{-1} \quad [4.2]
\]

\[
C_3H_8 + OH \rightarrow n-C_3H_7 + H_2O, \quad k = 1.44 \times 10^{-12} \left( \frac{T}{300} \right)^{1.0} \exp \left( -\frac{130}{T} \right) \text{cm}^3\text{s}^{-1} \quad [4.3]
\]

The reaction rate constants for the initial attack of propane by OH increase with increasing temperature and hence, more propane is converted at higher temperatures. There is no appreciable change in NO\textsubscript{x} conversion with temperature. The maximum conversion of propane was around 10% at the maximum temperature. The effects of temperature on the production of HCHO, propionaldehyde and methyl oxirane are shown in Fig. 4.4(b). As is the case for propene alone, an increase in temperature produced an increase in the final end products mainly owing to the increase in the reaction rate coefficients of the underlying reactions with the increase in temperature.

### 4.5 Concluding Remarks

In general, the addition of propane did not affect the overall product output distribution significantly. The presence of propane actually produced a decreased conversion of propene, since the initiator radicals are consumed by propane also. Increasing energy inputs with propane produced almost the same outputs as with propene alone. This was because of the high reactivity of propene as compared to propane. Varying reactor temperature followed the same trends with propene alone. Higher temperatures lead to more NO conversion. NO\textsubscript{x} conversion, however, remained almost unaffected by increasing gas temperatures.
Fig. 4.1 Reaction mechanism for NO$_x$ in the presence of propane
Fig. 4.2(a) Comparison of NO and NO$_2$ conversion levels with and without the addition of propane. All values correspond to a reactor residence time of 0.2 s.

Fig. 4.2(b) Comparison of percentage conversion levels for propene with and without the addition of propane, following 0.2 s.
Fig. 4.3(a) Effect of energy deposition on the production level of CO in the presence of propane. All values are for a residence time of 0.2 s.

Fig. 4.3(b) Effect of energy deposition on the production level of end products with the addition of propane. Values correspond to a residence time of 0.2 s.
Fig. 4.4(a) Change in species densities with reactor temperature for a system containing propane and propene. Values are for an energy deposition of 30 J/L and a residence time of 0.2 s.

Fig. 4.4(b) Final product concentrations as a function of reactor temperature following 0.2 s, with the system containing propane in addition to propene. Values correspond to an energy deposition of 30 J/L.
5. EFFECT OF MULTIPLE PULSES ON NO\textsubscript{x} PROCESSING

5.1 Introduction

Comparison of the results from GLOBAL\_KIN with experiments performed at Ford Research Laboratory showed that methyl nitrate (CH\textsubscript{3}ONO\textsubscript{2}) was experimentally produced (approx. 12 ppm) whereas only 1 ppm was predicted by the model. Simulations predicted the formation of significant amounts of methyl oxirane and methyl nitrite (CH\textsubscript{3}ONO), whereas these species were not found in the experiments by mass spectroscopy. These differences motivated us to analyze the effects that multiple discharge pulsing might have on the overall plasma chemistry. The role of multiple pulses in the plasma chemistry is discussed in Section 5.2. The time evolution of species during multiple pulsing is discussed in Section 5.3. Comparison of the effects of single and multiple pulse formats on the overall reaction mechanism is given in Section 5.4. Simulations were performed with varying propane in the inlet with multiple pulse inputs and these results are summarized and discussed in Section 5.5. Simulations were performed at different reactor temperatures with the multiple pulse format and these results are given in Section 5.6. Finally, concluding remarks are in Section 5.7.

5.2 Role of Multiple Pulses in Affecting the Overall Plasma Chemistry

CH\textsubscript{3}ONO\textsubscript{2} (methyl nitrate) was formed in significant amounts in the DBD processing experiments conducted at Ford Research Laboratories (approx. 12 ppm) with the gas mixture given in Table 3.2 while it was not formed in our simulations using a single pulse format. CH\textsubscript{3}ONO\textsubscript{2} could be produced by,
\[
\text{CH}_3\text{O} + \text{NO}_2 + \text{M} \rightarrow \text{CH}_3\text{ONO}_2 + \text{M}, \quad k = 1.5 \times 10^{-11} \left( \frac{T}{300} \right)^{0.5} \text{cm}^3\text{s}^{-1} \quad [\text{5.1}]
\]

Reaction 5.1 implies that CH\(_3\)O radicals and NO\(_2\) have to be present in significant quantities at the same time for the production of methyl nitrate. Since the feed does not contain NO\(_2\), for reaction 5.1 to occur at significant rates, CH\(_3\)O and NO\(_2\) must both be produced in significant quantities. There are other pathways for consumption of the CH\(_3\)O radical.

\[
\text{CH}_3\text{O} + \text{NO} \rightarrow \text{CH}_3\text{ONO}, \quad k = 2.0 \times 10^{-11} \left( \frac{T}{300} \right)^{0.5} \text{cm}^3\text{s}^{-1} \quad [\text{5.2}]
\]

\[
\text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{HCHO} + \text{HO}_2, \quad k = 1.13 \times 10^{-13} \exp \left( -\frac{1310}{T} \right) \text{cm}^3\text{s}^{-1} \quad [\text{5.3}]
\]

\[
\text{CH}_3\text{O} + \text{OH} \rightarrow \text{HCHO} + \text{H}_2\text{O}, \quad k = 3.0 \times 10^{-11} \left( \frac{T}{300} \right)^{0.5} \text{cm}^3\text{s}^{-1} \quad [\text{5.4}]
\]

\[
\text{CH}_3\text{O} + \text{CH}_3\text{O} \rightarrow \text{HCHO} + \text{CH}_3\text{OH}, \quad k = 1.0 \times 10^{-10} \left( \frac{T}{300} \right)^{0.5} \text{cm}^3\text{s}^{-1} \quad [\text{5.5}]
\]

When the rates of the reactions 5.2 – 5.5 at 453 K are compared, it is found that reaction 5.2 dominates by at least two orders of magnitude. The rates of reactions 5.1 and 5.2 can be written as

\[
r_{5.1} = -\frac{dN_{\text{CH}_3\text{O}}}{dt} = k_{5.1} [\text{CH}_3\text{O}] [\text{NO}_2] \quad [\text{5.6}]
\]

\[
r_{5.2} = -\frac{dN_{\text{CH}_3\text{O}}}{dt} = k_{5.2} [\text{CH}_3\text{O}] [\text{NO}] \quad [\text{5.7}]
\]

The rate constants being almost equal, the ratio of the rates are approximately the ratios of the concentrations of NO\(_2\) and NO. The time evolution of CH\(_3\)O radical, NO and NO\(_2\)
are shown in Fig. 5.1. Since the concentration of NO is always greater than NO2 at high values of CH₃O, one always expects more of methyl nitrite to be formed.

In order for the production of methyl nitrate in the model to match experiments, the concentration of NO₂ should be greater than NO when the concentration of CH₃O is maximum. With multiple discharge pulses, the concentration of NO is gradually reduced and that of NO₂ is gradually increased. CH₃O radicals are produced during each pulse. Hence there will eventually be a time when the concentration of NO₂ exceeds that of NO at which time one would expect the formation of CH₃ONO₂.

5.3 Time Evolution of Species Densities during the Multiple Pulsing of Gas Mixtures containing NOₓ

The effect of varying input voltage with multiple pulsing at a repetition rate of 75 s⁻¹ with an energy input of 76 J/L was investigated. The variations in the NO, NO₂ and NOₓ concentrations with time are shown in Fig. 5.2. Each of the points in the plots correspond to a density just prior to the next pulse. At the end of the processing time, almost 110 ppm of NOₓ is removed resulting in about 42% NOₓ conversion. After 0.12 s, [NO₂] decreases due to the formation of CH₃ONO₂, HNO₃ and HNO₂ during each of the pulse periods. The NO concentration does not decrease to zero as was seen in the case of a single pulse input due to the regeneration of NO, primarily from NO₂.

\[ \text{O + NO}_2 \rightarrow \text{NO} + \text{O}_2 \]  \[ 5.8 \]

This is shown in Fig. 5.3. Initially NO is removed, but at longer times, NO is regenerated. The variation of the N-containing products and energy deposition as a function of time are shown in Fig. 5.4. The multiple pulse format has resulted in the

54
production of CH$_3$ONO$_2$. The final products with propene are shown in Fig. 5.5 and include methyl oxirane, propionaldehyde, acetaldehyde and glyoxal (CHO-CHO). Methyl oxirane, acetaldehyde and glyoxal are mainly produced by reactions 3.33, 3.34 and 3.12 respectively. Propionaldehyde is produced by the reaction of O with C$_3$H$_6$.

\[ \text{O} + \text{C}_3\text{H}_6 \rightarrow \text{C}_2\text{H}_5\text{CHO} \]  

[ 5.9 ]

5.4 Comparison of Single and Multiple Pulse Inputs

The use of multiple pulse formats significantly affects the reaction chemistry. For example, in single pulse formats, one could neglect reaction [5.1] since the rate of this reaction at any point of time is much less when compared to reaction [5.2]. However, in the case of multiple pulse formats, the products generated from previous pulses are important in the reaction mechanism. A comparison between the products with a single pulse and multiple pulses is shown in Fig. 5.6 for the same total energy deposition. The NO$_2$ produced for the multiple pulse format is at least 40 ppm less than the NO$_2$ for a single pulse. The overall NO$_x$ reduction differs by about 35 ppm, in the favor of multiple pulse format. The acids HNO$_2$ and HNO$_3$ are produced in more amounts with multiple pulses. Production of methyl nitrate increases by a factor of 13 when using a multiple pulse format over a single pulse input. There is however only a small difference in the production of CH$_3$ONO.

The differences in the concentration of the C end products between single pulse and multiple pulse formats are shown in Fig. 5.7. With multiple pulses, propene conversion increases (for the same input energy) by 12%. The concentration of other products such as CHO-CHO, CH$_3$CHO, C$_2$H$_5$CHO and CO remain almost unchanged.
5.4 Combined Effect of Multiple Pulsing and Varying Propane Concentration on NO\textsubscript{x} Remediation

The effect of multiple pulsing with propane was investigated with the gas mixture in Table 3.1 with 500 ppm of propene and varying propane. The total number of pulses was fixed at 15 and the pulses were equally spaced over a period of 0.2 s. The total energy deposited was approximately 76 J/L.

With multiple pulsing, the results were not much different when compared with single pulsed inputs. The variation of [NO], [NO\textsubscript{2}] and [C\textsubscript{3}H\textsubscript{6}] as a function of propane is shown in Fig. 5.8. NO concentrations remained virtually a constant for different propane concentrations. Though small, propene conversion did decrease with increasing propane concentration. This is due to the increased competition for the radicals available for propene by propane. [NO\textsubscript{2}] also remained unaffected with propane. The final concentrations of the end products as a function of inlet propane concentration are shown in Fig. 5.9. With increasing propane, the concentrations of HCHO, C\textsubscript{2}H\textsubscript{5}CHO, methyl oxirane, glyoxal, methyl nitrate and methyl nitrite remained unaffected. However, CH\textsubscript{3}CHO decreased from 92 ppm to 76 ppm.

Thus, even with multiple pulse formats, propane does not affect the reactor outputs much, thereby implying that the contribution of propane to a secondary reaction chemistry is quite minimal.
5.5 Effect of Reactor Temperature on the Remediation of NO\textsubscript{x} with the Inclusion of Multiple Pulses

The combined effects of multiple pulses and reactor temperature were studied with the gas mixture in Table 3.1 with 500 ppm of propene and 175 ppm of propane. The total residence time of gas was fixed at 0.2 s and during this period, 15 equally spaced pulses were applied. The total energy deposition was approximately 76 J/L.

The trends in the temporal evolution of NO and NO\textsubscript{2} for varying reactor temperatures are shown in Fig. 5.10. With increasing reactor temperature, [NO] decreased and [NO\textsubscript{2}] increased at intermediate points in time. However, at longer times, the concentrations of NO and NO\textsubscript{2} approached a finite asymptotic value. At 0.1 s, the [NO]\textsubscript{T=360 K} was greater than [NO]\textsubscript{T=500 K} by 33 ppm and [NO\textsubscript{2}]\textsubscript{T=360 K} was less than [NO\textsubscript{2}]\textsubscript{T=500 K} by the same amount, whereas at 0.2 s, [NO\textsubscript{2}]\textsubscript{T=500 K} differed from [NO\textsubscript{2}]\textsubscript{T=360 K} only by 6 ppm and [NO]\textsubscript{T=360 K} \approx [NO]\textsubscript{T=500 K}.

The variation of the end products as a function of time is shown in Fig. 5.11. The solid line in the graphs represent results at T\textsubscript{GAS}=500 K while the dashed line corresponds to T\textsubscript{GAS}=360 K. Formaldehyde was produced more rapidly at higher temperatures but the rate of production decreased at longer times. At 0.2 s, there was almost no difference in the final [HCHO] between T\textsubscript{GAS}=360 K and T\textsubscript{GAS}=500 K. Acetaldehyde production increased with increase in temperature. There was almost a linear increase in glyoxal concentration with time, with higher temperatures resulting in it’s increased rates of production.

The effects of temperature on the production of methyl nitrate and methyl nitrite are shown in Fig. 5.12. At lower temperatures, equal amounts of CH\textsubscript{3}ONO and
CH₃ONO₂ are produced. This difference becomes larger at higher temperatures. The concentrations of HNO₃ and HNO₂ as a function of time are shown in Fig. 5.13. Unlike other end products, [HNO₂] decreases with increase in temperature. [HNO₃] on the other hand, increased with increase in temperature.

The variation of methyl oxirane with time for various reactor temperatures is shown in Fig. 5.14. As the temperature is increased, the rate of the reaction increases due to the positive energy of activation.

\[ C₃H₆ + O → \text{Methyl Oxirane}, \quad k = 9.051 \times 10^{-12} \exp\left(-\frac{609.9}{T}\right) \text{cm}^3\text{s}^{-1} \]  [5.10]

Temperature increases from 360 K to 500 K increased the final concentrations of methyl oxirane by 21 ppm. The time evolution of propane and propene for 360 K and 500 K are shown in Fig. 5.15. Increasing temperature increased the conversion of propene and propane. C₃H₆ showed a change in conversion from 57.2% at 360 K to 84.8% at 500 K. Propane conversion increased from 2.85% at 360 K to 15.42% at 500 K. This is expected since propene is more reactive than propane due to the presence of a double bond. Finally, CO production as a function of time for different gas temperatures is shown in Fig. 5.16. More CO is formed at higher temperatures indicating that the production channels for CO dominate over consumption channels at higher temperatures. The difference in the concentration of CO between the two temperatures is approximately 75 ppm. Thus, while considering the rise in temperature for improving the performance, one should also take into account the production of CO and other pollutants that might be produced in higher quantities.
5.6 Concluding Remarks

The effect of multiple discharge pulses on the plasma remediation of NO\textsubscript{x} in the presence of hydrocarbons was studied. When using multiple pulses, new reactions occur in the latter pulses due to the reaction products from previous pulses. CH\textsubscript{3}ONO\textsubscript{2}, which was not produced in noticeable quantities with single pulse format, was produced in significant amounts with multiple pulsing. Comparison of the products of single and multiple pulse discharges showed marked differences in final concentrations of NO\textsubscript{2}, HNO\textsubscript{x}, C\textsubscript{3}H\textsubscript{6} and CO. The effect of varying hydrocarbon (propane) concentration with multiple pulsing was investigated and results showed that propane’s contribution to NO\textsubscript{x} remediation did not increase with multiple pulse formats. Parameterizations of reactor temperature with multiple discharge formats indicated an increase in the conversion of NO, C\textsubscript{3}H\textsubscript{6} and C\textsubscript{3}H\textsubscript{8} with increase in temperatures. All end products except HNO\textsubscript{2} were produced in increasing amounts with increases in temperature. CO was also produced in higher quantities at higher temperatures and this should always be considered in varying the operating temperature for improving NO\textsubscript{x} remediation.
Fig. 5.1 Temporal evolution of NO, NO₂ and CH₃O radical during the plasma processing of NOₓ with a single discharge pulse.

Fig. 5.2: Variation of NO, NO₂ and NOₓ with time for a multiply pulsed discharge processing of NOₓ in a DBD.
Fig. 5.3  Variation of NO with NO$_2$. The curve corresponds to marching along a time line.

Fig. 5.4 : Variation of HNO$_3$, HNO$_2$, CH$_3$ONO$_2$ and energy deposition as a function of time during the multiply pulsed discharge processing of NO$_x$ in the presence of propene.
Fig. 5.5: Production levels of the typical end-products encountered in the plasma processing of NO\textsubscript{x} in the presence of propene as a function of time. Each of the symbols in the lines correspond to a pulsing at that point in time.

Fig. 5.6: Comparison of the exit level concentrations of various species after the plasma processing of NO\textsubscript{x} with single and multiple pulsed discharges.
Fig. 5.7 Comparison of concentrations of the end-products of plasma processing of Nox with single and multiple pulse inputs.

Fig. 5.8 Outlet concentrations of NO, NO\textsubscript{2} and C\textsubscript{3}H\textsubscript{6} as a function of inlet propane concentration for the multiple pulsed plasma processing of NO\textsubscript{x} in the presence of propane and propene.
Fig. 5.9 Production levels of typical end-products of the plasma processing of NO$_x$ with the variation in the inlet propane concentration. All values correspond to an energy deposition of 76 J/L and for a 15 pulse input.

Fig. 5.10 Variation of NO and NO$_2$ with time for varying reactor temperatures.
Fig. 5.11 Temporal evolution of end-products of the multiply pulsed plasma processing of NO$_x$ in a DBD. Solid lines represent operating conditions at 500 K and dashed lines correspond to reactor temperatures of 360 K.

Fig. 5.12 Variation of methyl nitrate and methyl nitrite as a function of time for two different reactor temperatures. Solid lines represent $T_{\text{GAS}}$=500 K while dashed lines correspond to $T_{\text{GAS}}$=360 K.
Fig. 5.13  HNO\textsubscript{2} and HNO\textsubscript{3} profiles as a function of time for T\textsubscript{GAS}=360 K (dashed lines) and T\textsubscript{GAS}=500 K.

Fig. 5.14  Methyl Oxirane variation as a function of time for different reactor gas temperatures for the multiply pulsed plasma processing of NO\textsubscript{x} in the presence of propane and propene.
Fig. 5.15 Variation of conversion levels of C\textsubscript{3}H\textsubscript{6} and C\textsubscript{3}H\textsubscript{8} as a function of time for different cases of gas temperatures: 360 K (dashed lines) and 500 K (solid lines).

Fig. 5.16 Production levels of CO during the multiply pulsed plasma processing of NO\textsubscript{x} in the presence of propane and propene.
6. CONCLUSIONS

We have used a zero-dimensional model, called GLOBAL_KIN, to investigate the dielectric barrier discharge (DBD) remediation of NO$_x$ in simulated diesel exhausts at atmospheric pressure. The model is capable of analyzing detailed reaction chemistries in the DBDs. Ultimately, the aim of the analysis is to obtain a set of operating conditions/ranges in which maximal and energy-efficient remediation of NO$_x$ is obtained.

Plasma remediation of NO$_x$ in the presence of hydrocarbons has been investigated. The results indicate that hydrocarbons play a significant role in the overall reaction chemistry of NO$_x$. With hydrocarbons, the energy efficiency of the process is found to improve. Increasing energy deposition through the application of higher voltages led to higher NO$_x$ remediation. Variation of temperature did not significantly affect the net NO$_x$ remediation. Alkanes, propane in particular, were analyzed to determine their role in NO$_x$ remediation. Alkanes being less reactive compared to alkenes, did not appreciably affect the process outputs.

Industrial systems for plasma remediation employ higher repetition rate discharges. Multiple discharge formats were implemented in GLOBAL_KIN. New reactions occur during the latter pulses due to the reaction products from previous pulses. Single and multiple pulse discharge processing of NO$_x$ were compared. The results obtained using the multiple pulse formats agreed more closely with the experiments.

One of the underlying assumptions of GLOBAL_KIN is the homogeneity of the gas mixture in the reactor. This is not the case in real time systems wherein spatial dependencies exist. Future improvements will account for these spatial dependencies.
Another improvement to the model will include heterogeneous reaction chemistries and particulate formation.
APPENDIX A : LIST OF SPECIES USED IN THE REMEDIATION OF NO\(_x\) IN 
\(\text{N}_2/\text{O}_2/\text{H}_2/\text{O}/\text{CO}/\text{CO}/\text{H}_2/\text{C}_3\text{H}_8/\text{C}_3\text{H}_8\)

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Methyl Oxirane
APPENDIX B. LIST OF REACTIONS USED IN THE REMEDIATION OF NOx

Electron impact reactions resulting in the production of new species

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<th>Reaction</th>
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<td>e + N$_2$ $\rightarrow$ N$_2$(A) + e</td>
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<td>e + O$_2$ $\rightarrow$ O$^+$ + O</td>
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<td>1</td>
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<td>e + O$_2$ $\rightarrow$ O$_2^+$ + e + e</td>
<td>1.961x10$^{-10}$</td>
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<td>e + O$_2$ $\rightarrow$ O + O + e</td>
<td>1.434x10$^{-9}$</td>
<td>2</td>
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<tr>
<td>e + O$_2$ $\rightarrow$ O($^1$D) + O + e</td>
<td>4.8x10$^{-9}$</td>
<td>2</td>
</tr>
<tr>
<td>e + N$_2^+$ $\rightarrow$ N($^2$D) + N</td>
<td>2x10$^{-7}$Te$^{-0.5}$</td>
<td>34</td>
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<td>e + H$_2$O $\rightarrow$ H$_2$O$^+$ + e + e</td>
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<td>e + N$_3^+$ $\rightarrow$ N + N$_2$</td>
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<td>b</td>
</tr>
<tr>
<td>e + H$_3$O$^+$.(H$_2$O)$_2$ $\rightarrow$ H + (H$_2$O)$_3$</td>
<td>2x10$^{-7}$Te$^{-0.5}$</td>
<td>b</td>
</tr>
<tr>
<td>e + NO$_2^+$ $\rightarrow$ NO + O</td>
<td>2x10$^{-7}$Te$^{-0.5}$</td>
<td>b</td>
</tr>
<tr>
<td>e + NO$_2^+$ $\rightarrow$ NO + O($^1$D)</td>
<td>2x10$^{-7}$Te$^{-0.5}$</td>
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<tr>
<td>e + H$_2$NO$^+$ $\rightarrow$ H$_2$O + N</td>
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<td>b</td>
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<tr>
<td>e + NO$^+$ $\rightarrow$ N($^2$D) + O</td>
<td>2x10$^{-7}$Te$^{-0.5}$</td>
<td>4</td>
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<tr>
<td>e + NO$^+$ $\rightarrow$ N + O($^1$D)</td>
<td>2x10$^{-7}$Te$^{-0.5}$</td>
<td>34</td>
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<tr>
<td>e + O$_2$ + M $\rightarrow$ O$_2^-$ + M</td>
<td>1x10$^{-31}$Te$^{-0.5}$</td>
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<tr>
<td>e + NO$^+$·O$_2$ $\rightarrow$ NO + O$_2$</td>
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<td>b</td>
</tr>
<tr>
<td>e + NO$_2$ $\rightarrow$ NO$_2^-$</td>
<td>4x10$^{-11}$</td>
<td>4</td>
</tr>
<tr>
<td>e + N$_4^+$ $\rightarrow$ N$_2$ + N$_2$</td>
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<td>b</td>
</tr>
<tr>
<td>e + NO$^+$·(H$_2$O)$_2$ $\rightarrow$ NO + H$_2$O + H$_2$O</td>
<td>2x10$^{-7}$Te$^{-0.5}$</td>
<td>b</td>
</tr>
</tbody>
</table>
\[ e + H_2O^+ \rightarrow OH + H \quad 6.6 \times 10^{-6} Te^{-0.5} \quad 5 \]
\[ e + H_2O^+ \rightarrow O + H + H \quad 2.88 \times 10^{-6} Te^{-0.5} \quad 5 \]
\[ e + H_2O^+ \rightarrow O + H_2 \quad 2.52 \times 10^{-6} Te^{-0.5} \quad 5 \]
\[ e + H_3O^+ \rightarrow H_2O + H \quad 2 \times 10^{-7} Te^{-0.5} \quad b \]
\[ e + O_2^+ \rightarrow O(1D) + O \quad 2 \times 10^{-7} Te^{-0.5} \quad b \]
\[ e + H_2^+ \rightarrow H_2 \quad 2 \times 10^{-7} Te^{-0.5} \quad b \]
\[ e + O_2^+ . H_2O \rightarrow O_2 + H_2O \quad 2 \times 10^{-7} Te^{-0.5} \quad b \]
\[ e + H_3O^+ . H_2O \rightarrow H + H_2O + H_2O \quad 2 \times 10^{-7} Te^{-0.5} \quad b \]
\[ e + NH_3^+ \rightarrow NH_2 + H \quad 2 \times 10^{-7} Te^{-0.5} \quad b \]
\[ e + NH_4^+ \rightarrow NH_3 + H \quad 2 \times 10^{-7} Te^{-0.5} \quad b \]
\[ e + NO^+ . H_2O \rightarrow NO + H_2O \quad 2 \times 10^{-7} Te^{-0.5} \quad b \]
\[ e + NO^+: (H_2O)_3 \rightarrow NO + H_2O + H_2O \quad 2 \times 10^{-7} Te^{-0.5} \quad b \]
\[ e + N_2(A) \rightarrow N_2^+ + e + e \quad 2.2 \times 10^{-7} x \quad 35 \]
\[ \text{(exp}(-9.33/Te)/(Te^{-0.5} (1+9.33)/Te)) x \]
\[ ((20+9.33/Te)^{-1} + \log (1.25(1+Te/9.33))) \]
\[ e + O_3 \rightarrow e + O_2 + O(1D) \quad 5 \times 10^{-10} \quad b \]
\[ e + CO_2 \rightarrow O + CO + e \quad 1.195 \times 10^{-9} \quad 6 \]
\[ e + CO_2 \rightarrow CO_2^+ + e + e \quad 1.693 \times 10^{-10} \quad 6 \]
\[ e + CO_2 \rightarrow O^- + CO \quad 6.565 \times 10^{-12} \quad 6 \]
\[ e + CO_2^+ \rightarrow CO + O \quad 2 \times 10^{-7} Te^{-0.5} \quad b \]
\[ e + C^+ \rightarrow C \quad 2 \times 10^{-7} Te^{-0.5} \quad 34 \]

**Reactions of N_2/O_2/H_2O/NO**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Coefficient</th>
<th>Ref.</th>
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<tbody>
<tr>
<td>O + O_2 + M → O_3 + M</td>
<td>(6.9 \times 10^{-34} (T/300)^{-1.25})</td>
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<td>H + OH + M → H_2O + M</td>
<td>(4.3 \times 10^{-31})</td>
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<tr>
<td>N_2O_5 → NO_2 + NO_3</td>
<td>(5.49 \times 10^{14} T^{0.1} \exp(-11080/T))</td>
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<tr>
<td>Reaction</td>
<td>Rate Constant</td>
<td>Units</td>
</tr>
<tr>
<td>-----------------------------------------------</td>
<td>---------------</td>
<td>-------</td>
</tr>
<tr>
<td>NO + O₂ + NO → NO₂ + NO₂</td>
<td>1.4x10⁻³⁸</td>
<td>b</td>
</tr>
<tr>
<td>NO + HO₂ → NO₂ + OH</td>
<td>3.7x10⁻¹² exp(240/T)</td>
<td>11</td>
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<tr>
<td>N²(D) + N₂ → N + N₂</td>
<td>2.4x10⁻¹⁴</td>
<td>4</td>
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<tr>
<td>NO + O + O₂ → NO₂ + O₂</td>
<td>2.44x10⁻²⁷T⁻¹.₈</td>
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<tr>
<td>N²(D) + O₂ → NO + O</td>
<td>6.8x10⁻¹²</td>
<td>4</td>
</tr>
<tr>
<td>NO + OH + M → HNO₂ + M</td>
<td>7.4x10⁻³¹(T/300)⁻².₄</td>
<td>11</td>
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<tr>
<td>N²(D) + NO → N₂ + O</td>
<td>6.3x10⁻¹¹</td>
<td>4</td>
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<tr>
<td>NO + H + M → HNO + M</td>
<td>3.4x10⁻³²</td>
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<td>N²(D) + N₂O → NO + N₂</td>
<td>2.6x10⁻¹²</td>
<td>4</td>
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<tr>
<td>NO + NO₃ → NO₂ + NO₂</td>
<td>1.6x10⁻¹¹ exp(150/T)</td>
<td>11</td>
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<tr>
<td>HO₂ + NO + M → HNO₃ + M</td>
<td>5.6x10⁻³³</td>
<td>b</td>
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<tr>
<td>HO₂ + NO → O₂ + HNO</td>
<td>9.0x10⁻₁⁹ exp(2819/T)</td>
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<td>N²(D) + NO₂ → N₂O + O</td>
<td>1.5x10⁻¹²</td>
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<td>NO + O₃ → NO₂ + O₂</td>
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<tr>
<td>H + O₂ + M → HO₂ + M</td>
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<tr>
<td>H + O₃ → OH + O₂</td>
<td>1.4x10⁻¹⁰ exp(-480/T)</td>
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<td>N₂(A) + NO → NO + N₂</td>
<td>3.6x10⁻¹⁰</td>
<td>36</td>
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<td>H + HNO → H₂ + NO</td>
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<tr>
<td>N₂(A) + O₂ → O + O + N₂</td>
<td>1.5x10⁻¹²</td>
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<tr>
<td>N + NO₂ → N₂O + O</td>
<td>2.4x10⁻¹²</td>
<td>4</td>
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<tr>
<td>N₂(A) + O₂ → O₂ + N₂</td>
<td>2.8x10⁻¹¹</td>
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<tr>
<td>Reaction</td>
<td>Rate Constant</td>
<td>Temperature</td>
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<tr>
<td>--------------------------------</td>
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<tr>
<td>$N + NO_2 \rightarrow NO + NO$</td>
<td>$6 \times 10^{-13}$</td>
<td>$4$</td>
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<tr>
<td>$N_2(A) + N_2O \rightarrow N_2 + N_2 + O$</td>
<td>$1.4 \times 10^{-11}$</td>
<td>$36$</td>
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<tr>
<td>$N_2(A) + N_2O \rightarrow N_2 + N_2O$</td>
<td>$1.7 \times 10^{-10}$</td>
<td>$36$</td>
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<tr>
<td>$N + N + M \rightarrow N_2 + M$</td>
<td>$3.9 \times 10^{-33}$</td>
<td>$4$</td>
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<tr>
<td>$N_2(A) + NO_2 \rightarrow NO + O + N_2$</td>
<td>$1 \times 10^{-12}$</td>
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<tr>
<td>$N_2(A) + H_2 \rightarrow N_2 + H_2$</td>
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<td>$N + OH \rightarrow NO + H$</td>
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<td>$N + O_3 \rightarrow NO + O_2$</td>
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<td>$O(1D) + H_2O \rightarrow O + H_2O$</td>
<td>$1.2 \times 10^{-11}$</td>
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<td>$O + NO_2 + M \rightarrow NO_3 + M$</td>
<td>$9.0 \times 10^{-32} (T/300)^{-2.0}$</td>
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<td>$NO_3 + NO_3 \rightarrow NO_2 + NO_2 + O_2$</td>
<td>$1.2 \times 10^{-15}$</td>
<td>$4$</td>
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<tr>
<td>$OH + OH \rightarrow O + H_2O$</td>
<td>$3.5 \times 10^{-16} T^{1.4} \text{exp}(200/T)$</td>
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<td>$NH + NO \rightarrow N_2O + H$</td>
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<td>$OH + NO_2 + N_2 \rightarrow HNO_3 + N_2$</td>
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<tr>
<td>$OH + HNO_3 \rightarrow NO_3 + H_2O$</td>
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<tr>
<td>$OH + HNO \rightarrow H_2O + NO$</td>
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<td>Unit</td>
</tr>
<tr>
<td>--------------------------------------------------------------------------</td>
<td>---------------</td>
<td>----------</td>
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<tr>
<td>( \text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2 )</td>
<td>(8 \times 10^{-11})</td>
<td>b</td>
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<tr>
<td>( \text{H}_2\text{O}^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{OH} )</td>
<td>(1.7 \times 10^{-9})</td>
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<td>( \text{OH} + \text{HNO}_2 \rightarrow \text{NO}_2 + \text{H}_2\text{O} )</td>
<td>(1.8 \times 10^{-11}\exp(-390/T))</td>
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<td>( \text{H}_2\text{O}^+ + \text{O}_2 \rightarrow \text{O}_2^+ + \text{H}_2\text{O} )</td>
<td>(4.3 \times 10^{-10})</td>
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<td>( \text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2 )</td>
<td>(1.9 \times 10^{-12}\exp(-1000/T))</td>
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<td>( \text{N}_3^+ + \text{O}_2 \rightarrow \text{NO}^+ + \text{N}_2\text{O} )</td>
<td>(3.6 \times 10^{-11})</td>
<td>4</td>
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<td>( \text{OH} + \text{N}_2\text{O} \rightarrow \text{HNO} + \text{NO} )</td>
<td>(3.8 \times 10^{-17})</td>
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<td>( \text{N}_3^+ + \text{O}_2 \rightarrow \text{NO}_2^+ + \text{N}_2 )</td>
<td>(1.5 \times 10^{-11})</td>
<td>4</td>
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<tr>
<td>( \text{HO}_2 + \text{NO}_2 + \text{N}_2 \rightarrow \text{HO}_2\text{NO}_2 + \text{N}_2 )</td>
<td>(1.5 \times 10^{-31}(T/300)^{-3.2})</td>
<td>11</td>
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<tr>
<td>( \text{N}_3^+ + \text{NO} \rightarrow \text{NO}^+ + \text{N} + \text{N}_2 )</td>
<td>(1.4 \times 10^{-10})</td>
<td>4</td>
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<td>( \text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + \text{O}_2 + \text{O}_2 )</td>
<td>(1.4 \times 10^{-14}\exp(-600/T))</td>
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<td>( \text{N}_3^+ + \text{NO}_2 \rightarrow \text{NO}^+ + \text{NO} + \text{N}_2 )</td>
<td>(7 \times 10^{-11})</td>
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<td>( \text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2 )</td>
<td>(1.2 \times 10^{-13}\exp(-2450/T))</td>
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<td>( \text{N}_3^+ + \text{NO}_2 \rightarrow \text{NO}_2^+ + \text{N} + \text{N}_2 )</td>
<td>(7 \times 10^{-11})</td>
<td>4</td>
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<td>( \text{N}_3^+ + \text{N}_2\text{O} \rightarrow \text{NO}^+ + \text{N}_2 + \text{N}_2 )</td>
<td>(5 \times 10^{-11})</td>
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<tr>
<td>( \text{O} + \text{NO}_2 \rightarrow \text{NO} + \text{O}_2 )</td>
<td>(6.5 \times 10^{-12}\exp(120/T))</td>
<td>11</td>
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<td>( \text{O} + \text{NO}_3 \rightarrow \text{O}_2 + \text{NO} )</td>
<td>(1 \times 10^{-11})</td>
<td>4</td>
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<tr>
<td>( \text{N}_3^+ + \text{NO}_2^- \rightarrow \text{N} + \text{N}_2 + \text{NO}_2 )</td>
<td>(2 \times 10^{-6}(T/300)^{-0.5})</td>
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<tr>
<td>( \text{O} + \text{OH} \rightarrow \text{H} + \text{O}_2 )</td>
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<td>( \text{O}^+ + \text{N}_2 \rightarrow \text{NO}^+ + \text{N} )</td>
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<td>4</td>
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<tr>
<td>( \text{OH} + \text{OH} + \text{O}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 )</td>
<td>(6.9 \times 10^{-31}(T/300)^{-0.8})</td>
<td>11</td>
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<tr>
<td>( \text{O}^+ + \text{NO} \rightarrow \text{NO}^+ + \text{O} )</td>
<td>(1.7 \times 10^{-12})</td>
<td>4</td>
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<tr>
<td>( \text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2 )</td>
<td>(2.9 \times 10^{-12}\exp(-160/T))</td>
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<tr>
<td>( \text{O}^+ + \text{O}_2 \rightarrow \text{O}_2^+ + \text{HO}_2 )</td>
<td>(1.9 \times 10^{-11})</td>
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<tr>
<td>( \text{H} + \text{HO}_2 \rightarrow \text{H}_2 + \text{O}_2 )</td>
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<td>( \text{O}^+ + \text{NO}_2 \rightarrow \text{NO}_2^+ + \text{O} )</td>
<td>(1.6 \times 10^{-9})</td>
<td>4</td>
</tr>
</tbody>
</table>
\[
\begin{align*}
\text{HO}_2\text{NO}_2 + \text{O}_2 & \rightarrow \text{HO}_2 + \text{NO}_2 + \text{O}_2 \\
3.6 \times 10^{-6} \exp(-10000/T) & \quad 24 \\
\text{O}^+ + \text{NO}_2^- & \rightarrow \text{O} + \text{NO}_2 \\
2 \times 10^{-6}(T/300)^{-0.5} & \quad 4 \\
\text{O}_2^+ + \text{NO} & \rightarrow \text{NO}^+ + \text{O}_2 \\
4.4 \times 10^{-10} & \quad 4 \\
\text{O}_2^+ + \text{NO}_2 & \rightarrow \text{NO}_2^+ + \text{O}_2 \\
8.8 \times 10^{-9} & \quad 4 \\
\text{O}_2^+ + \text{H}_2\text{O} + \text{H}_2\text{O} & \rightarrow \\
\text{H}_3\text{O}^+ + \text{OH} + \text{O}_2 \\
1.2 \times 10^{-9} & \quad 4 \\
\text{H}_3\text{O}^+ + \text{H}_2\text{O} + \text{M} & \rightarrow \\
\text{H}_3\text{O}^+ + \text{H}_2\text{O} + \text{M} \\
5 \times 10^{-27} & \quad 4 \\
\text{O}_2^+ + \text{NO}_2^- & \rightarrow \text{O}_2 + \text{NO}_2 \\
2 \times 10^{-6}(T/300)^{-0.5} & \quad 4 \\
\text{H}_3\text{O}^+\text{H}_2\text{O} + \text{H}_2\text{O} & \rightarrow \text{H}_3\text{O}^+(\text{H}_2\text{O})_2 \\
1 \times 10^{-9} & \quad 4 \\
\text{NO}_2^+ + \text{NO} & \rightarrow \text{NO}^+ + \text{NO}_2 \\
2.9 \times 10^{-10} & \quad 4 \\
\text{H}_3\text{O}^+(\text{H}_2\text{O})_2 + \text{NO}_2^- & \rightarrow \\
\text{H} + (\text{H}_2\text{O})_3 + \text{NO}_2 \\
2 \times 10^{-7}(T/300)^{-0.5} & \quad 4 \\
\text{H}_3\text{O}^+(\text{H}_2\text{O})_2 + \text{NO}_3^- & \rightarrow \\
\text{H} + (\text{H}_2\text{O})_3 + \text{NO}_3 \\
2 \times 10^{-7}(T/300)^{-0.5} & \quad 4 \\
\text{NO}_2^+ + \text{NO}_2^- & \rightarrow \text{NO}_2 + \text{NO}_2 \\
3 \times 10^{-6}(T/300)^{-0.5} & \quad 4 \\
\text{NO}_2^+ + \text{NO}_3^- & \rightarrow \text{NO}_2 + \text{NO}_3 \\
3 \times 10^{-6}(T/300)^{-0.5} & \quad 4 \\
\text{N}_2^+ + \text{NO} & \rightarrow \text{NO}^+ + \text{N}_2 \\
3.3 \times 10^{-10} & \quad 4 \\
\text{N}_3^+ + \text{H}_2\text{O} & \rightarrow \text{H}_2\text{NO}^+ + \text{N}_2 \\
3.3 \times 10^{-10} & \quad 4 \\
\text{N}_2^+ + \text{NO}_2 & \rightarrow \text{NO}_2^+ + \text{N}_2 \\
3.3 \times 10^{-10} & \quad 4 \\
\text{N}_2^+ + \text{NO}_2 & \rightarrow \text{NO}^+ + \text{N}_2\text{O} \\
5 \times 10^{-11} & \quad 4 \\
\text{H}_2\text{NO}^+ + \text{NO}_2^- & \rightarrow \\
\text{H}_2\text{O} + \text{N} + \text{NO}_2 \\
2 \times 10^{-6}(T/300)^{-0.5} & \quad 4 \\
\text{H}_2\text{NO}^+ + \text{NO}_3^- & \rightarrow \\
\text{H}_2\text{O} + \text{N} + \text{NO}_3 \\
2 \times 10^{-6}(T/300)^{-0.5} & \quad 4 \\
\text{NO}_2^- + \text{HNO}_3 & \rightarrow \\
\text{NO}_3^- + \text{HNO}_2 \\
1.6 \times 10^{-9} & \quad 4 \\
\text{N}_2^+ + \text{NO}_2^- & \rightarrow \text{N}_2 + \text{NO}_2 \\
3 \times 10^{-6}(T/300)^{-0.5} & \quad 4 
\end{align*}
\]
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<tr>
<th>Reaction</th>
<th>Rate Constant</th>
<th>Reaction Conditions</th>
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<td>( \text{NO}_2^- + \text{N}_2\text{O}_5 \rightarrow \text{NO}_3^- + \text{NO}_2 + \text{NO}_2 )</td>
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<td>( \text{N}(^2\text{D}) + \text{NH}_3 \rightarrow \text{NH} + \text{NH}_2 )</td>
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<td>( 2 \times 10^{-7}(T/300)^{-0.5} )</td>
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<td>( \text{NO}^+ + \text{O}_2 + \text{NO}_3^- \rightarrow \text{NO} + \text{O}_2 + \text{NO}_3 )</td>
<td>( 3 \times 10^{-6}(T/300)^{-0.5} )</td>
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<tr>
<td>( \text{OH} + \text{NH}_3 \rightarrow \text{NH}_2 + \text{H}_2\text{O} )</td>
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<td>( \text{O}(^1\text{D}) + \text{NH}_3 \rightarrow \text{NH}_2 + \text{OH} )</td>
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<td>( \text{NH}_2 + \text{NO} \rightarrow \text{N}_2 + \text{H}_2\text{O} )</td>
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<td>( \text{NH}_2 + \text{NO}_2 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O} )</td>
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</table>
\[
\begin{align*}
H_3O^+ + NH_3 &\rightarrow NH_4^+ + H_2O & 2.5 \times 10^{-9} & 4 \\
N^+ + NO &\rightarrow NO^+ + N & 9 \times 10^{-10} & 4 \\
N^+ + NH_3 &\rightarrow NH_3^+ + N & 2.4 \times 10^{-9} & 4 \\
N_2^+ + N_2 + M &\rightarrow N_4^+ + M & 1.1 \times 10^{-29} & 4 \\
N_3^+ + NH_3 &\rightarrow NH_3^+ + N + N_2 & 2.1 \times 10^{-9} & 4 \\
N_2^+ + O_2 &\rightarrow O_2^+ + N_2 & 5.1 \times 10^{-11} & 4 \\
N_2^+ + NH_3 &\rightarrow NH_3^+ + N_2 & 1.9 \times 10^{-9} & 4 \\
N_4^+ + NO &\rightarrow NO^+ + N_2 + N_2 & 1.8 \times 10^{-9} & 4 \\
N_4^+ + NO_2 &\rightarrow NO_2^+ + N_2 + N_2 & 2.5 \times 10^{-10} & 4 \\
NH_3^+ + NO_3^- &\rightarrow NH_3 + NO_3 & 5 \times 10^{-6}(T/300)^{-0.5} & b \\
N_4^+ + NO_2 &\rightarrow NO^+ + N_2O + N_2 & 5 \times 10^{-11} & 4 \\
NH_4^+ + NO_3^- &\rightarrow NH_3 + H + NO_3 & 3 \times 10^{-6}(T/300)^{-0.5} & 4 \\
N_4^+ + O_2 &\rightarrow O_2^+ + N_2 + N_2 & 2.5 \times 10^{-10} & 4 \\
NO^+ + H_2O + M &\rightarrow & 1.6 \times 10^{-28} & 4 \\
&NO^+ \cdot H_2O + M &\rightarrow & 1 \times 10^{-27} & 4 \\
&NO^+ \cdot (H_2O)_2 + M &\rightarrow & 3 \times 10^{-6}(T/300)^{-0.5} & 4 \\
&NO^+ \cdot (H_2O)_2 + M &\rightarrow & 1.3 \times 10^{-12} & 4 \\
&N_4^+ + NO_2^- &\rightarrow NO_2 + N_2 + N_2 & 3 \times 10^{-6}(T/300)^{-0.5} & 4 \\
&O_2^+ + H_2O + M &\rightarrow O_2^+ \cdot H_2O + M & 8 \times 10^{-11} & 4 \\
&NO^+ \cdot (H_2O)_2 + H_2O &\rightarrow H_3O^+ \cdot (H_2O)_2 + HNO_2 & 8 \times 10^{-11} & 4 \\
NH_2 + O &\rightarrow NH + OH & 1.2 \times 10^{-11} & 26 \\
NH_2 + O &\rightarrow HNO + H & 7.6 \times 10^{-11} & 26
\end{align*}
\]
\begin{align*}
\text{HO}_2\text{NO}_2 + \text{N}_2 & \rightarrow \text{HO}_2 + \text{NO}_2 + \text{N}_2 \\
\text{OH} + \text{NO}_2 + \text{O}_2 & \rightarrow \text{HNO}_3 + \text{O}_2 \\
\text{OH} + \text{H}_2 & \rightarrow \text{H}_2\text{O} + \text{H} \\
\text{O}^{(1D)} + \text{H}_2\text{O} & \rightarrow \text{H}_2 + \text{O}_2 \\
\text{O}^{(1D)} + \text{H}_2 & \rightarrow \text{OH} + \text{H} \\
\text{O} + \text{H}_2\text{O}_2 & \rightarrow \text{OH} + \text{HO}_2 \\
\text{O} + \text{H}_2 & \rightarrow \text{OH} + \text{H} \\
\text{H} + \text{HO}_2 & \rightarrow \text{H}_2\text{O} + \text{O} \\
\text{O} + \text{O}_2 + \text{N}_2 & \rightarrow \text{O}_2 + \text{O} + \text{N}_2 \\
\text{HO}_2 + \text{HO}_2 + \text{M} & \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 + \text{M} \\
\text{O} + \text{NO} + \text{N}_2 & \rightarrow \text{NO}_2 + \text{N}_2 \\
\text{NO}_2 + \text{NO}_3 + \text{M} & \rightarrow \text{N}_2\text{O}_5 + \text{M} \\
\text{N}^+ + \text{H}_2\text{O} & \rightarrow \text{H}_2\text{O}^+ + \text{N} \\
\text{H}_2\text{O}^+ + \text{NO}_2^- & \rightarrow \text{H}_2\text{O} + \text{NO}_2 \\
\text{H}_2\text{O}^+ + \text{NO}_3^- & \rightarrow \text{H}_2\text{O} + \text{NO}_3 \\
\text{H}_2\text{O}^+ + \text{O}_2^- & \rightarrow \text{H}_2\text{O} + \text{O}_2 \\
\text{H}_3\text{O}^+ + \text{NO}_2^- & \rightarrow \text{H}_2\text{O} + \text{H} + \text{NO}_2 \\
\text{H}_3\text{O}^+ + \text{NO}_3^- & \rightarrow \text{H}_2\text{O} + \text{H} + \text{NO}_3 \\
\text{H}_3\text{O}^+ + \text{O}_2^- & \rightarrow \text{H}_2\text{O} + \text{H} + \text{O}_2 \\
\text{O}_2^+ + \text{NO}_3^- & \rightarrow \text{O}_2 + \text{NO}_3 \\
\text{O}_2^+ + \text{O}_2^- & \rightarrow \text{O}_2 + \text{O}_2 \\
\text{N}_3^+ + \text{NO}_3^- & \rightarrow \text{N}_2 + \text{N} + \text{NO}_3 \\
\text{N}_3^+ + \text{O}_2^- & \rightarrow \text{N}_2 + \text{N} + \text{O}_2 \\
\text{NO}^+ + \text{O}_2^- & \rightarrow \text{NO} + \text{O}_2 \\
\text{NO}_2^+ + \text{O}_2^- & \rightarrow \text{NO}_2 + \text{O}_2 \\
\end{align*}

\text{OH} + \text{NO}_2 + \text{O}_2 \rightarrow 2.6 \times 10^{-30}(T/300)^{-2.9} \\
\text{OH} + \text{H}_2 \rightarrow 7.7 \times 10^{-12}\exp(-2100/T) \\
\text{O}^{(1D)} + \text{H}_2\text{O} \rightarrow 2.3 \times 10^{-12} \\
\text{O}^{(1D)} + \text{H}_2 \rightarrow 1.1 \times 10^{-10} \\
\text{O} + \text{H}_2\text{O}_2 \rightarrow 1.4 \times 10^{-12}\exp(-2000/T) \\
\text{O} + \text{H}_2 \rightarrow 1.6 \times 10^{-11}\exp(-4570/T) \\
\text{H} + \text{HO}_2 \rightarrow 9.4 \times 10^{-13} \\
\text{O} + \text{O}_2 + \text{N}_2 \rightarrow 6.2 \times 10^{-34}(T/300)^{-2.0} \\
\text{HO}_2 + \text{HO}_2 + \text{M} \rightarrow 1.9 \times 10^{-33}\exp(980/T) \\
\text{O} + \text{NO} + \text{N}_2 \rightarrow 9.1 \times 10^{-28}T^{-1.6} \\
\text{NO}_2 + \text{NO}_3 + \text{M} \rightarrow 2.7 \times 10^{-30}(T/300)^{-3.4} \\
\text{N}^+ + \text{H}_2\text{O} \rightarrow 5.55 \times 10^{-8}T^{-0.52} \\
\text{H}_2\text{O}^+ + \text{NO}_2^- \rightarrow 2 \times 10^{-6}(T/300)^{-0.5} \\
\text{H}_2\text{O}^+ + \text{NO}_3^- \rightarrow 2 \times 10^{-6}(T/300)^{-0.5} \\
\text{H}_2\text{O}^+ + \text{O}_2^- \rightarrow 2 \times 10^{-6}(T/300)^{-0.5} \\
\text{H}_3\text{O}^+ + \text{NO}_2^- \rightarrow 2 \times 10^{-6}(T/300)^{-0.5} \\
\text{H}_3\text{O}^+ + \text{NO}_3^- \rightarrow 2 \times 10^{-6}(T/300)^{-0.5} \\
\text{H}_3\text{O}^+ + \text{O}_2^- \rightarrow 2 \times 10^{-6}(T/300)^{-0.5} \\
\text{O}_2^+ + \text{NO}_3^- \rightarrow 2 \times 10^{-6}(T/300)^{-0.5} \\
\text{O}_2^+ + \text{O}_2^- \rightarrow 2 \times 10^{-6}(T/300)^{-0.5} \\
\text{N}_3^+ + \text{NO}_3^- \rightarrow 2 \times 10^{-6}(T/300)^{-0.5} \\
\text{N}_3^+ + \text{O}_2^- \rightarrow 2 \times 10^{-6}(T/300)^{-0.5} \\
\text{NO}^+ + \text{O}_2^- \rightarrow 2 \times 10^{-6}(T/300)^{-0.5} \\
\text{NO}_2^+ + \text{O}_2^- \rightarrow 2 \times 10^{-6}(T/300)^{-0.5}
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<td>$2 \times 10^{-6} (T/300)^{-0.5}$</td>
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<tr>
<td>$\text{NO}^+ \cdot \text{O}_2 + \text{O}_2^- \rightarrow \text{NO} + \text{O}_2 + \text{O}_2$</td>
<td>$2 \times 10^{-6} (T/300)^{-0.5}$</td>
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<tr>
<td>$\text{N}^+ + \text{O}_2^- \rightarrow \text{N}^+ \text{O}_2$</td>
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<td>$\text{H}_3\text{O}^+ \cdot \text{H}_2\text{O} + \text{NO}_3^- \rightarrow \text{H} + \text{H}_2\text{O} + \text{H}_2\text{O} + \text{NO}_3$</td>
<td>$2 \times 10^{-6} (T/300)^{-0.5}$</td>
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<td>$\text{H}_3\text{O}^+ \cdot \text{H}_2\text{O} + \text{O}_2^- \rightarrow \text{H} + \text{H}_2\text{O} + \text{H}_2\text{O} + \text{O}_2$</td>
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<td>$\text{H}_3\text{O}^+ \cdot (\text{H}_2\text{O})_2 + \text{O}_2^- \rightarrow \text{H} + (\text{H}_2\text{O})_3 + \text{O}_2$</td>
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\[
\begin{align*}
\text{NO} + \text{H}_2\text{O} + \text{NO}_2 & \quad \text{NO} + \text{H}_2\text{O} + \text{NO}_3 \\
\text{NO}^+\cdot \text{H}_2\text{O} + \text{NO}_3^- \rightarrow & \quad 2 \times 10^{-6} (T/300)^{-0.5} \quad \text{b} \\
\text{NO}^+\cdot \text{H}_2\text{O} + \text{O}_2^- \rightarrow & \quad 2 \times 10^{-6} (T/300)^{-0.5} \quad \text{b} \\
\text{NO}^+\cdot (\text{H}_2\text{O})_2 + \text{NO}_3^- \rightarrow & \quad 2 \times 10^{-6} (T/300)^{-0.5} \quad \text{b} \\
\text{NO}^+\cdot (\text{H}_2\text{O})_3 + \text{NO}_3^- \rightarrow & \quad 2 \times 10^{-6} (T/300)^{-0.5} \quad \text{b} \\
\text{NO}^+\cdot (\text{H}_2\text{O})_2 + \text{NO}_2^- \rightarrow & \quad 2 \times 10^{-6} (T/300)^{-0.5} \quad \text{b} \\
\text{NO}^+\cdot (\text{H}_2\text{O})_3 + \text{NO}_2^- \rightarrow & \quad 2 \times 10^{-6} (T/300)^{-0.5} \quad \text{b} \\
\text{NO}^+\cdot (\text{H}_2\text{O})_2 + \text{O}_2^- \rightarrow & \quad 2 \times 10^{-6} (T/300)^{-0.5} \quad \text{b} \\
\text{NO}^+\cdot (\text{H}_2\text{O})_3 + \text{O}_2^- \rightarrow & \quad 2.00 \times 10^{-6} (T/300)^{-0.5} \quad \text{b} \\
\text{O} + \text{H} + \text{M} \rightarrow \text{OH} + \text{M} & \quad 1.62 \times 10^{-32} \quad 28 \\
\text{H} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{OH} & \quad 4 \times 10^{-11} \exp(-2000/T) \quad 15 \\
\text{NO}_2 + \text{NO}_2 + \text{N}_2 \rightarrow & \quad 1.4 \times 10^{-33} (T/300)^{-3.8} \quad 17 \\
\text{N}_2\text{O}_4 + \text{N}_2 \rightarrow & \quad 1.29 \times 10^{-5} (T/300)^{-3.8} \quad 17 \\
\text{NH}_2 + \text{H}_2 \rightarrow \text{NH}_3 + \text{H} & \quad 5.98 \times 10^{-12} \exp(-2290/T) \quad 27 \\
\text{NH}_3 + \text{H} \rightarrow \text{NH}_2 + \text{H}_2 & \quad 1.35 \times 10^{-10} \exp(-3660/T) \quad 27 \\
\text{OH} + \text{NO}_3 \rightarrow \text{HO}_2 + \text{NO}_2 & \quad 2.6 \times 10^{-11} \quad 29 \\
\text{HO}_2 + \text{NO}_3 \rightarrow \text{OH} + \text{NO}_2 + \text{O}_2 & \quad 3.6 \times 10^{-12} \quad 29 \\
\text{HO}_2 + \text{NO}_3 \rightarrow \text{HNO}_3 + \text{O}_2 & \quad 9.2 \times 10^{-13} \quad 29 \\
\text{H} + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2 + \text{H}_2 & \quad 8 \times 10^{-11} \exp(-4000/T) \quad 15 \\
\text{HNO}_3 + \text{NO} \rightarrow \text{HNO}_2 + \text{NO}_2 & \quad 7.37 \times 10^{-21} \quad 25 
\end{align*}
\]
\begin{align*}
H_2 + O_2 & \rightarrow H + HO_2 & 2.4 \times 10^{-10} \exp(-28500/T) & 15 \\
H + O_2 & \rightarrow OH + O & 2.8 \times 10^{-7} \exp(-8750/T) & 15 \\
OH + M & \rightarrow O + H + M & 4 \times 10^{-9} \exp(-50000/T) & 15 \\
OH + O_2 & \rightarrow O + HO_2 & 3.7 \times 10^{-11} \exp(-26500/T) & 15 \\
OH + H & \rightarrow O + H_2 & 1.14 \times 10^{-12} T^{0.67} \exp(-518/T) & 5 \\
HO_2 + M & \rightarrow H + O_2 + M & 2 \times 10^{-5} T^{-1.18} \exp(-24363/T) & 15 \\
HO_2 + H_2 & \rightarrow H_2O_2 + H & 5 \times 10^{-11} \exp(-13100/T) & 15 \\
H_2O_2 + O_2 & \rightarrow HO_2 + HO_2 & 9 \times 10^{-11} \exp(-20000/T) & 15 \\
H_2O + H & \rightarrow H_2 + OH & 1.03 \times 10^{-16} T^{1.9} \exp(-9265/T) & 15 \\
H_2O + O & \rightarrow OH + OH & 7.6 \times 10^{-15} T^{1.3} \exp(-8605/T) & 15 \\
H^- + N_2^+ & \rightarrow H + N_2 & 3 \times 10^{-6} (T/300)^{-0.5} & b \\
O^- + N_2^+ & \rightarrow O + N_2 & 3 \times 10^{-6} (T/300)^{-0.5} & b \\
O^- + H_2^+ & \rightarrow O + H_2 & 3 \times 10^{-6} (T/300)^{-0.5} & 32 \\
O_2^- + H_2^+ & \rightarrow O_2 + H_2 & 3 \times 10^{-6} (T/300)^{-0.5} & 32 \\
H^- + H_2^+ & \rightarrow H + H_2 & 3 \times 10^{-6} (T/300)^{-0.5} & 32 \\
H^- + H_2O^+ & \rightarrow H + H_2O & 3 \times 10^{-6} (T/300)^{-0.5} & 32 \\
O^- + H_2O^+ & \rightarrow O + H_2O & 3 \times 10^{-6} (T/300)^{-0.5} & 32 \\
H^- + H_3O^+ & \rightarrow H_2 + H_2O & 3 \times 10^{-6} (T/300)^{-0.5} & b \\
O^- + H_3O^+ & \rightarrow OH + H_2O & 3 \times 10^{-6} (T/300)^{-0.5} & b \\
H^- + O_2^+ + M & \rightarrow H_2O + M & 1.2 \times 10^{-25} & b \\
O^- + O_2^+ & \rightarrow O + O_2 & 3 \times 10^{-6} (T/300)^{-0.5} & 32 \\
H^- + N_3^+ & \rightarrow NH + N_2 & 3 \times 10^{-6} (T/300)^{-0.5} & b \\
O^- + N_3^+ & \rightarrow NO + N_2 & 3 \times 10^{-6} (T/300)^{-0.5} & b \\
H^- + NO^+ + M & \rightarrow HNO + M & 1.2 \times 10^{-25} & b \\
O^- + NO^+ & \rightarrow NO + O & 3 \times 10^{-6} (T/300)^{-0.5} & b \\
H^- + NO_2^+ + M & \rightarrow HNO_2 + M & 1.2 \times 10^{-25} & b \\
O^- + NO_2^+ & \rightarrow NO_2 + O & 3 \times 10^{-6} (T/300)^{-0.5} & 32
\end{align*}
$\text{H}^- + \text{O}^+ + \text{M} \rightarrow \text{OH} + \text{M}$

$\text{O}^- + \text{O}^+ + \text{M} \rightarrow \text{O}_2 + \text{M}$

$\text{H}^- + \text{NO}^+\cdot\text{O}_2 \rightarrow \text{HNO} + \text{O}_2$

$\text{O}^- + \text{NO}^+\cdot\text{O}_2 \rightarrow \text{NO}_2 + \text{O}_2$

$\text{H}^- + \text{N}^+ + \text{M} \rightarrow \text{NH} + \text{M}$

$\text{O}^- + \text{N}^+ + \text{M} \rightarrow \text{NO} + \text{M}$

$\text{H}^- + \text{N}_4^+ \rightarrow \text{H} + \text{N}_2 + \text{N}_2$

$\text{O}^- + \text{N}_4^+ \rightarrow \text{O} + \text{N}_2 + \text{N}_2$

$\text{H}^- + \text{O}_2^+\cdot\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{H}_2\text{O}$

$\text{O}^- + \text{O}_2^+\cdot\text{H}_2\text{O} \rightarrow \text{O} + \text{O}_2 + \text{H}_2\text{O}$

$\text{H}^- + \text{H}_3\text{O}^+\cdot\text{H}_2\text{O} \rightarrow \text{H}_2 + \text{H}_2\text{O} + \text{H}_2\text{O}$

$\text{O}^- + \text{H}_3\text{O}^+\cdot\text{H}_2\text{O} \rightarrow \text{OH} + \text{H}_2\text{O} + \text{H}_2\text{O}$

$\text{H}^- + \text{H}_3\text{O}^+\cdot(\text{H}_2\text{O})_2 \rightarrow \text{H}_2 + (\text{H}_2\text{O})_3$

$\text{O}^- + \text{H}_3\text{O}^+\cdot(\text{H}_2\text{O})_2 \rightarrow \text{OH} + (\text{H}_2\text{O})_3$

$\text{H}^- + \text{H}_2\text{NO}^+ \rightarrow \text{H}_2 + \text{HNO}$

$\text{O}^- + \text{H}_2\text{NO}^+ \rightarrow \text{OH} + \text{HNO}$

$\text{H}^- + \text{NH}_3^+ \rightarrow \text{H} + \text{NH}_3$

$\text{O}^- + \text{NH}_3^+ \rightarrow \text{O} + \text{NH}_3$

$\text{H}^- + \text{NH}_4^+ \rightarrow \text{H}_2 + \text{NH}_3$

$\text{O}^- + \text{NH}_4^+ \rightarrow \text{OH} + \text{NH}_3$

$\text{H}^- + \text{NO}^+\cdot\text{H}_2\text{O} \rightarrow \text{H} + \text{NO} + \text{H}_2\text{O}$

$\text{O}^- + \text{NO}^+\cdot\text{H}_2\text{O} \rightarrow \text{O} + \text{NO} + \text{H}_2\text{O}$

$\text{H}^- + \text{NO}^+\cdot(\text{H}_2\text{O})_2 \rightarrow \text{HNO} + \text{H}_2\text{O} + \text{H}_2\text{O}$

$\text{O}^- + \text{NO}^+\cdot(\text{H}_2\text{O})_2 \rightarrow \text{NO}_2 + \text{H}_2\text{O} + \text{H}_2\text{O}$
H\(^+\) + NO\(^+\)·(H\(_2\)O\(_3\)) \rightarrow \\
HNO + H\(_2\)O + H\(_2\)O + H\(_2\)O

O\(^-\) + NO\(^+\)·(H\(_2\)O\(_3\)) \rightarrow \\
NO\(_2\) + H\(_2\)O + H\(_2\)O + H\(_2\)O

(H\(_2\)O\(_3\)) \rightarrow H\(_2\)O + H\(_2\)O + H\(_2\)O

OH + NO\(_2\) + H\(_2\)O \rightarrow HNO\(_3\) + H\(_2\)O

N\(_2\)\(^+\) + H\(_2\)O \rightarrow H\(_2\)O\(^+\) + N\(_2\)

O + OH + M \rightarrow HO\(_2\) + M

O\(^{1\text{D}}\) + O\(_3\) \rightarrow O\(_2\) + O + O

O\(^{1\text{D}}\) + NO \rightarrow O\(_2\) + N

NH + NO \rightarrow N\(_2\) + OH

N\(_3\) + NO \rightarrow N\(_2\)O\(_2\) + N\(_2\)

NH\(_2\) + O \rightarrow H\(_2\) + NO

OH + NO\(_2\) \rightarrow HO\(_2\) + NO

NO\(_3\) + NO\(_2\) \rightarrow NO + NO\(_2\) + O\(_2\)

O\(^{1\text{D}}\) + NO\(_2\) \rightarrow O\(_2\) + NO

O\(^{1\text{D}}\) + N\(_2\)O \rightarrow NO + NO

NO\(_2\) + O\(_3\) \rightarrow O\(_2\) + O\(_2\) + NO

O + N\(_3\) \rightarrow NO + N\(_2\)

O + HNO \rightarrow OH + NO

HNO + O\(_2\) \rightarrow NO + HO\(_2\)

O + O + M \rightarrow O\(_2\) + M

Additional reactions of N\(_2\)/O\(_2\)/H\(_2\)O/CO\(_2\)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Coefficient (^c)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(_2)(A) + CO(_2) \rightarrow N(_2) + CO(_2)</td>
<td>2.5x10(^{-11})</td>
<td>36</td>
</tr>
<tr>
<td>N(_2)(A) + CO \rightarrow N(_2) + CO</td>
<td>1.1x10(^{-10})</td>
<td>36</td>
</tr>
<tr>
<td>O(^{1\text{D}}) + CO(_2) \rightarrow O + CO(_2)</td>
<td>7.4x10(^{-11})</td>
<td>b</td>
</tr>
<tr>
<td>Reaction</td>
<td>Rate Constant</td>
<td>Temperature ( T )</td>
</tr>
<tr>
<td>-----------------------------------------------</td>
<td>--------------------------------</td>
<td>---------------------</td>
</tr>
<tr>
<td>( \text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{H} )</td>
<td>( 1.12 \times 10^{-13} \exp(-9.1 \times 10^{-4} \times T) )</td>
<td>15</td>
</tr>
<tr>
<td>( \text{CO}_2^+ + \text{NO} \rightarrow \text{NO}^+ + \text{CO}_2 )</td>
<td>( 1.2 \times 10^{-10} )</td>
<td>4</td>
</tr>
<tr>
<td>( \text{CO}_2^+ + \text{O}_2 \rightarrow \text{O}_2^+ + \text{CO}_2 )</td>
<td>( 5.6 \times 10^{-11} )</td>
<td>4</td>
</tr>
<tr>
<td>( \text{CO}_2^+ + \text{NO}_2^- \rightarrow \text{CO}_2 + \text{NO}_2 )</td>
<td>( 2 \times 10^{-6} (T/300)^{-0.5} )</td>
<td>32</td>
</tr>
<tr>
<td>( \text{CO}_2^+ + \text{NO}_3^- \rightarrow \text{CO}_2 + \text{NO}_3 )</td>
<td>( 2 \times 10^{-6} (T/300)^{-0.5} )</td>
<td>32</td>
</tr>
<tr>
<td>( \text{CO}_2^+ + \text{O}_2^- \rightarrow \text{CO}_2 + \text{O}_2 )</td>
<td>( 2 \times 10^{-6} (T/300)^{-0.5} )</td>
<td>32</td>
</tr>
<tr>
<td>( \text{OH} + \text{CO} \rightarrow \text{HOCO}^* )</td>
<td>( 1.55 \times 10^{-13} )</td>
<td>b</td>
</tr>
<tr>
<td>( \text{CO}_2 + \text{H} \rightarrow \text{CO} + \text{OH} )</td>
<td>( 2.5 \times 10^{-10} \exp(-13300/T) )</td>
<td>15</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>
<td>15</td>
</tr>
<tr>
<td>( \text{CO} + \text{O}_2 \rightarrow \text{CO}_2 + \text{O} )</td>
<td>( 4.2 \times 10^{-12} \exp(-24000/T) )</td>
<td>15</td>
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<tr>
<td>( \text{CO} + \text{M} \rightarrow \text{CO}_2 + \text{M} )</td>
<td>( 1.7 \times 10^{-33} \exp(-1510/T) )</td>
<td>15</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>15</td>
</tr>
<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>
<td>15</td>
</tr>
<tr>
<td>( \text{HCO} + \text{H}_2 \rightarrow \text{CH}_2\text{O} + \text{H} )</td>
<td>( 3 \times 10^{-18} T^{2.0} \exp(-8972/T) )</td>
<td>15</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>
<td>15</td>
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<tr>
<td>( \text{HCO} + \text{H}_2 \rightarrow \text{H}_2 + \text{CO} )</td>
<td>( 2 \times 10^{-10} )</td>
<td>15</td>
</tr>
<tr>
<td>( \text{HCO} + \text{O} \rightarrow \text{H} + \text{CO}_2 )</td>
<td>( 5 \times 10^{-11} )</td>
<td>15</td>
</tr>
<tr>
<td>( \text{HCO} + \text{O} \rightarrow \text{OH} + \text{CO} )</td>
<td>( 5 \times 10^{-11} )</td>
<td>15</td>
</tr>
<tr>
<td>( \text{HCO} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{CO} )</td>
<td>( 5 \times 10^{-11} )</td>
<td>15</td>
</tr>
<tr>
<td>( \text{HCO} + \text{HO}_2 \rightarrow \text{OH} + \text{H} + \text{CO}_2 )</td>
<td>( 5 \times 10^{-11} )</td>
<td>15</td>
</tr>
<tr>
<td>( \text{HCO} + \text{H}_2\text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{H}_2\text{O} )</td>
<td>( 1.7 \times 10^{-13} \exp(-3486/T) )</td>
<td>15</td>
</tr>
<tr>
<td>( \text{HCO} + \text{H}_2\text{O} \rightarrow \text{CH}_2\text{O} + \text{OH} )</td>
<td>( 3 \times 10^{-16} T^{1.35} \exp(-13146/T) )</td>
<td>15</td>
</tr>
<tr>
<td>( \text{HCO} + \text{HCO} \rightarrow \text{CH}_2\text{O} + \text{CO} )</td>
<td>( 3 \times 10^{-11} )</td>
<td>15</td>
</tr>
<tr>
<td>( \text{HCO} + \text{HCO} \rightarrow \text{H}_2 + \text{CO} + \text{CO} )</td>
<td>( 5 \times 10^{-12} )</td>
<td>15</td>
</tr>
<tr>
<td>( \text{H}^- + \text{CO}_2^+ \rightarrow \text{H} + \text{CO}_2 )</td>
<td>( 3 \times 10^{-6} (T/300)^{-0.5} )</td>
<td>b</td>
</tr>
<tr>
<td>( \text{O}^- + \text{CO}_2^+ \rightarrow \text{O} + \text{CO}_2 )</td>
<td>( 3 \times 10^{-6} (T/300)^{-0.5} )</td>
<td>b</td>
</tr>
<tr>
<td>( \text{CH}_2\text{O} + \text{OH} \rightarrow \text{H} + \text{HCOOH} )</td>
<td>( 2 \times 10^{-13} )</td>
<td>31</td>
</tr>
<tr>
<td>Reaction</td>
<td>Rate Constant</td>
<td>Notes</td>
</tr>
<tr>
<td>-------------------------------------------------------------------------</td>
<td>-------------------</td>
<td>-------</td>
</tr>
<tr>
<td>HCOOH + OH → H₂O + CO₂ + H</td>
<td>4.8x10⁻¹³</td>
<td></td>
</tr>
<tr>
<td>CN + O → CO + N</td>
<td>1.7x10⁻¹¹</td>
<td></td>
</tr>
<tr>
<td>CN + N → N₂ + C</td>
<td>3x10⁻¹⁰</td>
<td>b</td>
</tr>
<tr>
<td>CN + N + M → CNN + M</td>
<td>2.76x10⁻³²</td>
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</tr>
<tr>
<td>CN + NO → N₂ + CO</td>
<td>1.2x10⁻¹³</td>
<td></td>
</tr>
<tr>
<td>CN + N₂O → CNN + NO</td>
<td>6.40x10⁻²¹T².6exp(-1860/T)</td>
<td></td>
</tr>
<tr>
<td>CN + HCN → NCCN + H</td>
<td>6.31x10⁻¹⁷T¹.57exp(-50/T)</td>
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<tr>
<td>CN + H₂O → HCN + OH</td>
<td>1.33x10⁻¹¹exp(-3752/T)</td>
<td></td>
</tr>
<tr>
<td>CN + H₂ → HCN + H</td>
<td>1.13x10⁻¹⁰exp(-2700/T)</td>
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<tr>
<td>CN + O₂ → NCO + O</td>
<td>1.1x10⁻¹¹exp(205/T)</td>
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<tr>
<td>CN + CO₂ → NCO + CO</td>
<td>2x10⁻¹⁵</td>
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</tr>
<tr>
<td>HCN + O → OH + CN</td>
<td>4.5x10⁻¹⁵T¹.58exp(-13386/T)</td>
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<tr>
<td>HCN + O → H + NCO</td>
<td>3.3x10⁻¹⁶T¹.47exp(-3774/T)</td>
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<tr>
<td>HCN + O → CO + NH</td>
<td>9.0x10⁻¹⁶T¹.21exp(-3824/T)</td>
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<tr>
<td>HCN + OH → H₂O + CN</td>
<td>1.28x10⁻¹¹exp(-4161/T)</td>
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</tr>
<tr>
<td>HCN + OH → HOHCN + H</td>
<td>2.01x10⁻¹¹exp(-8516/T)</td>
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<tr>
<td>HCN + OH → HNCO + H</td>
<td>2.84x10⁻¹³exp(-4397/T)</td>
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</tr>
<tr>
<td>HCN + OH → NH₂ + CO</td>
<td>1.07x10⁻¹³exp(-5892/T)</td>
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<tr>
<td>HCN + H → CN + H₂</td>
<td>6.31x10⁻¹⁰exp(-12400/T)</td>
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</tr>
<tr>
<td>NCO + H₂ → H + HNCO</td>
<td>1.26x10⁻²¹T³exp(-2012/T)</td>
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</tr>
<tr>
<td>NCO + O → NO + CO</td>
<td>1.48x10⁻¹¹</td>
<td></td>
</tr>
<tr>
<td>NCO + O₂ → NO + CO</td>
<td>1.32x10⁻¹²</td>
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</tr>
<tr>
<td>NCO + NO → CO + N₂ + O</td>
<td>7.61x10⁻¹²</td>
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<tr>
<td>NCO + NO → CO₂ + N₂</td>
<td>1.45x10⁻¹¹</td>
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<tr>
<td>NCO + NO → N₂O + CO</td>
<td>1.09x10⁻¹¹</td>
<td></td>
</tr>
<tr>
<td>NCCN + O → CN + NCO</td>
<td>4.15x10⁻¹¹exp(-5500/T)</td>
<td></td>
</tr>
</tbody>
</table>
NCCN + H → NCN + CN  \quad 8.59 \times 10^{-16}  \\
CO + H + M → HCO + M  \quad 1.99 \times 10^{-33} \ exp(-842/T)  \\
CO + NO₂ → CO₂ + NO  \quad 1.48 \times 10^{-10} \ exp(-17009/T)  \\
CO + O₃ → O₂ + CO₂  \quad 4 \times 10^{-25}  \\
C + CO + M → C₂O + M  \quad 6.3 \times 10^{-32}  \\
C₂O + O → CO + CO  \quad 9.51 \times 10^{-11}  \\
C₂O + O₂ → C₂O + CO  \quad 3.3 \times 10^{-13}  \\
C₂O + N → CO + CN  \quad 5.5 \times 10^{-10}  \\
C + N + M → CN + M  \quad 9.41 \times 10^{-33}  \\
C + NCCN → CN + CCN  \quad 3 \times 10^{-11}  \\
C + NO → CN + O  \quad 4.8 \times 10^{-11}  \\
C + N₂ + M → CNN + M  \quad 3.1 \times 10^{-33}  \\
C + N₃ → CN + N₂  \quad 1.10 \times 10^{-10}  \\
C + O₂ → CO + O  \quad 2.6 \times 10^{-11}  \\
CCN + O → CO + CN  \quad 6 \times 10^{-12}  \\
CCN + N → CN + CN  \quad 1 \times 10^{-10}  \\
CO₂ + N → CO + NO  \quad 3.2 \times 10^{-13} \ exp(-1710/T)  \\
C^+ + H^- → C + H  \quad 5 \times 10^{-8} \ (T/300)^{-0.5}  \\
C^+ + O^- → C + O  \quad 5 \times 10^{-8} \ (T/300)^{-0.5}  \\
C^+ + O₂^- → C + O₂  \quad 5 \times 10^{-8} \ (T/300)^{-0.5}
Additional reactions due to the presence of C$_3$H$_6$/C$_3$H$_8$

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$k^a$</th>
<th>$n$</th>
<th>$E_a$ (K)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_3$H$_8$ + H $\rightarrow$ n-C$_3$H$_7$ + H$_2$</td>
<td>4.31x10$^{-12}$</td>
<td>2.54</td>
<td>3.40x10$^{+03}$</td>
<td>7</td>
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<tr>
<td>C$_3$H$_8$ + H $\rightarrow$ i-C$_3$H$_7$ + H$_2$</td>
<td>1.90x10$^{-12}$</td>
<td>2.4</td>
<td>2.25x10$^{+03}$</td>
<td>7</td>
</tr>
<tr>
<td>C$_3$H$_8$ + O $\rightarrow$ n-C$_3$H$_7$ + OH</td>
<td>1.39x10$^{-12}$</td>
<td>2.68</td>
<td>1.87x10$^{+03}$</td>
<td>7</td>
</tr>
<tr>
<td>C$_3$H$_8$ + O $\rightarrow$ i-C$_3$H$_7$ + OH</td>
<td>4.08x10$^{-13}$</td>
<td>2.71</td>
<td>1.06x10$^{+03}$</td>
<td>7</td>
</tr>
<tr>
<td>C$_3$H$_8$ + C$_2$H$_5$ $\rightarrow$ n-C$_3$H$_7$ + C$_2$H$_6$</td>
<td>1.65x10$^{-15}$</td>
<td>3.65</td>
<td>4.60x10$^{+03}$</td>
<td>7</td>
</tr>
<tr>
<td>C$_3$H$_8$ + C$_2$H$_5$ $\rightarrow$ i-C$_3$H$_7$ + C$_2$H$_6$</td>
<td>9.31x10$^{-16}$</td>
<td>3.46</td>
<td>3.76x10$^{+03}$</td>
<td>7</td>
</tr>
<tr>
<td>C$_3$H$_8$ + CH$_3$ $\rightarrow$ n-C$_3$H$_7$ + CH$_4$</td>
<td>1.65x10$^{-15}$</td>
<td>3.65</td>
<td>3.60x10$^{+03}$</td>
<td>7</td>
</tr>
<tr>
<td>C$_3$H$_8$ + CH$_3$ $\rightarrow$ i-C$_3$H$_7$ + CH$_4$</td>
<td>9.31x10$^{-16}$</td>
<td>3.46</td>
<td>2.76x10$^{+03}$</td>
<td>7</td>
</tr>
<tr>
<td>C$_3$H$_8$ + OH $\rightarrow$ n-C$_3$H$_7$ + H$_2$O</td>
<td>7.95x10$^{-13}$</td>
<td>2</td>
<td>2.27x10$^{+02}$</td>
<td>7</td>
</tr>
<tr>
<td>C$_3$H$_8$ + OH $\rightarrow$ i-C$_3$H$_7$ + H$_2$O</td>
<td>1.44x10$^{-12}$</td>
<td>1</td>
<td>1.30x10$^{+02}$</td>
<td>7</td>
</tr>
<tr>
<td>n-C$_3$H$_7$ + O$_2$ $\rightarrow$ n-C$_3$H$_7$O$_2$</td>
<td>5.64x10$^{-12}$</td>
<td>-2.7</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>i-C$_3$H$_7$ + O$_2$ $\rightarrow$ (CH$_3$)$_2$CHO$_2$</td>
<td>1.50x10$^{-11}$</td>
<td>7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-C$_3$H$_7$O$_2$ + NO $\rightarrow$ n-C$_3$H$_7$O + NO$_2$</td>
<td>8.69x10$^{-12}$</td>
<td>18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-C$_3$H$_7$O$_2$ + NO $\rightarrow$ n-C$_3$H$_7$ONO$_2$</td>
<td>1.80x10$^{-13}$</td>
<td>18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(CH$_3$)$_2$CHO$_2$ + NO $\rightarrow$ (CH$_3$)$_2$CHO + NO$_2$</td>
<td>2.70x10$^{-12}$</td>
<td>-3.60x10$^{+02}$</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>(CH$_3$)$_2$CHO$_2$ + NO $\rightarrow$ (CH$_3$)$_2$CHONO$_2$</td>
<td>3.80x10$^{-13}$</td>
<td>18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-C$_3$H$_7$O$_2$ + HO$_2$ $\rightarrow$ n-C$_3$H$_7$OOH + O$_2$</td>
<td>1.90x10$^{-13}$</td>
<td>-1.30x10$^{+03}$</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>(CH$_3$)$_2$CHO$_2$ + HO$_2$ $\rightarrow$ (CH$_3$)$_2$CHOOH + O$_2$</td>
<td>1.90x10$^{-13}$</td>
<td>-1.30x10$^{+03}$</td>
<td>33</td>
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</tr>
<tr>
<td>n-C$_3$H$_7$O + O$_2$ $\rightarrow$ C$_2$H$_5$CHO + HO$_2$</td>
<td>6.00x10$^{-14}$</td>
<td>5.50x10$^{+02}$</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>(CH$_3$)$_2$CHO + O$_2$ $\rightarrow$ CH$_3$COCH$_3$ + HO$_2$</td>
<td>1.50x10$^{-14}$</td>
<td>2.00x10$^{+02}$</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>n-C$_3$H$_7$ $\rightarrow$ C$_2$H$_4$ + CH$_3$</td>
<td>1.20x10$^{+13}$</td>
<td>1.53x10$^{+04}$</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>n-C$_3$H$_7$ $\rightarrow$ C$_3$H$_6$ + H</td>
<td>1.09x10$^{+13}$</td>
<td>1.78x10$^{+04}$</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>Reaction</td>
<td>Rate Constant</td>
<td>Pressure (bar)</td>
<td>Temperature (K)</td>
<td>Notes</td>
</tr>
<tr>
<td>-------------------------------------------------------------------------</td>
<td>---------------</td>
<td>----------------</td>
<td>-----------------</td>
<td>-------</td>
</tr>
<tr>
<td>n-C$_3$H$_7$ + H$_2$ → C$_3$H$_8$ + H</td>
<td>$3.25\times10^{14}$</td>
<td>2.84</td>
<td>4.60$\times10^{03}$</td>
<td>7</td>
</tr>
<tr>
<td>n-C$_3$H$_7$ + H → C$_3$H$_6$ + H$_2$</td>
<td>$3.00\times10^{12}$</td>
<td></td>
<td></td>
<td>7</td>
</tr>
<tr>
<td>n-C$_3$H$_7$ + OH → C$_3$H$_6$ + H$_2$O</td>
<td>$4.00\times10^{11}$</td>
<td></td>
<td></td>
<td>7</td>
</tr>
<tr>
<td>n-C$_3$H$_7$ + OH → n-C$_3$H$_7$OH</td>
<td>$4.00\times10^{11}$</td>
<td></td>
<td></td>
<td>7</td>
</tr>
<tr>
<td>n-C$_3$H$_7$ + HO$_2$ → C$_3$H$_5$ + OH + HCHO</td>
<td>$4.00\times10^{11}$</td>
<td></td>
<td></td>
<td>7</td>
</tr>
<tr>
<td>n-C$_3$H$_7$ + H$_2$O → HO$_2$ + C$_3$H$_8$</td>
<td>$5.23\times10^{15}$</td>
<td>2.11</td>
<td>1.29$\times10^{03}$</td>
<td>7</td>
</tr>
<tr>
<td>n-C$_3$H$_7$ + CH$_4$ → C$_3$H$_8$ + CH$_3$</td>
<td>$3.63\times10^{16}$</td>
<td>4.2</td>
<td>5.47$\times10^{03}$</td>
<td>7</td>
</tr>
<tr>
<td>n-C$_3$H$_7$ + C$_2$H$_6$ → C$_3$H$_8$ + C$_2$H$_5$</td>
<td>$1.22\times10^{15}$</td>
<td>3.82</td>
<td>4.55$\times10^{03}$</td>
<td>7</td>
</tr>
<tr>
<td>n-C$_3$H$_7$ + HCHO → C$_3$H$_8$ + HCO</td>
<td>$7.63\times10^{14}$</td>
<td>2.9</td>
<td>2.95$\times10^{03}$</td>
<td>7</td>
</tr>
<tr>
<td>n-C$_3$H$_7$ + HCO → C$_3$H$_8$ + CO</td>
<td>$1.00\times10^{10}$</td>
<td></td>
<td></td>
<td>7</td>
</tr>
<tr>
<td>n-C$_3$H$_7$ + HCO → C$_3$H$_7$CHO</td>
<td>$2.00\times10^{11}$</td>
<td></td>
<td></td>
<td>7</td>
</tr>
<tr>
<td>n-C$_3$H$_7$ + CH$_3$ → CH$_4$ + C$_3$H$_6$</td>
<td>$3.06\times10^{12}$</td>
<td>-0.32</td>
<td></td>
<td>7</td>
</tr>
<tr>
<td>n-C$_3$H$_7$ + C$_2$H$_5$ → C$_3$H$_6$ + C$_2$H$_6$</td>
<td>$2.40\times10^{12}$</td>
<td></td>
<td></td>
<td>7</td>
</tr>
<tr>
<td>n-C$_3$H$_7$ + C$_2$H$_5$ → C$_3$H$_8$ + C$_2$H$_4$</td>
<td>$1.90\times10^{12}$</td>
<td></td>
<td></td>
<td>7</td>
</tr>
<tr>
<td>n-C$_3$H$_7$ + C$_3$H$_8$ → C$_3$H$_8$ + i-C$_3$H$_7$</td>
<td>$1.13\times10^{17}$</td>
<td>4</td>
<td>2.38$\times10^{03}$</td>
<td>7</td>
</tr>
<tr>
<td>n-C$_3$H$_7$ + n-C$_3$H$_7$ → C$_3$H$_6$ + C$_3$H$_8$</td>
<td>$2.80\times10^{12}$</td>
<td></td>
<td></td>
<td>7</td>
</tr>
<tr>
<td>n-C$_3$H$_7$O → C$_2$H$_5$ + HCHO</td>
<td>$5.01\times10^{13}$</td>
<td>7.85$\times10^{03}$</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>i-C$_3$H$_7$ → C$_3$H$_6$ + H</td>
<td>$1.60\times10^{13}$</td>
<td>1.80$\times10^{04}$</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>i-C$_3$H$_7$ + H$_2$ → C$_3$H$_8$ + H</td>
<td>$7.73\times10^{14}$</td>
<td>3.28</td>
<td>4.36$\times10^{03}$</td>
<td>7</td>
</tr>
<tr>
<td>i-C$_3$H$_7$ + H → C$_3$H$_6$ + H$_2$</td>
<td>$6.00\times10^{12}$</td>
<td></td>
<td></td>
<td>7</td>
</tr>
<tr>
<td>i-C$_3$H$_7$ + OH → C$_3$H$_6$ + H$_2$O</td>
<td>$4.00\times10^{11}$</td>
<td></td>
<td></td>
<td>7</td>
</tr>
<tr>
<td>i-C$_3$H$_7$ + HO$_2$ → CH$_3$CHO + CH$_3$ + OH</td>
<td>$4.00\times10^{11}$</td>
<td></td>
<td></td>
<td>7</td>
</tr>
<tr>
<td>i-C$_3$H$_7$ + H$_2$O → C$_3$H$_8$ + HO$_2$</td>
<td>$4.92\times10^{15}$</td>
<td>2.83</td>
<td>2.04$\times10^{03}$</td>
<td>7</td>
</tr>
<tr>
<td>i-C$_3$H$_7$ + C$_2$H$_6$ → C$_3$H$_8$ + C$_2$H$_5$</td>
<td>$3.55\times10^{16}$</td>
<td>4.2</td>
<td>4.39$\times10^{03}$</td>
<td>7</td>
</tr>
<tr>
<td>i-C$_3$H$_7$ + HCHO → C$_3$H$_8$ + HCO</td>
<td>$1.80\times10^{13}$</td>
<td>3.50$\times10^{03}$</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>i-C$_3$H$_7$ + HCO → C$_3$H$_8$ + CO</td>
<td>$2.00\times10^{10}$</td>
<td></td>
<td></td>
<td>7</td>
</tr>
<tr>
<td>i-C$_3$H$_7$ + HCO → C$_3$H$_7$CHO</td>
<td>$3.00\times10^{11}$</td>
<td></td>
<td></td>
<td>7</td>
</tr>
</tbody>
</table>
\[
\begin{array}{llll}
\text{i-C}_3\text{H}_2 + \text{CH}_3 & \rightarrow & \text{CH}_4 + \text{C}_3\text{H}_6 & 7.52 \times 10^{-12} \\
\text{i-C}_3\text{H}_2 + \text{C}_2\text{H}_5 & \rightarrow & \text{C}_3\text{H}_8 + \text{C}_2\text{H}_4 & 4.16 \times 10^{-12} \\
\text{i-C}_3\text{H}_2 + \text{C}_2\text{H}_5 & \rightarrow & \text{C}_3\text{H}_6 + \text{C}_2\text{H}_6 & 5.20 \times 10^{-12} \\
\text{i-C}_3\text{H}_2 + \text{C}_2\text{H}_4 & \rightarrow & \text{C}_3\text{H}_6 + \text{C}_2\text{H}_5 & 4.40 \times 10^{-14} \\
\text{i-C}_3\text{H}_2 + \text{C}_3\text{H}_8 & \rightarrow & \text{C}_3\text{H}_8 + \text{n-C}_3\text{H}_7 & 3.55 \times 10^{-16} \\
\text{i-C}_3\text{H}_2 + \text{n-C}_3\text{H}_7 & \rightarrow & \text{C}_3\text{H}_6 + \text{C}_3\text{H}_8 & 1.16 \times 10^{-11} \\
\text{i-C}_3\text{H}_2 + \text{i-C}_3\text{H}_7 & \rightarrow & \text{C}_3\text{H}_6 + \text{C}_3\text{H}_8 & 6.50 \times 10^{-12} \\
\text{\textit{CH}}_4 + \text{H} & \rightarrow & \text{\textit{CH}}_3 + \text{H}_2 & 1.01 \times 10^{-12} \\
\text{\textit{CH}}_4 + \text{HO}_2 & \rightarrow & \text{\textit{CH}}_3 + \text{H}_2\text{O}_2 & 3.00 \times 10^{-13} \\
\text{\textit{C}}_2\text{H}_6 + \text{H} & \rightarrow & \text{\textit{C}}_2\text{H}_5 + \text{H}_2 & 4.03 \times 10^{-12} \\
\text{\textit{C}}_2\text{H}_6 + \text{O} & \rightarrow & \text{\textit{C}}_2\text{H}_5 + \text{OH} & 2.91 \times 10^{-12} \\
\text{\textit{C}}_2\text{H}_6 + \text{OH} & \rightarrow & \text{\textit{C}}_2\text{H}_5 + \text{H}_2\text{O} & 1.62 \times 10^{-12} \\
\text{\textit{C}}_2\text{H}_6 + \text{HO}_2 & \rightarrow & \text{\textit{H}}_2\text{O}_2 + \text{\textit{C}}_2\text{H}_5 & 4.90 \times 10^{-13} \\
\text{HCHO} + \text{HO}_2 & \rightarrow & \text{\textit{H}}_2\text{O}_2 + \text{HCO} & 3.30 \times 10^{-12} \\
\text{HCHO} + \text{NO}_2 & \rightarrow & \text{\textit{H}}_2\text{O}_2 + \text{HNO}_2 & 8.29 \times 10^{-16} \\
\text{HCHO} + \text{NO}_3 & \rightarrow & \text{\textit{H}}_2\text{O}_2 + \text{HNO}_3 & 5.80 \times 10^{-16} \\
\text{CO}_2 + \text{N} & \rightarrow & \text{CO} + \text{NO} & 3.20 \times 10^{-13} \\
\text{\textit{CH}}_3 + \text{H}_2 & \rightarrow & \text{\textit{CH}}_4 + \text{H} & 2.61 \times 10^{-14} \\
\text{\textit{CH}}_3 + \text{O}_2 & \rightarrow & \text{HCHO} + \text{OH} & 1.60 \times 10^{-15} \\
\text{\textit{CH}}_3 + \text{OH} & \rightarrow & \text{\textit{CH}}_3\text{OH} & 1.15 \times 10^{-08} \\
\text{\textit{CH}}_3 + \text{OH} & \rightarrow & \text{\textit{CH}}_2\text{OH} + \text{H} & 1.25 \times 10^{-05} \\
\text{\textit{CH}}_3 + \text{H}_2\text{O}_2 & \rightarrow & \text{\textit{CH}}_4 + \text{HO}_2 & 2.00 \times 10^{-14} \\
\text{\textit{CH}}_3 + \text{C}_2\text{H}_6 & \rightarrow & \text{\textit{CH}}_4 + \text{\textit{C}}_2\text{H}_5 & 9.79 \times 10^{-17} \\
\text{\textit{CH}}_3 + \text{HCHO} & \rightarrow & \text{\textit{CH}}_4 + \text{HCO} & 1.87 \times 10^{-15} \\
\text{\textit{CH}}_3 + \text{CO} & \rightarrow & \text{\textit{CH}}_3\text{CO} & 1.98 \times 10^{-10} \\
\text{\textit{CH}}_3 + \text{HCO} & \rightarrow & \text{\textit{CH}}_4 + \text{CO} & 2.00 \times 10^{-10} \\
\text{\textit{CH}}_3 + \text{HCO} & \rightarrow & \text{\textit{CH}}_3\text{CHO} & 3.00 \times 10^{-11}
\end{array}
\]
\begin{align*}
\text{CH}_3 + \text{N} & \rightarrow \text{H} + \text{H} + \text{HCN} \quad 3.32 \times 10^{-13} \quad 18 \\
\text{CH}_3 + \text{N} & \rightarrow \text{HCN} + \text{H}_2 \quad 8.59 \times 10^{-12} \quad 18 \\
\text{CH}_3 + \text{NO}_2 & \rightarrow \text{CH}_3\text{NO}_2 \quad 3.44 \times 10^{-11} \quad -0.6 \quad 18 \\
\text{CH}_3 + \text{NO}_2 & \rightarrow \text{HCHO} + \text{HNO} \quad 5.39 \times 10^{-12} \quad 18 \\
\text{CH}_3 + \text{NO}_2 & \rightarrow \text{CH}_3\text{ONO} \quad 1.16 \times 10^{-13} \quad 18 \\
\text{CH}_3 + \text{NO}_2 & \rightarrow \text{CH}_3\text{O} + \text{NO} \quad 2.50 \times 10^{-11} \quad 18 \\
\text{C}_2\text{H}_5 & \rightarrow \text{C}_2\text{H}_4 + \text{H} \quad 4.44 \times 10^{-12} \quad 1.19 \quad 1.87 \times 10^{+04} \quad 19 \\
\text{C}_2\text{H}_5 + \text{H}_2 & \rightarrow \text{C}_2\text{H}_6 + \text{H} \quad 4.22 \times 10^{-15} \quad 3.6 \quad 4.25 \times 10^{+03} \quad 19 \\
\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} \quad 1.95 \times 10^{+03} \quad 19 \\
\text{C}_2\text{H}_5 + \text{O}_2 & \rightarrow \text{C}_2\text{H}_3\text{O}_2 \quad 7.66 \times 10^{-10} \quad -5.12 \quad 1.49 \times 10^{+03} \quad 19 \\
\text{C}_2\text{H}_5 + \text{O}_2 & \rightarrow \text{CH}_3\text{CHO} + \text{OH} \quad 1.14 \times 10^{-13} \quad -0.12 \quad 4.28 \times 10^{+03} \quad 19 \\
\text{C}_2\text{H}_5 + \text{H} & \rightarrow \text{C}_2\text{H}_6 \quad 1.66 \times 10^{-10} \quad 0 \quad 19 \\
\text{C}_2\text{H}_5 + \text{H} & \rightarrow \text{CH}_3 + \text{CH}_3 \quad 6.05 \times 10^{-10} \quad -1.4 \quad 6.59 \times 10^{+02} \quad 19 \\
\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 19 \\
\text{C}_2\text{H}_5 + \text{O} & \rightarrow \text{CH}_3\text{CHO} + \text{H} \quad 1.33 \times 10^{-10} \quad 19 \\
\text{C}_2\text{H}_5 + \text{O} & \rightarrow \text{HCHO} + \text{CH}_3 \quad 2.67 \times 10^{-11} \quad 19 \\
\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 19 \\
\text{C}_2\text{H}_5 + \text{OH} & \rightarrow \text{CH}_3 + \text{H} + \text{HCHO} \quad 4.00 \times 10^{-11} \quad 19 \\
\text{C}_2\text{H}_5 + \text{HO}_2 & \rightarrow \text{CH}_3 + \text{HCHO} + \text{OH} \quad 4.00 \times 10^{-11} \quad 19 \\
\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 19 \\
\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 19 \\
\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} \quad 4.90 \times 10^{+02} \quad 19 \\
\text{C}_2\text{H}_5 + \text{HCHO} & \rightarrow \text{C}_2\text{H}_6 + \text{HCO} \quad 8.33 \times 10^{-14} \quad 2.81 \quad 2.95 \times 10^{+03} \quad 19 \\
\text{C}_2\text{H}_5 + \text{HCO} & \rightarrow \text{C}_2\text{H}_6 + \text{CO} \quad 2.00 \times 10^{-10} \quad 19 \\
\text{C}_2\text{H}_5 + \text{HCO} & \rightarrow \text{C}_2\text{H}_5\text{CHO} \quad 3.00 \times 10^{-11} \quad 19 \\
\text{C}_2\text{H}_5 + \text{CH}_3 & \rightarrow \text{C}_3\text{H}_8 \quad 4.70 \times 10^{-11} \quad -0.5 \quad 19 \\
\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} \quad -0.5 \quad 19
\end{align*}
$C_2H_5 + C_2H_5 \rightarrow C_2H_4 + C_2H_6$  
$2.30 \times 10^{-12}$  
$C_2H_4 + H \rightarrow C_2H_5$  
$6.87 \times 10^{-12}$  
$1.49$  
$4.99 \times 10^{+02}$  
$C_2H_4 + H \rightarrow C_2H_3 + H_2$  
$4.07 \times 10^{-12}$  
$2.53$  
$6.16 \times 10^{+03}$  
$C_2H_4 + O \rightarrow CH_3 + HCO$  
$1.52 \times 10^{-12}$  
$1.55$  
$2.15 \times 10^{+02}$  
$C_2H_4 + O \rightarrow CH_2CHO + H$  
$6.24 \times 10^{-13}$  
$C_2H_4 + O \rightarrow CH_2CO + H_2$  
$3.81 \times 10^{-14}$  
$C_2H_4 + O \rightarrow C_2H_3 + OH$  
$1.33 \times 10^{-12}$  
$1.91$  
$1.88 \times 10^{+03}$  
$C_2H_4 + OH \rightarrow C_2H_3 + H_2O$  
$1.69 \times 10^{-13}$  
$2.75$  
$2.10 \times 10^{+03}$  
$C_2H_4 + OH \rightarrow C_2H_4OH$  
$9.00 \times 10^{-12}$  
$C_2H_4 + HO_2 \rightarrow CH_3CHO + OH$  
$1.00 \times 10^{-14}$  
$4.00 \times 10^{+03}$  
$C_2H_3 + H_2 \rightarrow C_2H_4 + H$  
$1.64 \times 10^{-13}$  
$2.63$  
$4.30 \times 10^{+03}$  
$C_2H_3 + O_2 \rightarrow C_2H_2 + HO_2$  
$2.00 \times 10^{-13}$  
$C_2H_3 + H \rightarrow C_2H_2 + H_2$  
$1.60 \times 10^{-10}$  
$C_2H_3 + O \rightarrow CH_2CO + H$  
$1.60 \times 10^{-10}$  
$C_2H_3 + OH \rightarrow H_2O + C_2H_2$  
$5.00 \times 10^{-11}$  
$C_2H_3 + OH \rightarrow CH_3CHO$  
$5.00 \times 10^{-11}$  
$C_2H_3 + HO_2 \rightarrow OH + CH_3 + CO$  
$5.00 \times 10^{-11}$  
$C_2H_3 + H_2O_2 \rightarrow C_2H_4 + HO_2$  
$2.00 \times 10^{-14}$  
$3.00 \times 10^{+02}$  
$C_2H_3 + CH_4 \rightarrow C_2H_4 + CH_3$  
$2.18 \times 10^{-14}$  
$4.02$  
$2.75 \times 10^{+03}$  
$C_2H_3 + C_2H_6 \rightarrow C_2H_4 + C_2H_5$  
$1.50 \times 10^{-13}$  
$3.3$  
$5.29 \times 10^{+03}$  
$C_2H_3 + HCHO \rightarrow C_2H_4 + HCO$  
$8.22 \times 10^{-14}$  
$2.81$  
$2.95 \times 10^{+03}$  
$C_2H_3 + CO \rightarrow C_2H_3CO$  
$2.50 \times 10^{-13}$  
$2.42 \times 10^{+03}$  
$C_2H_3 + HCO \rightarrow C_2H_4 + CO$  
$1.50 \times 10^{-10}$  
$C_2H_3 + HCO \rightarrow C_2H_3CHO$  
$3.00 \times 10^{-11}$  
$C_2H_3 + CH_3 \rightarrow C_2H_2 + CH_4$  
$3.40 \times 10^{-11}$  
$C_2H_3 + CH_3 \rightarrow C_3H_6$  
$1.20 \times 10^{-10}$  
$C_2H_3 + C_2H_5 \rightarrow C_2H_4 + C_2H_4$  
$8.00 \times 10^{-13}$
\[ \text{C}_2\text{H}_3 + \text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_2 + \text{C}_2\text{H}_6 \quad 8.00 \times 10^{-13} \]

\[ \text{C}_2\text{H}_3 + \text{C}_2\text{H}_3 \rightarrow \text{C}_2\text{H}_4 + \text{C}_2\text{H}_2 \quad 1.60 \times 10^{-12} \]

\[ \text{C}_2\text{H}_2 + \text{O} \rightarrow \text{CH}_2 + \text{CO} \quad 5.15 \times 10^{-12} \quad 1.17 \quad 1.07 \times 10^{+03} \]

\[ \text{C}_2\text{H}_2 + \text{O} \rightarrow \text{C}_2\text{HO} + \text{H} \quad 1.50 \times 10^{-11} \quad 2.29 \times 10^{+03} \]

\[ \text{C}_2\text{H}_2 + \text{OH} \rightarrow \text{C}_2\text{H} + \text{H}_2\text{O} \quad 1.04 \times 10^{-13} \quad 2.68 \quad 6.06 \times 10^{+03} \]

\[ \text{C}_2\text{H}_2 + \text{HO}_2 \rightarrow \text{CH}_2\text{CO} + \text{OH} \quad 1.00 \times 10^{-14} \quad 4.00 \times 10^{+03} \]

\[ \text{C}_2\text{H}_2 + \text{CH}_3 \rightarrow \text{C}_3\text{H}_5 \quad 1.00 \times 10^{-12} \quad 3.88 \times 10^{+03} \]

\[ \text{C}_2\text{H}_2 + \text{OH} \rightarrow \text{C}_2\text{H}_2\text{OH} \quad 8.50 \times 10^{-12} \quad 7.05 \times 10^{+02} \]

\[ \text{C}_2\text{H} + \text{H}_2 \rightarrow \text{C}_2\text{H}_2 + \text{H} \quad 1.90 \times 10^{-11} \quad 1.45 \times 10^{+03} \]

\[ \text{C}_2\text{H} + \text{O}_2 \rightarrow \text{CO} + \text{HCO} \quad 4.00 \times 10^{-12} \]

\[ \text{C}_2\text{H} + \text{O}_2 \rightarrow \text{C}_2\text{HO} + \text{O} \quad 1.00 \times 10^{-12} \]

\[ \text{C}_2\text{H} + \text{H} \rightarrow \text{C}_2\text{H}_2 \quad 3.00 \times 10^{-10} \]

\[ \text{C}_2\text{H} + \text{O} \rightarrow \text{CH} + \text{CO} \quad 3.00 \times 10^{-11} \]

\[ \text{C}_2\text{H} + \text{OH} \rightarrow \text{C}_2\text{H}_2 + \text{O} \quad 3.00 \times 10^{-11} \]

\[ \text{C}_2\text{H} + \text{OH} \rightarrow \text{CH}_2 + \text{CO} \quad 3.00 \times 10^{-11} \]

\[ \text{C}_2\text{H} + \text{HO}_2 \rightarrow \text{C}_2\text{H}_2 + \text{O}_2 \quad 3.00 \times 10^{-11} \]

\[ \text{C}_2\text{H} + \text{HO}_2 \rightarrow \text{C}_2\text{HO} + \text{OH} \quad 3.00 \times 10^{-11} \]

\[ \text{C}_2\text{H} + \text{CH}_4 \rightarrow \text{C}_2\text{H}_2 + \text{CH}_3 \quad 3.00 \times 10^{-12} \quad 2.50 \times 10^{+02} \]

\[ \text{C}_2\text{H} + \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_2 + \text{C}_2\text{H}_5 \quad 6.00 \times 10^{-12} \]

\[ \text{C}_2\text{H} + \text{CO} \rightarrow \text{C}_2\text{HCO} \quad 2.50 \times 10^{-13} \quad 2.42 \times 10^{+03} \]

\[ \text{C}_2\text{H} + \text{HCO} \rightarrow \text{C}_2\text{H}_2 + \text{CO} \quad 1.00 \times 10^{-10} \]

\[ \text{C}_2\text{H} + \text{CH}_3 \rightarrow \text{C}_3\text{H}_3 + \text{H} \quad 4.00 \times 10^{-11} \]

\[ \text{C}_2\text{H} + \text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_2 + \text{C}_2\text{H}_4 \quad 3.00 \times 10^{-12} \]

\[ \text{C}_2\text{H} + \text{C}_2\text{H}_5 \rightarrow \text{C}_3\text{H}_3 + \text{CH}_3 \quad 3.00 \times 10^{-11} \]

\[ \text{C}_2\text{H} + \text{C}_2\text{H}_3 \rightarrow \text{C}_2\text{H}_2 + \text{C}_2\text{H}_2 \quad 1.60 \times 10^{-12} \]

\[ \text{C}_2\text{H} + \text{C}_2\text{H} \rightarrow \text{C}_2\text{H}_2 + \text{C}_2 \quad 3.00 \times 10^{-12} \]

\[ \text{CH}_3\text{CO} + \text{M} \rightarrow \text{CH}_3 + \text{CO} + \text{M} \quad 6.44 \times 10^{-03} \quad -8.62 \quad 1.13 \times 10^{+04} \]
\[
CH_3CO + O_2 \rightarrow CH_3COO_2 \quad 3.00 \times 10^{-12}
\]
\[
CH_3CO + H \rightarrow CH_3 + HCO \quad 1.60 \times 10^{-10}
\]
\[
CH_3CO + O \rightarrow CH_3 + CO_2 \quad 1.60 \times 10^{-11}
\]
\[
CH_3CO + OH \rightarrow CH_2CO + H_2O \quad 2.00 \times 10^{-11}
\]
\[
CH_3CO + OH \rightarrow CH_3 + CO + OH \quad 5.00 \times 10^{-11}
\]
\[
CH_3CO + HO_2 \rightarrow CH_3 + CO_2 + OH \quad 5.00 \times 10^{-11}
\]
\[
CH_3CO + H_2O_2 \rightarrow CH_3CHO + HO_2 \quad 3.00 \times 10^{-13} \quad 4.14 \times 10^{+03}
\]
\[
CH_3CO + HCO \rightarrow CH_3CHO + CO \quad 1.50 \times 10^{-11}
\]
\[
CH_3CO + HCO \rightarrow CH_3COCHO \quad 3.00 \times 10^{-11}
\]
\[
CH_3CO + CH_3 \rightarrow CH_3COCH_3 \quad 6.70 \times 10^{-09} -0.8
\]
\[
CH_3CO + C_2H_5 \rightarrow C_2H_5COCH_3 \quad 5.19 \times 10^{-10}
\]
\[
CH_3CO + C_2H_3 \rightarrow CH_3 + CH_2CHCO \quad 3.00 \times 10^{-11}
\]
\[
CH_3CO + C_2H \rightarrow C_2HCO + CH_3 \quad 3.00 \times 10^{-11}
\]
\[
CH_3O_2 + H \rightarrow CH_3O + OH \quad 1.60 \times 10^{-10}
\]
\[
CH_3O_2 + O \rightarrow CH_3O + O_2 \quad 6.00 \times 10^{-11}
\]
\[
CH_3O_2 + OH \rightarrow CH_3OH + O_2 \quad 1.00 \times 10^{-10}
\]
\[
CH_3O_2 + HO_2 \rightarrow CH_3OOH + OH \quad 7.70 \times 10^{-14} \quad -1.30 \times 10^{+03}
\]
\[
CH_3O_2 + H_2O_2 \rightarrow CH_3OOH + HO_2 \quad 4.00 \times 10^{-12} \quad 5.00 \times 10^{+03}
\]
\[
CH_3O_2 + HCO \rightarrow CH_3O + H + CO_2 \quad 5.00 \times 10^{-11}
\]
\[
CH_3O_2 + CH_3 \rightarrow CH_3O + CH_3O \quad 4.00 \times 10^{-11}
\]
\[
CH_3O_2 + C_2H_5 \rightarrow CH_3O + C_2H_5O \quad 4.00 \times 10^{-11}
\]
\[
CH_3O_2 + C_2H_3 \rightarrow CH_3O + C_2H_3O \quad 4.00 \times 10^{-11}
\]
\[
CH_3O_2 + C_2H \rightarrow CH_3O + C_2HO \quad 4.00 \times 10^{-11}
\]
\[
CH_3O_2 + CH_3CO \rightarrow CH_3 + CO_2 + CH_3O \quad 4.00 \times 10^{-11}
\]
\[
CH_3O_2 + CH_3O \rightarrow CH_3O + CH_3O + O_2 \quad 1.30 \times 10^{-13}
\]
\[
CH_3O_2 + CH_3O \rightarrow CH_3OH + HCHO + O_2 \quad 2.10 \times 10^{-13}
\]
\[
CH_3O_2 + NO \rightarrow CH_3O + NO_2 \quad 4.20 \times 10^{-12} \quad -1.80 \times 10^{+02}
\]
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
<th>Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{HCHO} + \text{HO}_2$</td>
<td>$1.10 \times 10^{-13}$</td>
<td>1.31 $\times 10^{03}$</td>
</tr>
<tr>
<td>$\text{CH}_3\text{O} + \text{H} \rightarrow \text{HCHO} + \text{H}_2$</td>
<td>$3.30 \times 10^{-11}$</td>
<td>19</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>19</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>19</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>19</td>
</tr>
<tr>
<td>$\text{CH}_3\text{O} + \text{CH}_4 \rightarrow \text{CH}_3\text{OH} + \text{CH}_3$</td>
<td>$2.60 \times 10^{-13}$</td>
<td>4.45 $\times 10^{03}$</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>$4.00 \times 10^{-13}$</td>
<td>3.57 $\times 10^{03}$</td>
</tr>
<tr>
<td>$\text{CH}_3\text{O} + \text{HCHO} \rightarrow \text{CH}_3\text{OH} + \text{HCO}$</td>
<td>$1.70 \times 10^{-13}$</td>
<td>1.50 $\times 10^{03}$</td>
</tr>
<tr>
<td>$\text{CH}_3\text{O} + \text{CO} \rightarrow \text{CH}_3 + \text{CO}_2$</td>
<td>$2.60 \times 10^{-11}$</td>
<td>5.94 $\times 10^{03}$</td>
</tr>
<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>
<td>19</td>
</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>19</td>
</tr>
<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>19</td>
</tr>
<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>19</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>19</td>
</tr>
<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>19</td>
</tr>
<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>19</td>
</tr>
<tr>
<td>$\text{CH}_3\text{O} + \text{CH}_3\text{CO} \rightarrow \text{HCHO} + \text{CH}_3\text{CHO}$</td>
<td>$1.00 \times 10^{-11}$</td>
<td>19</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>19</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>19</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>18</td>
</tr>
<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>18</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>18</td>
</tr>
<tr>
<td>$\text{CH}_3\text{O} + \text{NO} \rightarrow \text{HCHO} + \text{HNO}$</td>
<td>$4.00 \times 10^{-12}$</td>
<td>-0.7</td>
</tr>
<tr>
<td>$\text{CH}_3\text{OH} + \text{O} \rightarrow \text{CH}_2\text{OH} + \text{OH}$</td>
<td>$4.63 \times 10^{-14}$</td>
<td>3.77</td>
</tr>
<tr>
<td>$\text{CH}_3\text{OH} + \text{O} \rightarrow \text{CH}_3\text{O} + \text{OH}$</td>
<td>$7.08 \times 10^{-13}$</td>
<td>1.54</td>
</tr>
<tr>
<td>$\text{CH}_3\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{CH}_3\text{OH}$</td>
<td>$8.79 \times 10^{-13}$</td>
<td>20</td>
</tr>
<tr>
<td>$\text{CH}_3\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{CH}_3\text{O}$</td>
<td>$1.66 \times 10^{-11}$</td>
<td>8.54 $\times 10^{02}$</td>
</tr>
</tbody>
</table>
\[
\begin{align*}
\text{CH}_3\text{OH} + \text{H} & \rightarrow \text{CH}_2\text{OH} + \text{H}_2 \quad 1.39 \times 10^{-11} \quad 20 \\
\text{CH}_3\text{OH} + \text{H} & \rightarrow \text{CH}_3\text{O} + \text{H}_2 \quad 6.64 \times 10^{-11} \quad 3.07 \times 10^{+03} \quad 20 \\
\text{C}_2\text{H}_5 + \text{NO} & \rightarrow \text{C}_2\text{H}_5\text{NO} \quad 6.49 \times 10^{-11} \quad -3.37 \quad 1.74 \times 10^{+03} \quad 18 \\
\text{C}_3\text{H}_6 + \text{O} & \rightarrow \text{Methyl Oxirane} \quad 9.05 \times 10^{-12} \quad 6.10 \times 10^{+02} \quad 33 \\
\text{C}_3\text{H}_6 + \text{O} & \rightarrow \text{CH}_2\text{CHO} + \text{CH}_3 \quad 9.05 \times 10^{-12} \quad 6.10 \times 10^{+02} \quad 33 \\
\text{C}_3\text{H}_6 + \text{O} & \rightarrow \text{C}_2\text{H}_5 + \text{HCO} \quad 6.03 \times 10^{-12} \quad 6.10 \times 10^{+02} \quad 33 \\
\text{C}_3\text{H}_6 + \text{OH} & \rightarrow \text{CH}_3\text{CH}CH\text{CH}_2\text{OH} \quad 6.56 \times 10^{-11} \quad -1.48 \quad 3.61 \times 10^{+02} \quad 33 \\
\text{C}_3\text{H}_6 + \text{OH} & \rightarrow \text{CH}_3\text{CHOHCH}_2 \quad 3.53 \times 10^{-11} \quad -1.48 \quad 3.61 \times 10^{+02} \quad 33 \\
\text{C}_3\text{H}_6 + \text{H} & \rightarrow \text{CH}_3 + \text{C}_2\text{H}_4 \quad 1.20 \times 10^{-11} \quad 6.55 \times 10^{+02} \quad 34 \\
\text{C}_3\text{H}_6 + \text{H} & \rightarrow \text{i-C}_3\text{H}_7 \quad 1.00 \times 10^{-11} \quad 0.25 \quad 5.93 \times 10^{+02} \quad 34 \\
\text{CH}_3\text{CH(OH)CH}_2 + \text{O}_2 \rightarrow & \quad 3.90 \times 10^{-12} \quad 33 \\
\text{CH}_3\text{CH(OH)CH}_2\text{OO} & \quad \text{CH}_3\text{CH(OH)CH}_2\text{OH} \quad 1.16 \times 10^{-11} \quad 33 \\
\text{CH}_3\text{CHCH}_2\text{OH} + \text{O}_2 \rightarrow & \quad 1.16 \times 10^{-11} \quad 33 \\
\text{CH}_3\text{CH(OO)CH}_2\text{OH} & \quad \text{CH}_3\text{CH(OH)CH}_2\text{OO} + \text{NO} \rightarrow \text{NO}_2 + \text{CH}_3\text{CH(OH)CH}_2\text{O} \quad 1.00 \times 10^{-14} \quad 33 \\
\text{CH}_3\text{CH(OO)CH}_2\text{OH} + \text{NO} \rightarrow \text{NO}_2 + \text{CH}_3\text{CH(O)CH}_2\text{O} \quad 1.00 \times 10^{-14} \quad 33 \\
\text{CH}_3\text{CH(OH)CH}_2\text{O} \rightarrow \text{HCHO} + \text{CH}_3\text{CHOH} \quad 7.94 \times 10^{+13} \quad 1.05 \times 10^{+04} \quad 33 \\
\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} \quad 1.00 \times 10^{-11} \quad 33 \\
\text{CH}_3\text{CHOH} + \text{O}_2 \rightarrow \text{CH}_3\text{CHO} + \text{HO}_2 \quad 1.00 \times 10^{-11} \quad 33 \\
\text{CH}_2\text{OH} + \text{O}_2 \rightarrow \text{HCHO} + \text{HO}_2 \quad 1.06 \times 10^{-10} \quad -1.58 \quad 8.01 \times 10^{+02} \quad 33 \\
\text{CH}_2\text{CHO} + \text{NO} \rightarrow \text{ONCH}_2\text{CHO} \quad 2.51 \times 10^{-11} \quad 37 \\
\text{CH}_2\text{CHO} + \text{O}_2 \rightarrow \text{CHOCHO} + \text{OH} \quad 2.20 \times 10^{+13} \quad 37 \\
\text{CH}_2\text{CHO} + \text{O}_2 \rightarrow \text{HCHO} + \text{CO} + \text{OH} \quad 3.00 \times 10^{-14} \quad 37
\end{align*}
\]
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂CHCHO + OH → H₂O + CH₂CHCO</td>
<td>2.66×10⁻¹¹</td>
<td>37</td>
</tr>
<tr>
<td>Methyl Oxirane + OH → H₂O + Products</td>
<td>4.95×10⁻¹³</td>
<td>18</td>
</tr>
<tr>
<td>C₂H₆ + N → CH₃NCH₃</td>
<td>4.00×10⁻¹⁶</td>
<td>18</td>
</tr>
<tr>
<td>C₂H₅O₂ + NO → C₂H₅O + NO₂</td>
<td>8.90×10⁻¹²</td>
<td>18</td>
</tr>
<tr>
<td>C₂H₅O₂ + NO → C₂H₅ONO₂</td>
<td>1.30×10⁻¹³</td>
<td>18</td>
</tr>
<tr>
<td>C₂H₅O₂ + NO₂ → C₂H₅OONO₂</td>
<td>2.59×10⁻¹⁰⁻³.₇₄ 1.03×10⁴₀³</td>
<td>18</td>
</tr>
<tr>
<td>C₂H₅O → C₂H₄ + HO₂</td>
<td>2.69×10⁻³⁶</td>
<td>18</td>
</tr>
<tr>
<td>C₂H₅O + NO → C₂H₅ONO</td>
<td>2.63×10⁻¹¹</td>
<td>18</td>
</tr>
<tr>
<td>C₂H₅O + NO → CH₃CHO + HNO</td>
<td>1.30×10⁻¹¹</td>
<td>18</td>
</tr>
<tr>
<td>C₂H₅O + NO₂ → C₂H₅ONO₂</td>
<td>2.80×10⁻¹¹</td>
<td>18</td>
</tr>
<tr>
<td>C₂H₅O + NO₂ → CH₃CHO + HNO₂</td>
<td>6.61×10⁻¹²</td>
<td>18</td>
</tr>
<tr>
<td>C₂H₄ + N → HCN + CH₃</td>
<td>2.46×10⁻¹²⁻³.₂₈ 1.36×10⁴₀³</td>
<td>18</td>
</tr>
<tr>
<td>CH₄ + N → HCN + H₂ + H</td>
<td>2.50×10⁻¹⁴</td>
<td>18</td>
</tr>
<tr>
<td>CH₃CHO + N → HCN + H₂ + HCO</td>
<td>1.99×10⁻¹⁴</td>
<td>18</td>
</tr>
<tr>
<td>CH₃CHO + NO₃ → HNO₃ + CH₃CO</td>
<td>2.73×10⁻¹⁵</td>
<td>18</td>
</tr>
<tr>
<td>CH₃COO₂ + NO → CH₃ + CO₂ + NO₂</td>
<td>2.00×10⁻¹¹</td>
<td>18</td>
</tr>
<tr>
<td>CH₃COO₂ + NO → CH₃COO + NO₂</td>
<td>1.40×10⁻¹¹</td>
<td>18</td>
</tr>
<tr>
<td>CH₃COO₂ + NO₂ → CH₃CO₃NO₂</td>
<td>1.75×10⁻¹²⁻₃.₉₃×10⁴₀²</td>
<td>18</td>
</tr>
<tr>
<td>CH₃CO + NO → CH₃CONO</td>
<td>3.32×10⁻¹³</td>
<td>18</td>
</tr>
<tr>
<td>CH₃CO + NO₂ → CH₃ + CO₂ + NO</td>
<td>1.66×10⁻¹²</td>
<td>18</td>
</tr>
<tr>
<td>CH₃CO + NO₂ → CH₃COO + NO</td>
<td>2.50×10⁻¹¹</td>
<td>18</td>
</tr>
<tr>
<td>CH₂OH + NO → CH₂OHNO</td>
<td>2.50×10⁻¹¹</td>
<td>18</td>
</tr>
<tr>
<td>CH₂OH + NO₂ → HOCH₂NO₂</td>
<td>2.30×10⁻¹¹</td>
<td>18</td>
</tr>
<tr>
<td>CH₂OH + O → HCHO + OH</td>
<td>1.50×10⁻¹⁰</td>
<td>18</td>
</tr>
<tr>
<td>CH₂OH + CH₃ → CH₄ + HCHO</td>
<td>4.00×10⁻¹²</td>
<td>20</td>
</tr>
<tr>
<td>CH₂OH + CH₃ → C₂H₅OH</td>
<td>2.00×10⁻¹¹</td>
<td>20</td>
</tr>
<tr>
<td>CH₂CHO + NO₂ → CH₂CO + HNO₂</td>
<td>1.48×10⁻¹¹⁻₈.₀₀×10⁴₀¹</td>
<td>18</td>
</tr>
</tbody>
</table>
\[ \text{CH}_2 + \text{NO} \rightarrow \text{CONH}_2 \quad 5.76 \times 10^{-12} \quad -1.90 \times 10^{+02} \quad 18 \]
\[ \text{CH}_2\text{CO} + \text{OH} \rightarrow \text{CH}_2\text{OH} + \text{CO} \quad 1.08 \times 10^{-11} \quad 18 \]
\[ \text{CH}_2\text{CO} + \text{OH} \rightarrow \text{HCO} + \text{HCHO} \quad 4.65 \times 10^{-11} \quad 18 \]
\[ \text{CH}_2\text{CO} + \text{H} \rightarrow \text{CH}_3 + \text{CO} \quad 1.88 \times 10^{-11} \quad 1.73 \times 10^{+03} \quad 18 \]
\[ \text{CH} + \text{NO} \rightarrow \text{CO} + \text{NH} \quad 2.50 \times 10^{-10} \quad 18 \]
\[ \text{HCO} + \text{NO} \rightarrow \text{CO} + \text{HNO} \quad 1.20 \times 10^{-11} \quad 18 \]
\[ \text{HCO} + \text{NO} \rightarrow \text{H} + \text{CO}_2 + \text{NO} \quad 1.95 \times 10^{-10} \quad -0.75 \quad 9.70 \times 10^{+02} \quad 18 \]
\[ \text{HCO} + \text{NO}_2 \rightarrow \text{HCOO} + \text{NO} \quad 2.71 \times 10^{-11} \quad 18 \]
\[ \text{HCO} + \text{NO}_2 \rightarrow \text{CO} + \text{HNO}_2 \quad 8.73 \times 10^{-11} \quad 3.19 \times 10^{+02} \quad 18 \]
\[ \text{CH}_3\text{ONO} \rightarrow \text{HCHO} + \text{HNO} \quad 3.98 \times 10^{+13} \quad 1.94 \times 10^{+04} \quad 18 \]
\[ \text{HO}_2 + \text{NO}_2 \rightarrow \text{HNO}_2 + \text{O}_2 \quad 1.20 \times 10^{-13} \quad 18 \]
\[ \text{O} + \text{HNO}_2 \rightarrow \text{NO}_2 + \text{OH} \quad 2.00 \times 10^{-11} \quad 3.00 \times 10^{+03} \quad 18 \]

\( \text{a} \) Rate coefficients have units of cm\(^3\)s\(^{-1}\). Electron impact reactions without specific electron temperature dependencies are given for typical values of E/N.

\( \text{b} \) Estimated.

\( \text{c} \) Rate coefficients have units of s\(^{-1}\) for 1 body reaction, cm\(^3\)s\(^{-1}\) for 2 body reactions, and cm\(^6\)s\(^{-1}\) for 3 body reactions. Activation energies have equivalent units of K. T is the gas temperature. Two body reactions which do not have specific temperature dependencies were scaled by \((T/300)^{1/2}\) to account for changes in the reaction rate due to thermal speeds. Three body reactions were similarly scaled by \((T/300)^{-3/2}\).

\( \text{d} \) Estimated based on Lennard-Jones parameters. Value shown for T = 300K.
B.1 References


