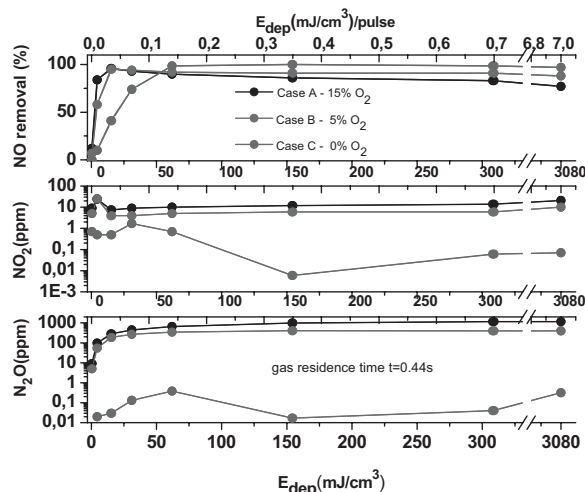


# The Effect of O<sub>2</sub> in a Humid O<sub>2</sub>/N<sub>2</sub>/NO<sub>x</sub> Gas Mixture on NO<sub>x</sub> and N<sub>2</sub>O Remediation by an Atmospheric Pressure Dielectric Barrier Discharge

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A numerical model for N<sub>x</sub>O<sub>y</sub> remediation in humid air plasma produced with a dielectric barrier discharge at atmospheric pressure is presented. Special emphasis is given to NO<sub>2</sub> and N<sub>2</sub>O reduction with the decrease of O<sub>2</sub> content in the feedstock gas. A detailed reaction mechanism including electronic and ionic processes, as well as the contribution of radicals and excited atomic/molecular species is proposed. The temporal evolution of the densities of NO, NO<sub>2</sub> and N<sub>2</sub>O species, and some other by-products, is analyzed, and the major pathways for the N<sub>x</sub>O<sub>y</sub> remediation are discussed for one pulse. Subsequently, simulations are presented for a multi-pulses case, where three O<sub>2</sub> contents are tested for optimization of the remediation process. It is found that when the gas mixture O<sub>2</sub>/N<sub>2</sub>/H<sub>2</sub>O/NO<sub>x</sub> has no initial O<sub>2</sub> content, the best NO<sub>x</sub> and N<sub>2</sub>O remediation is achieved.



## 1. Introduction

The remediation of different nitrogen oxides N<sub>x</sub>O<sub>y</sub> from diesel exhaust and gas turbines has been extensively studied in the last decade for their major role to atmospheric pollution and human health.<sup>[1–13]</sup> In this paper, special attention is given to NO<sub>x</sub> (x = 1, 2) and N<sub>2</sub>O. The pollutant

NO<sub>x</sub>, which represents both NO and NO<sub>2</sub>, plays an important role in the acid rain, photochemical smog, and stratospheric ozone chemistry.<sup>[14]</sup> These toxins penetrate deeply into lung tissue, leading to respiratory diseases. N<sub>2</sub>O is known as a greenhouse gas which can trap the heat in the atmosphere contributing to global warming. Its “global warming potential” is about 300 times higher than for CO<sub>2</sub>. Also, it is one of the end gas products in air ozonizers and nitric acid plants, difficult to diminish in concentration.

In general three methods are known for fuel exhaust remediation: (1) pre-combustion gas treatment, which leads to cleaner fuel, eliminating the problem of fuel bound nitrogen;<sup>[1]</sup> (2) combustion modification, which attacks the production of thermal NO<sub>x</sub> by lowering the temperature inside the engine or burner,<sup>[2,3]</sup> and (3) post-combustion

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gas treatment, including both classical catalytic processes,<sup>[4,5]</sup> but also innovative methods such as plasma technology, either in combination with catalytic processes<sup>[6]</sup> or not.<sup>[7–13]</sup>

In the present paper, we will investigate the potential of plasma technology for NO<sub>x</sub> remediation, not in combination with catalysis. Indeed, because of the high cost of rare metal catalysts, a low-cost, and catalyst-free post-treatment process would be of interest for NO<sub>x</sub> and N<sub>2</sub>O remediation. Dielectric barrier discharges (DBDs) and corona plasmas are suitable candidates for this application, for their robustness and compactness in producing low temperature non-equilibrium plasmas, which makes them easy to apply for mobile emission sources as diesel engines.<sup>[7,10,11,15,16]</sup>

In general, however, it is claimed<sup>[10]</sup> that plasma alone cannot provide an efficient NO<sub>x</sub> removal for two reasons: (i) high energy cost and (ii) high concentrations of by-products NO<sub>2</sub> and N<sub>2</sub>O. To overcome these problems, several attempts were made using water in the gas mixture (in vapor or liquid state) together with lower O<sub>2</sub> concentrations in the gas mixture at not very high gas temperatures (less than 400 K).<sup>[7–11,15,17,18]</sup> We have investigated the optimum water concentration and gas temperature of a NO/NO<sub>2</sub>/O<sub>2</sub>/N<sub>2</sub>/H<sub>2</sub>O mixture, and the simulation results suggest that at least 25% water and a gas temperature of 350 K are needed to obtain 100% removal of NO<sub>x</sub> and N<sub>2</sub>O pollutants in a DBD.<sup>[19]</sup>

Many experiments have been performed for NO<sub>x</sub> removal using pulsed non-thermal plasmas<sup>[7,8,17,18]</sup> when water was present on the electrode surface or in vapor state, as well as for dry gas mixtures,<sup>[11,20]</sup> but very limited information is available on the fundamental oxidation and reduction processes during NO<sub>x</sub> removal. It is known that the presence of water in the carrier gas makes the N<sub>x</sub>O<sub>y</sub> remediation process more efficient, by introducing besides O and N radicals also OH and HO<sub>2</sub>, controlling better the concentration of the pollutant gases.<sup>[5,15,18,19,21–24]</sup> However, it also produces NH radicals as potential reactants for N<sub>2</sub>O production.

Fujii et al.<sup>[8]</sup> have shown that 95% NO<sub>x</sub> removal in both diesel exhaust and blended dry NO gas can be achieved by a positive DC corona discharge with water surface electrodes. Mizuno et al.<sup>[7]</sup> have tested the performance of several wet-type reactors in the DeNO<sub>x</sub> efficiency for a gas mixture of O<sub>2</sub>/N<sub>2</sub>/NO/CO<sub>2</sub>. They obtained 90% NO<sub>x</sub> removal for a reactor whose inner walls have a thin film of water, suggesting the importance of water for the best possible removal process. In these two papers, however, the N<sub>2</sub>O concentration was not discussed.

Tas et al.<sup>[17]</sup> have shown experimentally that the most energy efficient NO removal is achieved at higher O<sub>2</sub> and H<sub>2</sub>O concentrations in both N<sub>2</sub> and He as background

gases, but the implications of NO<sub>2</sub> and N<sub>2</sub>O pollutants were not discussed.

Yan et al.<sup>[18]</sup> investigated experimentally the influence of O<sub>2</sub>, H<sub>2</sub>O and NH<sub>3</sub> content on the produced NO<sub>2</sub> concentration, connected with the NO removal. When the O<sub>2</sub> content drops from 11 to 0% in the gas mixture, the NO<sub>2</sub> concentration was reduced by 50%, suggesting the importance of O<sub>2</sub> concentration on this by-product. Again the pollutant N<sub>2</sub>O was not discussed.

Penetrante et al.<sup>[11]</sup> reported a 100% NO removal with a NO<sub>2</sub> production of about 0.52 ppm in pure N<sub>2</sub> having 100 ppm NO. The by-product N<sub>2</sub>O was accounted for in the reaction set and it results from the conversion of NO and NO<sub>2</sub> pollutants, but it was not detected in the measurements.

Concerning the chemical kinetics of NO<sub>x</sub> removal by non-thermal plasmas, several models have been developed to estimate the radical production and plasma chemistry.<sup>[11,15,17,24–26]</sup> Herron<sup>[24]</sup> calculated the temporal profile of N<sub>x</sub>O<sub>y</sub> concentrations in humid nitrogen/air, where for the pulse chemistry the electron interaction with water and the ion chemistry was omitted, but the NO<sub>2</sub> and N<sub>2</sub>O by-products were accounted for. Gentile and Kushner<sup>[15]</sup> presented a comprehensive plasma kinetic model of NO<sub>x</sub> removal from a gas stream of N<sub>2</sub>/O<sub>2</sub>/H<sub>2</sub>O/NO. It was demonstrated that a lower power deposition results in a more effective use of the radicals in the remediation. The reported N<sub>2</sub>O concentration was about 0.25 ppm after four pulses. The plasma model, however, did not include the reaction N<sub>2</sub>(A) + O<sub>2</sub> → N<sub>2</sub>O + O which appears to be the dominant N<sub>2</sub>O production source, as will be explained below. Penetrante et al.<sup>[11]</sup> also proposed a simplified model for the gas-phase plasma chemistry, where the electrons have an equivalent energy of 3–5 eV in a pulsed streamer corona and DBD.

The existing chemical models usually couple the role of the electrons and ions to radical production and describe the link between radicals and NO<sub>x</sub> pollutants, but not much is known about the N<sub>2</sub>O optimization with the plasma-catalyst free method. Nevertheless, the N<sub>2</sub>O production in the NO<sub>x</sub> remediation process should also be kept under control.

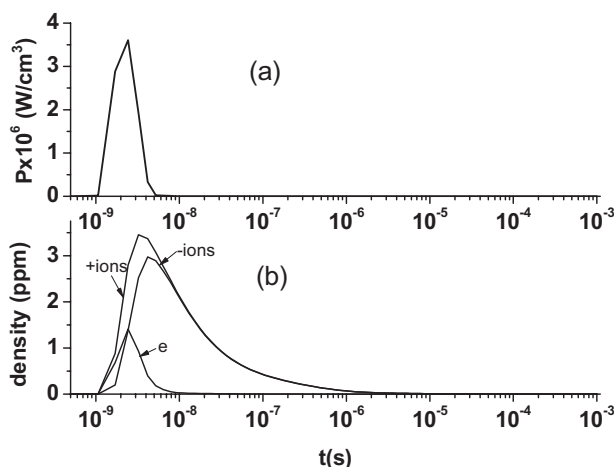
Therefore, we propose a global plasma kinetic model for a DBD plasma, accounting for electrons, various types of ions, excited species and radicals, besides molecules, and including also the electric field variation in time. The aim is to investigate the influence of O<sub>2</sub> content in a humid O<sub>2</sub>/N<sub>2</sub> gas mixture on the NO, NO<sub>2</sub> and N<sub>2</sub>O removal, assuming initial pollutant concentrations of 100 ppm NO and 1 ppm NO<sub>2</sub>. These particular pollutant concentrations were chosen, because they are in the range of the typical diesel exhaust NO<sub>x</sub> concentrations with a density ratio of 100 between NO and NO<sub>2</sub>.<sup>[27]</sup> We also want to understand which plasma species are playing a role in the loss and

production mechanisms of these pollutants. The water content in the gas mixture is kept at 25%, and the O<sub>2</sub> content is varied from 15 to 5 and 0%, corresponding to a transition from humid ambient air to humid nitrogen gas. It will be demonstrated that plasma technology without catalyst can efficiently remediate NO pollutants with minimum by-product concentrations (around 0.01 ppm), when there is no initial O<sub>2</sub> present in the humid N<sub>2</sub> gas. The implications of the input energy needed to remove NO molecules are discussed as well.

## 2. Description of the Model

The computational model is based on the zero-dimensional global model, called GLOBAL\_KIN, developed at University of Illinois by Kushner and co-workers.<sup>[28]</sup> The code calculates the temporal profiles of volume-averaged species densities, based on balance equations describing the production and loss of the species due to chemical reactions. The electron energy distribution is determined from the Boltzmann equation which provides also the electron rate coefficients for the electron impact reactions. The rate coefficients for the heavy particle chemical reactions are estimated from Arrhenius expressions, based on the gas temperature (see Appendix 1). The gas temperature is computed by accounting for the heat from electron impact collisions and enthalpy of heavy particle reactions.<sup>[28]</sup> More information about this model can be found in ref.<sup>[28]</sup>

In order to simulate the transient glow phase in a microdischarge, the calculations are initially applied to one pulse and afterglow; the shape and duration of the pulse were chosen according to the calculations of Eliasson et al.<sup>[29]</sup> for a DBD plasma: it is a pulse, with a rise time of 2.4 ns and a decreasing time of 3 ns (see Figure 1a), followed



**Figure 1.** The power pulse (a) and the electron and total positive and negative ion densities (b) as a function of time, in case A.

by an afterglow of 1ms, until the next pulse would start (for a repetition rate of 1 kHz). However, our calculations stop for one pulse at the end of this afterglow. The input energy of the pulse is 7 mJ cm<sup>-3</sup>. The pulse has a maximum power density of 3.6 × 10<sup>6</sup> W cm<sup>-3</sup>. The values of *E/N* assumed in the model follow the power pulse variation, with a maximum of 140 Td at the peak of the triangular pulse, and they become constant (i.e., 50 Td) in the afterglow of the pulse. This single pulse regime is considered here to investigate in detail the underlying mechanisms in the remediation process. However, it has been demonstrated<sup>[16]</sup> that the NO<sub>x</sub> remediation process is more efficient when a given energy is deposited in multiple shorter pulses. Therefore, we will also consider a multi-pulse regime, with pulses of variable maximum power and duration, as will be explained in Section 3.3 below.

The DBD geometry consists of two parallel plate electrodes of 50 mm length and 50 mm width, with a gap distance of 5 mm.

The plasma kinetic analysis considers 56 species, including electrons, several types of molecules, radicals, ions as well as excited atomic and molecular species. The species included in the model are shown in Table 1. For simplification, for the vibrational and electronically excited molecular states we use the following notations:

$$O_2(v) = \sum_{i=1}^6 O_2(v_i)$$

$$O_2(a) = O_2(a^1\Delta_g), \quad O_2(b) = O_2(b^1\Sigma_g^+)$$

$$N_2(A) = N_2(A^3\Sigma_g^+), \quad N_2(B) = N_2(B^3\Pi_g)$$

$$N_2(a') = N_2(a'^1\Sigma_u^-)$$

Our model includes 541 chemical reactions listed in the Appendix 1. They can be divided in 95 electron impact reactions, 21 electron-ion recombination reactions, 97 ion-ion recombination reactions, 139 ion-neutral reactions, and 189 neutral-neutral reactions. The chemistry set combines the databases of Gaens,<sup>[30]</sup> Kushner,<sup>[31]</sup> Herron and Green,<sup>[32]</sup> Kossyi et al.,<sup>[33]</sup> Gentile,<sup>[34]</sup> Liu et al.<sup>[21]</sup> and Atkinson et al.<sup>[35]</sup> for a gas mixture of O<sub>2</sub>/N<sub>2</sub>/H<sub>2</sub>O with initial concentrations of 100 ppm NO and 1 ppm NO<sub>2</sub>, 25% water concentration (absolute volume v.v) and different O<sub>2</sub> contents at a gas temperature of 350 K and atmospheric pressure. At this temperature, 1 ppm = 2.44 × 10<sup>13</sup> cm<sup>-3</sup> and the relative humidity at 25% water content is RH = 60.

## 3. Results and Discussion

The N<sub>x</sub>O<sub>y</sub> remediation process is determined by the plasma conditions, and hence, it depends on the concentration of

**Table 1.** Species considered in the global model.

Molecules	O <sub>2</sub> , O <sub>3</sub> , N <sub>2</sub> , NO, NO <sub>2</sub> , NO <sub>3</sub> , N <sub>2</sub> O <sub>4</sub> , N <sub>2</sub> O <sub>5</sub> , N <sub>2</sub> O <sub>3</sub> , N <sub>2</sub> O, H <sub>2</sub> O, H <sub>2</sub> O <sub>2</sub> , HNO, HNO <sub>2</sub> , HNO <sub>3</sub> , HNO <sub>4</sub>
Radicals	O <sup>•</sup> , N <sup>•</sup> , H <sup>•</sup> , OH <sup>•</sup> , HO <sub>2</sub> <sup>•</sup> , NH <sup>•</sup>
Excited species	O( <sup>1</sup> D), O( <sup>1</sup> S), N( <sup>2</sup> D), N( <sup>2</sup> P), O <sub>2</sub> (a), O <sub>2</sub> (b), O <sub>2</sub> (v), N <sub>2</sub> (A), N <sub>2</sub> (B), N <sub>2</sub> (a')
Positive ions	O <sup>+</sup> , O <sub>2</sub> <sup>+</sup> , N <sup>+</sup> , N <sub>2</sub> <sup>+</sup> , N <sub>4</sub> <sup>+</sup> , NO <sup>+</sup> , NO <sub>2</sub> <sup>+</sup> , N <sub>2</sub> O <sup>+</sup> , H <sup>+</sup> , H <sub>2</sub> <sup>+</sup> , H <sub>3</sub> <sup>+</sup> , OH <sup>+</sup> , HO <sub>2</sub> <sup>+</sup> , H <sub>2</sub> O <sup>+</sup> , H <sub>3</sub> O <sup>+</sup>
Negative ions	O <sup>-</sup> , O <sub>2</sub> <sup>-</sup> , O <sub>3</sub> <sup>-</sup> , NO <sup>-</sup> , NO <sub>2</sub> <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , H <sup>-</sup> , OH <sup>-</sup>
Electrons	e <sup>-</sup>

electrons, ions, radicals, and excited species in the plasma. Table 2 gives an overview of the different plasma species playing a role in the production and loss for NO, NO<sub>2</sub> and N<sub>2</sub>O, as obtained from our simulations (see details below). Therefore, in order to understand the N<sub>x</sub>O<sub>y</sub> remediation, we will first analyze the densities of these plasma species as a function of time during one pulse. Subsequently, the temporal evolution of the NO density, as well as the densities of the NO<sub>2</sub> and N<sub>2</sub>O by-products and some other minor by-products of the remediation will be discussed, and the most important pathways in this remediation process will be presented. We focus first on one pulse, because we want to understand the remediation reaction mechanism in a microdischarge. In the last section, calculation results will be shown for a multi-pulses case, mimicking closer the conditions of a DBD plasma, which typically consists of thousands of microdischarges for a gas residence time of a few seconds.

It is well known<sup>[15,25]</sup> that the ions and electrons do not influence directly the production/loss processes of the N<sub>x</sub>O<sub>y</sub>

pollutants, due to their small densities (at least two times lower) compared to the pollutants. The input energy per pulse can be increased to balance the differences between the density of electrons, ions, and pollutants, but the NO remediation process will then become too costly and it is therefore not of interest. On the other hand, the radicals and excited species are the main candidates which can influence the production and loss mechanism of the above mentioned pollutants. More O radicals in the carrier gas will determine a better NO remediation, but also a stronger NO<sub>2</sub> production and indirectly also N<sub>2</sub>O production.

The combination of O<sub>2</sub> and N<sub>2</sub> gases with water vapor was intensively studied<sup>[7,8,17,18,24]</sup> being a favorable gas mixture for the NO remediation process, generating the radicals O, N, and OH, which are active in the loss process of NO molecules. It also forms HO<sub>2</sub> radicals which are a potential source of OH radicals, as well as unwanted NH radicals, producing a high concentration of the N<sub>2</sub>O pollutant. The plasma species which take part in the OH, HO<sub>2</sub>, and NH radical reaction mechanisms are presented in Table 3.

**Table 2.** Overview of the plasma species playing a role in the production and loss of NO<sub>x</sub> and N<sub>2</sub>O.

Species	NO mechanism		NO <sub>2</sub> mechanism		N <sub>2</sub> O mechanism	
	Production	Loss	Production	Loss	Production	Loss
Excited species	N <sub>2</sub> (A), N( <sup>2</sup> P)	N( <sup>2</sup> P)		N <sub>2</sub> (A)	N <sub>2</sub> (A)	N <sub>2</sub> (A)
Radicals	O, N, OH, NH, HO <sub>2</sub> , O <sub>3</sub>	O, N, OH, HO <sub>2</sub>	O, HO <sub>2</sub>	O, H, OH	N, NH	
Molecules	NO <sub>2</sub> , N <sub>2</sub> O <sub>3</sub>	NO <sub>2</sub>	NO, N <sub>2</sub> O <sub>3</sub>	NO	O <sub>2</sub> , NO, NO <sub>2</sub>	

**Table 3.** Overview of the plasma species playing a role in the production and loss of OH, HO<sub>2</sub> and NH radicals.

Species	OH mechanism		HO <sub>2</sub> mechanism		NH mechanism	
	Production	Loss	Production	Loss	Production	Loss
Electrons	e	e		e	–	
Negative ions	OH <sup>-</sup>	–	H <sup>-</sup> , OH <sup>-</sup>	–	–	–
Positive ions	O <sub>2</sub> <sup>+</sup> , N <sub>4</sub> <sup>+</sup> , H <sub>3</sub> O <sup>+</sup> , NO <sup>+</sup>	–	–	–	–	–
Excited species	O( <sup>1</sup> D), O( <sup>1</sup> S), N( <sup>2</sup> D)	–	–	–	N( <sup>2</sup> D)	–
Radicals	O, H, HO <sub>2</sub>	O, N, HO <sub>2</sub>	O, H, OH	O, H, OH		O, OH
Molecules	H <sub>2</sub> O, NO, NO <sub>2</sub>	NO, NO <sub>2</sub>	O <sub>2</sub> , O <sub>3</sub> , H <sub>2</sub> O <sub>2</sub>	NO, NO <sub>2</sub>	H <sub>2</sub> O	O <sub>2</sub> , NO

Recent mass spectrometry investigations by Sabo et al.<sup>[36]</sup> revealed the presence of water cluster ions  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$  in a positive corona discharge in a gas mixture of  $\text{O}_2/\text{H}_2\text{O}/\text{NH}_3$  diluted in pure  $\text{N}_2$  at atmospheric pressure, while pulsed high-pressure mass spectrometry<sup>[37]</sup> studies of the cationic chemistry of an ionized humid air sample, have shown the existence of protonated water clusters  $\text{H}^+(\text{H}_2\text{O})_n$ , both formed when the hydronium ion  $\text{H}_3\text{O}^+$  reacts with water. In this case, the dominant positive plasma ions were  $\text{H}_3\text{O}^+(\text{H}_2\text{O})$ <sup>[36]</sup> or  $\text{H}^+(\text{H}_2\text{O})_3$ .<sup>[37]</sup> Similar results as obtained by Sabo et al.<sup>[36]</sup> can be found in the numerical studies of Dorai and Kushner<sup>[38]</sup> for  $\text{NO}_x$  remediation in soot laden exhaust using a DBD. The depletion time of the ions  $\text{H}_3\text{O}^+(\text{H}_2\text{O})$  was found to be about  $3 \times 10^{-7}$  s, as they rapidly recombine with the negative ions such  $\text{O}^-$ ,  $\text{H}^-$ ,  $\text{O}_2^-$  or with the electrons. Therefore, we believe that the water cluster ions are not so chemically active with regard to the  $\text{N}_x\text{O}_y$  remediation process, given the short time when they dominate the plasma characteristics. Thus in the present kinetic model they are not being considered.

From Table 3 it can be observed also that the electrons and several ions are indirectly important in the  $\text{N}_x\text{O}_y$  removal process, as they contribute directly to the loss/production mechanisms of the radicals. Moreover, the electrons are involved in the production of the excited species  $\text{N}_2(\text{A})$  which are mainly responsible for the  $\text{N}_2\text{O}$  loss process, as will be explained below.

Given the high concentration of  $\text{N}_2\text{O}$  pollutant formed in this gas mixture, it is aimed to find a better gas combination where NO remediation occurs with a minimum amount of  $\text{NO}_2$  and  $\text{N}_2\text{O}$  by-products. It can be seen from Table 2 that O radicals and  $\text{O}_2$  molecules are potential sources for  $\text{NO}_2$  and  $\text{N}_2\text{O}$  production, respectively. Therefore a decrease in  $\text{O}_2$  content in the carrier gas is expected to lead to smaller concentrations of these by-products, even if the NO remediation process will be slowed down in time. Moreover, it will be demonstrated below that in the multi-pulse regime the maximum NO remediation can be achieved when the gas does not contain oxygen molecules.

In order to investigate the effect of oxygen in the gas mixture, we will consider three different cases, with the following gas mixing ratios of  $\text{N}_2/\text{O}_2/\text{H}_2\text{O}/\text{NO}/\text{NO}_2 = 60/15/25/0.01/10^{-4}$  (case A),  $70/5/25/0.01/10^{-4}$  (case B), and  $75/0/25/0.01/10^{-4}$  (case C). Hence, the  $\text{H}_2\text{O}$  concentration (humidity), and NO and  $\text{NO}_2$  concentrations stay the same;

only the  $\text{O}_2$  concentration is varied from 15 (i.e., humid air) to 5 and 0% (humid  $\text{N}_2$  gas).

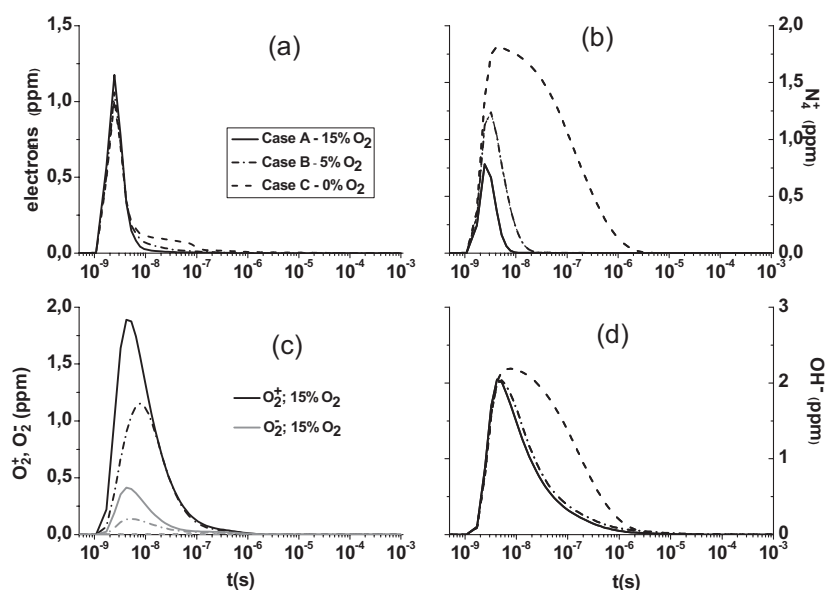
### 3.1. Influence of $\text{O}_2$ Content on the Plasma Species Behavior During One Pulse

#### 3.1.1. Electrons

As mentioned before, the electrons are directly contributing to the production of radicals and excited species, and therefore it is worth to investigate the temporal evolution of their density (or concentration) in cases A–C.

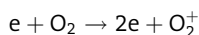
The evolution in concentration (in ppm) of electrons and of the most important ions is plotted as a function of time during one pulse in Figure 2, for the three different cases (i.e.,  $\text{O}_2$  contents in the carrier gas: 0, 5 and 15%).

It is clear that the electron concentration (or number density) exactly follows the pulse profile (see also Figure 1): it rises significantly in the beginning of the pulse, and drops to very low values when the pulse is over. According to Figure 2a, the electron density is somewhat higher at the highest  $\text{O}_2$  content during the pulse (case A), but it drops also most quickly after the pulse. Indeed, in cases B and C the electron density has some non-zero values until about 100 ns after pulse termination. This can be explained when looking at the production and loss processes of the electrons (see Appendix 2: Table A1 and Figure A1). Indeed, at the maximum of the power pulse (i.e., at  $t_1$  in Appendix 2),



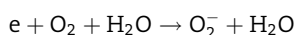
**Figure 2.** Calculated density as a function of time for the electrons (a) and the most important positive and negative ions (b–d), for three different oxygen concentrations in the carrier gas, as indicated in the legend. The  $\text{H}_3\text{O}^+$  ion density has the same profile as the  $\text{OH}^-$  density, and is therefore not shown.

electron impact ionization of O<sub>2</sub> is a quite important production process for the electrons:



and its rate obviously decreases with lower O<sub>2</sub> concentration.

On the other hand, in the afterglow (i.e., in the time interval ( $t_2-t_4$ ) of Appendix 2), the following loss process is very important for the electrons:



and it becomes of lower importance at lower O<sub>2</sub> contents, explaining the longer lifetime of electrons after pulse termination in cases B and C.

### 3.1.2. Most Important Ions

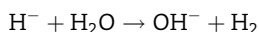
The ion densities also rise in the beginning of the pulse, as is shown in Figure 2b–d, but they have a longer lifetime than the electrons, typically up to a few μs. In general, this can be explained by their lower mobility and diffusion coefficients, due to their larger mass.

Regarding the absolute values of the ion and electron densities, it is clear from Figure 1b that the plasma is dominated by the positive and negative ions, since the electron density is about three times lower than the total ion density.

The N<sub>4</sub><sup>+</sup>, O<sub>2</sub><sup>+</sup> and H<sub>3</sub>O<sup>+</sup> ions appear to be the dominant positive ions, whereas the negative ions with highest density are OH<sup>-</sup> and O<sub>2</sub><sup>-</sup>. Note that the H<sub>3</sub>O<sup>+</sup> density is not shown in Figure 2, because it has exactly the same behavior as the OH<sup>-</sup> ions. The densities of these dominant ions are all in the order of 1–2 ppm, hence 2–5 × 10<sup>13</sup> cm<sup>-3</sup>. Compared to the sum of the N<sub>2</sub> and O<sub>2</sub> gas densities, which is about 1.6 × 10<sup>19</sup> cm<sup>-3</sup> for atmospheric pressure and a temperature of 350 K, this gives an ionization degree of about 4.5 × 10<sup>-6</sup>, which corresponds to a weakly ionized plasma.

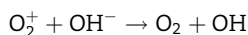
The N<sub>4</sub><sup>+</sup> ion density drops with rising O<sub>2</sub> content in the gas mixture (Figure 2b), which is logical because this corresponds to a drop of nitrogen content in the gas (see above). At the same time, the densities of O<sub>2</sub><sup>+</sup> and O<sub>2</sub><sup>-</sup> ions (Figure 2c) increase, which is again logical due to the higher O<sub>2</sub> content.

Finally, the OH<sup>-</sup> density (Figure 2d) appears not to be affected by the O<sub>2</sub> content in the beginning of the pulse, but shortly after the maximum of the pulse, the density of these ions increases a bit in case C, when the O<sub>2</sub> content is 0%, whereas it drops when the O<sub>2</sub> content is 15 or 5%. Hence, the OH<sup>-</sup> density is clearly higher in the case of 0% O<sub>2</sub>, compared to the two other cases. This can again be explained from the production and loss processes of these ions (see Table A2 and Figure A2 in Appendix 2). For all cases, the dominant production of OH<sup>-</sup> ions during the power pulse is through reaction:



whose contribution increases for lower O<sub>2</sub> content at the end of the pulse and in the early afterglow.

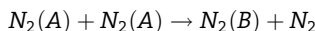
The principal loss of OH<sup>-</sup> ions during the pulse and in the early afterglow for cases A and B is the recombination reaction:



which does obviously not occur for case C. The recombination reaction with N<sub>4</sub><sup>+</sup> ions is then the dominant loss process, but it occurs at a lower rate, so the total loss rate of OH<sup>-</sup> ions is clearly lower than in cases A and B, explaining why the density drops much more slowly, as appears from Figure 2d.

### 3.1.3. Excited Species

Figure 3 illustrates the temporal density profiles of the excited species playing a role in the NO<sub>x</sub> remediation, either directly (i.e., N<sub>2</sub>(A) and N<sup>(2)P</sup>; see Table 2) or indirectly through the OH radical production (i.e., O<sup>(1)S</sup>, O<sup>(1)D</sup>, N<sup>(2)D</sup>). The N<sub>2</sub>(A) density (Figure 3a) is 100 times higher than the electron and ion densities, thus this species plays an important role in the gas phase reactions. It also has a long lifetime after the pulse, which is attributed to the N<sub>2</sub> and NO molecules, representing the major sources of N<sub>2</sub>(A) in the afterglow. The loss of N<sub>2</sub>(A) molecules is mainly through the following reaction:



The densities of excited N and O atoms are plotted in Figure 3b and c, respectively. The N<sup>(2)P</sup> and O<sup>(1)D</sup> densities are comparable to the electron and ion densities, whereas the N<sup>(2)D</sup> and O<sup>(1)S</sup> densities are about three orders of magnitude lower. Indeed, the energy needed to populate the O<sup>(1)S</sup> excited state is two times higher than for the O<sup>(1)D</sup>

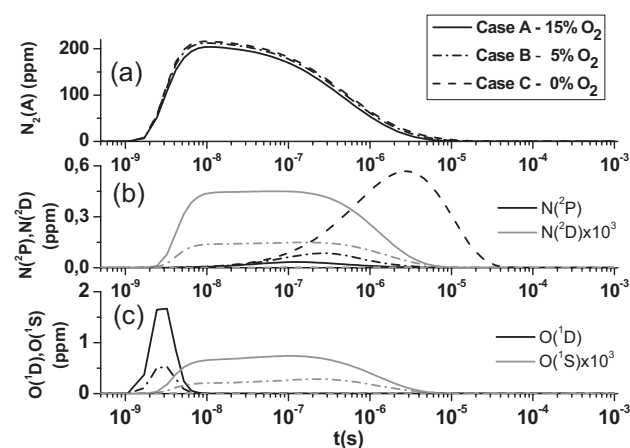
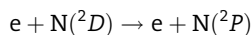


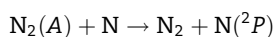
Figure 3. Calculated density of the excited species N<sub>2</sub>(A), N<sup>(2)D</sup>, N<sup>(2)P</sup> and O<sup>(1)D</sup>, O<sup>(1)S</sup> as a function of time, for three different oxygen concentrations in the carrier gas, as indicated in the legend.

excited state, explaining the greater  $O(^1D)$  density compared with the  $O(^1S)$  density. For the N excited states, the majority of  $N(^2D)$  is converted into  $N(^2P)$  through the electron impact reaction:



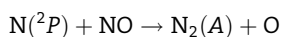
leading to a higher  $N(^2P)$  density compared with the  $N(^2D)$  density.

The  $N(^2P)$  density increases with decreasing  $O_2$  content (see Figure 3b), as it is produced upon collision of N atoms with  $N_2(A)$  molecules:

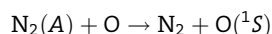
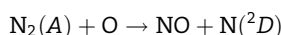


and these two species have a higher density at lower  $O_2$  content.

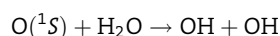
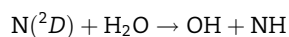
In cases A and B, the  $N(^2P)$  atoms are lost in a reaction with  $O_2$  molecules to form NO, while the opposite effect is noticed in case C where they are consumed by NO molecules to form O atoms and  $N_2(A)$  molecules:



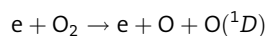
From Figure 3b and c it can be observed that the  $N(^2D)$  and  $O(^1S)$  excited atoms exhibit a similar variation in time and a life time comparable with the  $N_2(A)$  molecules, which are their main production source:



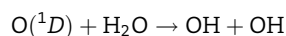
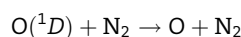
Furthermore, they are both mainly consumed by  $H_2O$  molecules to form OH and NH radicals:



Finally, it is clear from Figure 3c that the  $O(^1D)$  excited atoms follow the time-evolution of the pulse, and their density is in the same order of magnitude as the ion and electron densities. Indeed, they are mainly populated by the electron impact reaction:



while they are mainly consumed in reactions with  $N_2$  and  $H_2O$  molecules:



### 3.1.4. Most Important Radicals

Figure 4 presents the density evolution as a function of time of the most important radicals in the NO,  $NO_2$  and  $N_2O$  reaction mechanism (see Table 2). The radicals O and OH are the most abundant (with densities about one order of magnitude higher than the electron and important ion densities), followed by the radicals  $HO_2$ , H and N (with

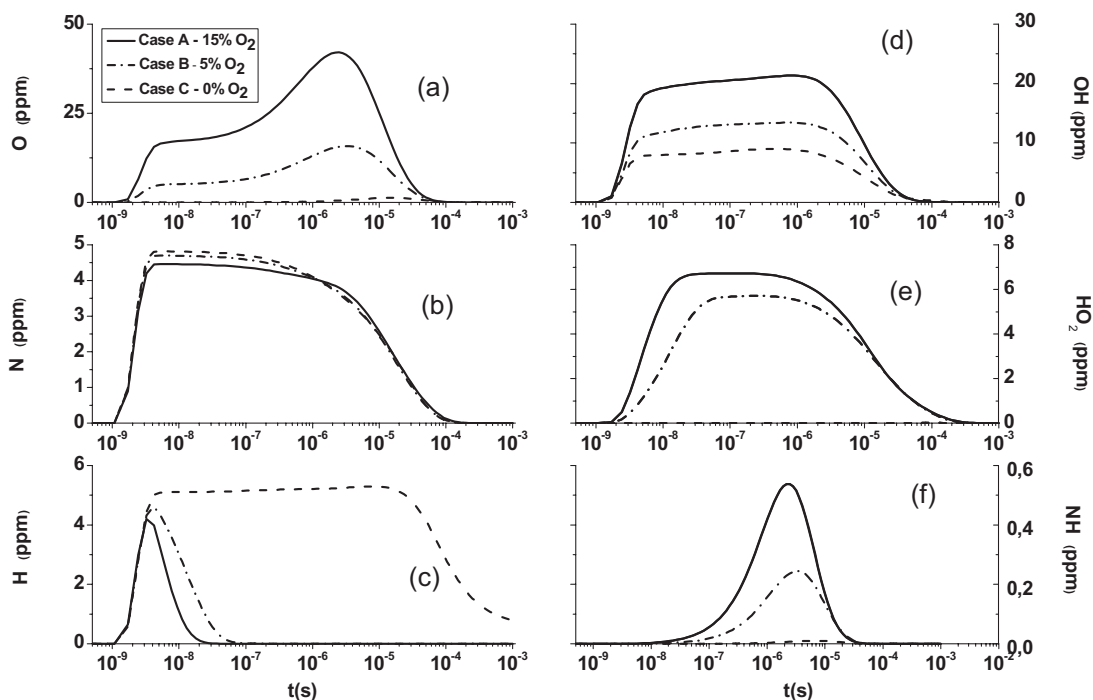


Figure 4. Calculated density of several radicals as a function of time, for three different oxygen concentrations in the carrier gas, as indicated in the legend.

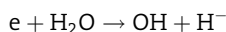
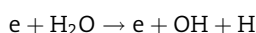
densities slightly higher than the electron and important ion densities). The NH density is lower than the electron and ion densities.

When the O<sub>2</sub> content is decreasing in the carrier gas, the O radical density obviously drops significantly (Figure 4a), while the N radical density increases slightly (Figure 4b) because of the increasing N<sub>2</sub> content for the same H<sub>2</sub>O concentration. Furthermore, in a gas mixture with 0% O<sub>2</sub>, the H radicals are not consumed in the oxidation reactions, leading to a greater density and especially a much longer lifetime (1 ms) compared to the case of 15 and 5% O<sub>2</sub>, when the H radicals are depleted earlier (0.3 μs) (see Figure 4c).

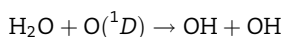
On the other hand, from Figure 4d–f it can be observed that the OH, HO<sub>2</sub> and NH radical concentrations drop when the O<sub>2</sub> content is reduced. In the case of the OH radicals, the trend is gradual, whereas for the HO<sub>2</sub> and NH radicals, the difference between 15 and 5% O<sub>2</sub> is rather small, but a significant drop is seen to 0% O<sub>2</sub>.

To better understand these trends of the OH, HO<sub>2</sub> and NH radical densities, we have again analyzed the production and loss pathways for these species, to examine the implications of lower O<sub>2</sub> content for the same H<sub>2</sub>O concentration (see details in Table A3–A5 and Figure A3–A5 in Appendix 2).

At the maximum of the power pulse, the major production path of OH radicals is established by the electrons via reactions:

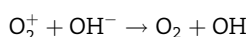


which have the same rate for cases A–C. However, another important source of OH production in case A is the reaction:



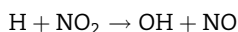
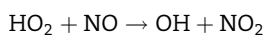
while this process occurs at a lower rate in case B, and is completely absent in case C. This explains why less OH radicals are formed in cases B and C compared to case A.

Further, in the early afterglow, in cases A and B, the recombination between O<sub>2</sub><sup>+</sup> and OH<sup>-</sup> ions is the dominant production process for the OH radicals:

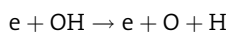


while this process does not occur in case C, explaining again the lower OH concentration. Note that these ions play a role in the OH mechanism only in the early afterglow, when they have a maximum density (cf. Figure 2c and d).

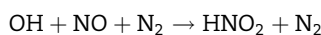
Finally, in the late afterglow, the OH radicals are formed from HO<sub>2</sub> radicals, in cases A and B, and from H radicals in case C:



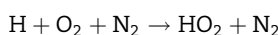
At the maximum of the power pulse, the OH radicals are mainly converted into O and H radicals upon reaction with electrons:



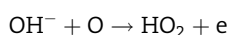
whereas in the afterglow, they are mostly consumed by NO molecules transforming into HNO<sub>2</sub>:



For the HO<sub>2</sub> radicals, the production occurs mainly via O<sub>2</sub> molecules and H radicals in cases A and B, both during the pulse and in the (early) afterglow:

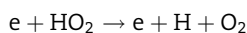


In case C, for 0% O<sub>2</sub>, this path is absent, and the reaction:

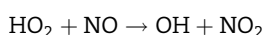


appears to be the dominant production process. However, because of the low OH<sup>-</sup> and O densities in this case, it obviously occurs at a very low rate (see Figure A4 in Appendix 2), explaining the lower HO<sub>2</sub> density in case C (Figure 4e).

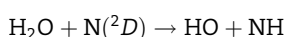
Regarding the HO<sub>2</sub> loss process, at the maximum of the power pulse, electron impact dissociation is the main path for all three cases A–C:



In the early afterglow (time interval (*t*<sub>2</sub>, *t*<sub>3</sub>)), the HO<sub>2</sub> radicals recombine with either OH, O, HO<sub>2</sub> or H radicals, or with NO molecules, and the latter process becomes dominant in the later afterglow, producing NO<sub>2</sub> molecules:

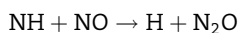


Finally, the NH radicals are exclusively produced by:



The rate of this reaction clearly drops for lower O<sub>2</sub> content (see Figure A5 in Appendix 2), explaining the lower NH density in cases B and especially case C.

The loss of NH radicals is due to collision with NO molecules, forming the by-product N<sub>2</sub>O:



The contribution of this loss path increases for case C versus case B versus case A, due to the greater NO density, thus explaining again the lower NH density for cases B and C compared to case A (Figure 4f).

### 3.2. Influence of O<sub>2</sub> Content on the NO<sub>x</sub> and N<sub>2</sub>O Remediation During One Pulse

Here, we analyze how the O<sub>2</sub> content in the carrier gas can affect the NO remediation process in connection with the by-product formation. Indeed, the optimum conditions for



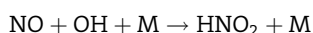
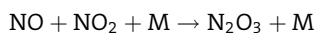
NO remediation are achieved when not only the NO concentration has dropped, but when also the formation of the by-products, i.e., mainly NO<sub>2</sub> and N<sub>2</sub>O, and to a lower extent also N<sub>2</sub>O<sub>3</sub>, HNO<sub>2</sub>, N<sub>2</sub>O<sub>4</sub>, N<sub>2</sub>O<sub>5</sub> and HNO<sub>3</sub>, is minimized.

### 3.2.1. Production and Loss Mechanisms for NO, NO<sub>2</sub> and N<sub>2</sub>O

Figure 5 and 6 illustrate the most important pathways yielding the production and loss of the various species, integrated in time, for the cases A–B and C, respectively, focusing especially on NO, meant to be remediated, and its by-products. The co-reacting species (radicals, molecules, and excited species) involved in each pathway are indicated next to each arrow. Note that indeed electron and ion reactions are not so important when integrated over time (i.e., pulse and afterglow). The arrows are drawn in bold when the contribution of the pathway is more than 10% for the production or loss of the corresponding species.

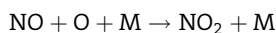
A detailed analysis of the important production and loss processes for NO and for the two major by-products, i.e., NO<sub>2</sub> and N<sub>2</sub>O, for cases A–C, at different times, is presented in Table A6–A8 and Figure A6–A8 of Appendix 2.

From this analysis, it is clear that besides NO<sub>2</sub>, also HNO<sub>2</sub> and N<sub>2</sub>O<sub>3</sub> are produced to some extent from NO via the reactions:



where the third body (M) can be each plasma species, but most typically N<sub>2</sub> gas molecules, because of their highest density in the plasma.

The major pathway from NO to NO<sub>2</sub> is through a three-body collision with O atoms:



NO<sub>2</sub>, in turn, gives rise to the formation of N<sub>2</sub>O<sub>3</sub> and N<sub>2</sub>O<sub>5</sub>, and to a lower extent to HNO<sub>3</sub>, and N<sub>2</sub>O<sub>4</sub>, through the

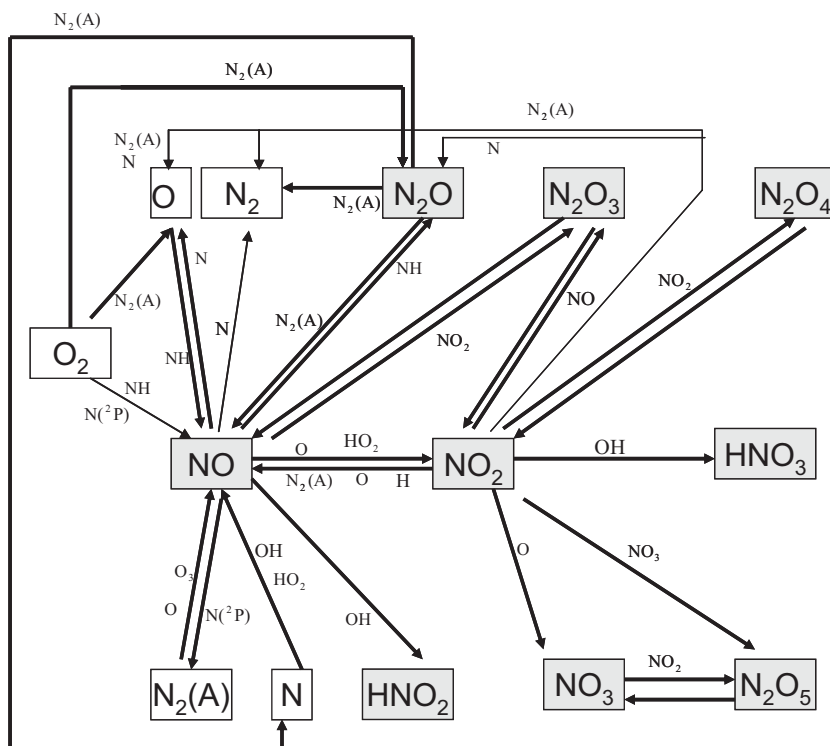


Figure 5. Schematic diagram of the important reaction pathways, integrated over time, for the NO remediation in cases A and B. The dominant pathways are drawn in bold.

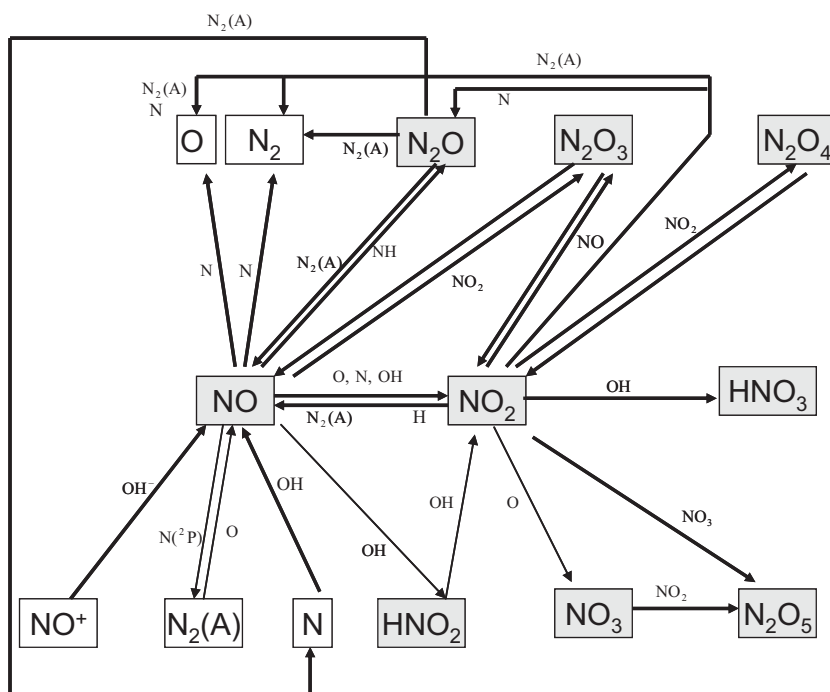
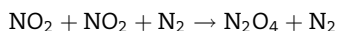
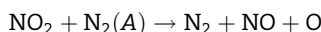
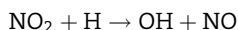


Figure 6. Schematic diagram of the important reaction pathways, integrated over time, for the NO remediation in case C. The dominant pathways are drawn in bold.

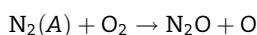
reactions:



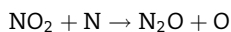
In addition, a small part of NO<sub>2</sub> is converted back into NO molecules through reactions:



The N<sub>2</sub>O molecules are mainly formed upon collision of excited N<sub>2</sub>(A) molecules with O<sub>2</sub> gas molecules:



Obviously, the latter process does not occur in the absence of O<sub>2</sub> (case C), explaining why N<sub>2</sub>O is not formed in large amounts in case C (see below: Figure 7 and 8). In the latter case, the dominant production process for N<sub>2</sub>O, but hence not so important in absolute terms, is through the collision of NO<sub>2</sub> with N atoms:



This process also becomes important at the end of the afterglow in cases A and B, when the excited N<sub>2</sub>(A) density has dropped to low values (see Figure 3a above).

It should be mentioned that part of N<sub>2</sub>O is also formed from NO in a reaction with NH radicals, but only in the late afterglow:

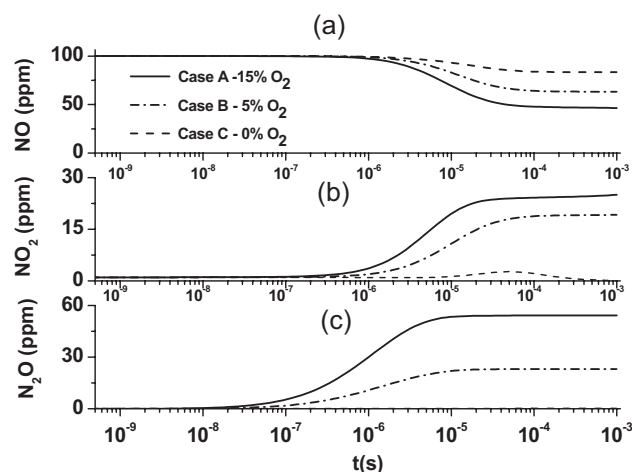
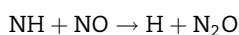


Figure 7. Calculated densities of NO (a), NO<sub>2</sub> (b) and N<sub>2</sub>O (c) as a function of time, for three different concentrations in the carrier gas, as indicated in the legend.

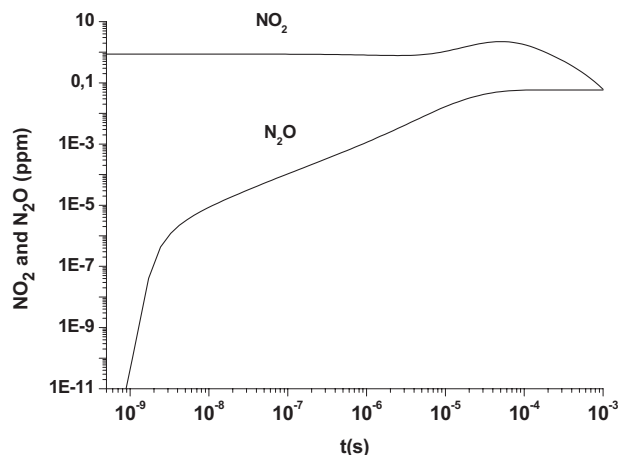
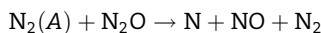


Figure 8. Calculated density of NO<sub>2</sub> and N<sub>2</sub>O as a function of time, for case C.

For the N<sub>2</sub>O loss during the pulse and in the early afterglow, N<sub>2</sub>(A) molecules are the main reactants assisting the conversion of N<sub>2</sub>O into N radicals and NO molecules:



### 3.2.2. Densities of NO, NO<sub>2</sub> and N<sub>2</sub>O, and the Other By-products, as a Function of Time

The temporal profiles of the NO density, as well as of the densities of the two major by-products, NO<sub>2</sub> and N<sub>2</sub>O, are plotted in Figure 7, for the three cases investigated (A–B–C). It is clear from this figure that for all cases investigated the NO remediation only starts after roughly 1 μs, i.e., in the afterglow, long after the power pulse, when the electron and most ion densities have already dropped to negligible values. Furthermore, only NO is remediated during one pulse and corresponding afterglow, while the NO<sub>2</sub> and N<sub>2</sub>O by-products continuously increase in time and converge to a constant value around  $t = 30 \mu\text{s}$  for cases A and B.

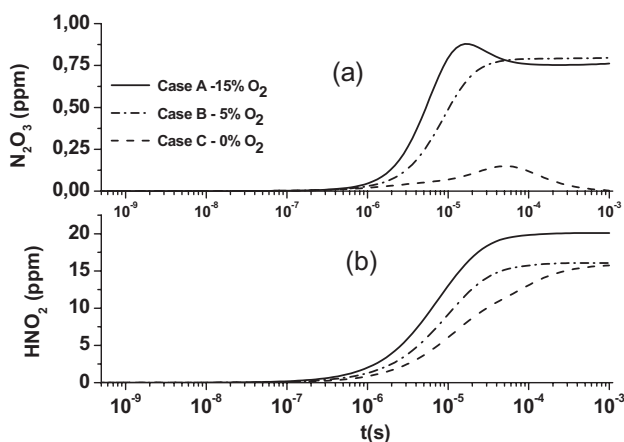
Figure 7 illustrates that less O<sub>2</sub> in the carrier gas leads to a lower reduction of NO, but also to lower by-product formation. Indeed, in case B, a 10% decrease in the O<sub>2</sub> content (compared to case A) results in 17% lower NO remediation, but the densities of the NO<sub>2</sub> and N<sub>2</sub>O by-products are also lower by 24 and 57%, respectively. This can be explained from above, because the major pathway for NO<sub>2</sub> formation is through a three-body collision of NO with O atoms, and the density of the latter obviously drops with lower O<sub>2</sub> contents. Similarly, N<sub>2</sub>O is mainly formed from collisions of N<sub>2</sub>(A) with O<sub>2</sub> molecules (see above), and the rate of this process also becomes negligible at low O<sub>2</sub> contents.

In case C, when the gas contains no initial pure O<sub>2</sub>, an interesting variation in the NO<sub>2</sub> profile is observed: it starts

to increase at 7  $\mu\text{s}$ , reaches a maximum at 50  $\mu\text{s}$  and then it decreases again until the end of the simulation. Indeed, in this case less NO molecules are converted into  $\text{NO}_2$  compared with cases A and B. This behavior is shown in more detail in Figure 8, which is a logarithmic representation of Figure 7b and c, for the  $\text{NO}_2$  and  $\text{N}_2\text{O}$  profiles in case C. At the end of the afterglow, i.e., just before the next pulse would start, the densities of  $\text{NO}_2$  and  $\text{N}_2\text{O}$  are only 0.073 ppm, which is 2–3 orders of magnitude lower than in case A. Hence, in spite of the fact that the NO remediation was about 37% lower in this case compared to case A, the formation of by-products is much more limited, suggesting that case C represents a more efficient gas mixture for NO remediation. Furthermore, it will be demonstrated in Section 3.3 below that by applying multi-pulses, the NO can be reduced by 100% under these conditions.

As mentioned above, besides  $\text{NO}_2$  and  $\text{N}_2\text{O}$ , some other by-products are formed in the remediation of NO, i.e.,  $\text{N}_2\text{O}_3$  and  $\text{HNO}_2$ , as is illustrated in Appendix 2. The acid  $\text{HNO}_2$  can in practice be collected by some methods (using scrubber technology) and disposed off from the pollutants. The species  $\text{NO}_2$  and  $\text{N}_2\text{O}_3$  are toxic and therefore they should not be produced at high amounts.

In case A, the concentration of the above-mentioned by-products at the end of the pulse is 24 ppm for  $\text{NO}_2$ , 0.75 ppm for  $\text{N}_2\text{O}_3$  and 20 ppm for  $\text{HNO}_2$ . The  $\text{NO}_2$  density as a function of time was presented in Figure 7b and 8 above. Figure 9 illustrates the temporal profiles of the other by-products, i.e.,  $\text{N}_2\text{O}_3$  and  $\text{HNO}_2$ , for the three cases (A–B–C). It can be seen from this figure that in case B the concentration of  $\text{N}_2\text{O}_3$  has increased by 5% at the end of the afterglow, compared to case A, while the concentrations of  $\text{NO}_2$  (cf. Figure 7b) and  $\text{HNO}_2$  (Figure 9b) are lowered by 22% and 20%, respectively. In case C, the concentrations of  $\text{NO}_2$  and  $\text{N}_2\text{O}_3$  were lowered by more than two orders of



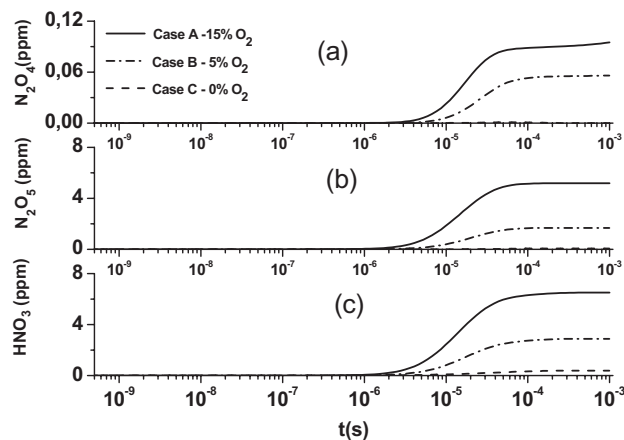
**Figure 9.** Calculated density of  $\text{N}_2\text{O}_3$  and  $\text{HNO}_2$  by-products as a function of time, for three different oxygen concentrations in the gas mixture, as indicated in the legend.

magnitude, while for  $\text{HNO}_2$  a 22% smaller concentration was obtained compared to case A (hence more or less the same as in case B). Therefore, it can be concluded that case C results in the lowest formation of by-products from NO.

The secondary by-products formed out of  $\text{NO}_2$  are  $\text{NO}_3$ ,  $\text{N}_2\text{O}_3$ ,  $\text{N}_2\text{O}_4$ ,  $\text{N}_2\text{O}_5$  and  $\text{HNO}_3$  (see detailed analysis in Appendix 2). These by-products are also toxic and it is aimed to optimize the  $\text{NO}_2$  reduction to a level from where the production of these pollutants is less than 1 ppm.  $\text{NO}_3$  is formed at negligible concentrations (i.e., far below 1 ppm), and will therefore not be analyzed here.  $\text{N}_2\text{O}_3$  was already discussed above. Figure 10 illustrates the evolution in time of the densities of the three other by-products,  $\text{N}_2\text{O}_4$ ,  $\text{N}_2\text{O}_5$  and  $\text{HNO}_3$ , in cases A, B and C. The amount of  $\text{N}_2\text{O}_5$  and  $\text{HNO}_3$  is noticeable at the end of the pulse in case A as their concentrations reach values of 5 and 6.5 ppm, respectively, while the concentration of  $\text{N}_2\text{O}_4$  is fairly small, i.e., only about 0.11 ppm. The formation of these by-products becomes clearly less prominent at lower  $\text{O}_2$  contents in the carrier gas. Indeed, in case B, the  $\text{N}_2\text{O}_5$  and  $\text{HNO}_3$  concentrations at the end of the pulse are about 1.6 and 2.8 ppm, respectively, i.e., a reduction by a factor of 3 for  $\text{N}_2\text{O}_5$  and a factor of 2.3 for  $\text{HNO}_3$  compared to case A, while in case C, the concentrations of these by-products are only 0.06 and 0.38 ppm, hence about two or one order of magnitude lower, respectively, than in case A. This is a promising result, because the concentrations of all by-products should be kept below 1 ppm in the NO remediation process.<sup>[39]</sup>

### 3.3. Influence of $\text{O}_2$ Content and Input Energy on $\text{NO}_x$ and $\text{N}_2\text{O}$ Remediation for a Multi-pulse Regime

In order to couple back our calculation results to real experimental conditions, we have also studied a number



**Figure 10.** Calculated density of  $\text{N}_2\text{O}_4$ ,  $\text{N}_2\text{O}_5$  and  $\text{HNO}_3$  by-products as a function of time, for three different oxygen concentrations in the gas mixture, as indicated in the legend.

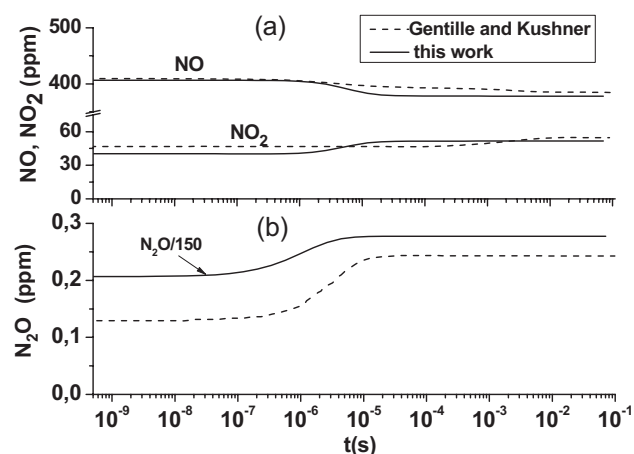
of cases consisting of multi-pulses for different input energies, when the pollutant gas has a residence time of at least 0.1 s.

First, to validate our calculation results, we have compared them with data obtained from literature. We are not aware of data available for case A, i.e., 15% O<sub>2</sub> present in the carrier gas, however, our results obtained for case B, i.e., 5% O<sub>2</sub>, can be compared with the simulation results by Gentile and Kushner.<sup>[15]</sup> Likewise, our results for case C, i.e., no O<sub>2</sub> present in the carrier gas, can be compared with the experimental and simulation results by Penetrante et al.<sup>[11]</sup>

Figure 11 presents the comparison between our calculation results and the data from Gentile and Kushner,<sup>[15]</sup> for the NO, NO<sub>2</sub>, and N<sub>2</sub>O concentrations as a function of time. In their paper, Gentile and Kushner considered a DBD with an input energy of 3 mJ/cm<sup>3</sup>/pulse, a repetition frequency of 10 Hz in a gas mixture of NO/N<sub>2</sub>/O<sub>2</sub>/H<sub>2</sub>O = 0.05/85/5/10 at a temperature of 400 K, so we applied our model to exactly the same conditions.

As is clear from Figure 11a, the agreement between our calculated NO and NO<sub>2</sub> concentrations and the results from Gentile and Kushner is very good. We obtained 2% more for the NO remediation and 5.5% less for the NO<sub>2</sub> production. On the other hand, for the N<sub>2</sub>O production (Figure 11b), we predict 150 times larger values compared to the results of Gentile and Kushner.

This difference in the N<sub>2</sub>O concentration arises from the omission of reaction N<sub>2</sub>(A) + O<sub>2</sub> → N<sub>2</sub>O + O in ref.,<sup>[15]</sup> whereas this reaction is found to be the dominant

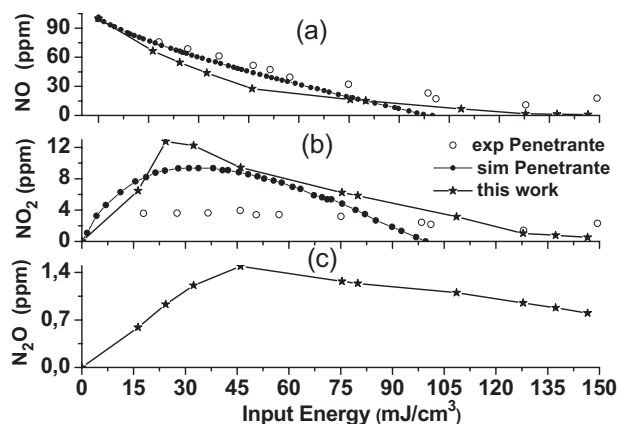


**Figure 11.** Comparison between our calculation results and the calculation results by Gentile and Kushner,<sup>[15]</sup> for a gas mixture N<sub>2</sub>/O<sub>2</sub>/H<sub>2</sub>O = 85/5/10 (hence resembling our case B) and 500 ppm NO at 400 K, a pulse frequency of 10 Hz and an input energy of 3 mJ cm<sup>-3</sup>. The results are plotted as obtained after the fourth pulse.

production process for N<sub>2</sub>O in our work, with a relative contribution of 100% in time up to *t* = 7 μs, when the density of this species converges to a constant value.

In Figure 12 our results are compared with the work of Penetrante et al. (both experiments and simulations), where a plasma was produced in a DBD at 372 K for input energies varying between 0 and 150 mJ cm<sup>-3</sup> and a gas residence time of 169 ms (169 pulses). The pulse frequency in this work was 1 kHz, and the gas mixture was N<sub>2</sub>/NO. Again we applied our simulations to exactly the same conditions. The reduced electric field (*E*/*N*) in this case was 150 Td; at this value, we calculated an electron energy of 3.46 eV, in good agreement with the value calculated by Penetrante et al.<sup>[11]</sup> (i.e., 4 eV). Furthermore, as can be observed from Figure 12, our calculation results for the NO and NO<sub>2</sub> concentrations are in good agreement with the simulations of Penetrante et al., as well as with their experimental results, predicting the same trends in the variation of NO and NO<sub>2</sub> concentrations with the input energy. For the NO concentration, the agreement is very good, while for the NO<sub>2</sub> concentration, our simulations agree rather well with the simulations of,<sup>[11]</sup> illustrating a maximum concentration around 20–30 mJ cm<sup>-3</sup> but the experimental data do not exhibit this maximum. Nevertheless, looking at the absolute values, the agreement can still be considered reasonable, at least in the correct order of magnitude.

The N<sub>2</sub>O production was not mentioned in ref.<sup>[11]</sup> Nevertheless, the variation of N<sub>2</sub>O density with the total input energy, as calculated with our model, is illustrated in Figure 12c. It is interesting to notice that the N<sub>2</sub>O production reaches a maximum when the input energy increases to 46 mJ cm<sup>-3</sup> and then it decreases by 50% at 146 mJ cm<sup>-3</sup>. Hence, our calculations predict that NO can be remediated by 99% with NO<sub>2</sub> production of about 0.52 ppm and



**Figure 12.** Comparison between our calculation results and the experiments and simulation results by Penetrante et al.,<sup>[11]</sup> after 169 pulses, for a gas mixture of N<sub>2</sub>/NO = 100/0.01 at 372 K and a pulse frequency of 1 kHz.

N<sub>2</sub>O production of about 0.8 ppm, for a total input energy of 146 mJ cm<sup>-3</sup>, when O<sub>2</sub> and H<sub>2</sub>O are not present in the gas mixture.

We investigated the reaction mechanism for one pulse, assuming different external input energies, and observed that the reaction mechanism does not really change by varying the input energy. However, the densities of the N<sub>x</sub>O<sub>y</sub> pollutants will change since the electron, ion, and radical densities are directly correlated with the applied energy.

For the analysis of the reaction mechanism during one pulse, a case of high input energy (i.e., 7 mJ cm<sup>-3</sup>) was preferred to clearly see the temporal trends of the most important species playing a role in the NO abatement process. However, Dorai and Kushner<sup>[15]</sup> have shown that it is more efficient to apply 20 pulses having in total the same input energy as for a single pulse. Therefore, we performed a set of simulations, assuming a multi-pulse regime with 440 pulses, and varying the input energy per pulse between 10<sup>-3</sup> and 7 mJ cm<sup>-3</sup>. The pulse repetition frequency was 1 kHz, so that the total gas residence time after the 440 pulses amounted to 0.44 s.

Figure 13 illustrates the NO removal efficiency after 440 pulses, as a function of energy per pulse (top x-axis) and total energy input (bottom x-axis). It is clear from this figure that in cases A and B a better NO removal is obtained for a lower input energy per pulse, hence for a lower total energy cost (except at very low energies, below 0.35 mJ/cm<sup>3</sup>/pulse, where the removal efficiency drops drastically). The highest NO removal efficiency of about 96% was achieved for 0.035 mJ/cm<sup>3</sup>/pulse at a total energy cost of 15.4 mJ cm<sup>-3</sup>.

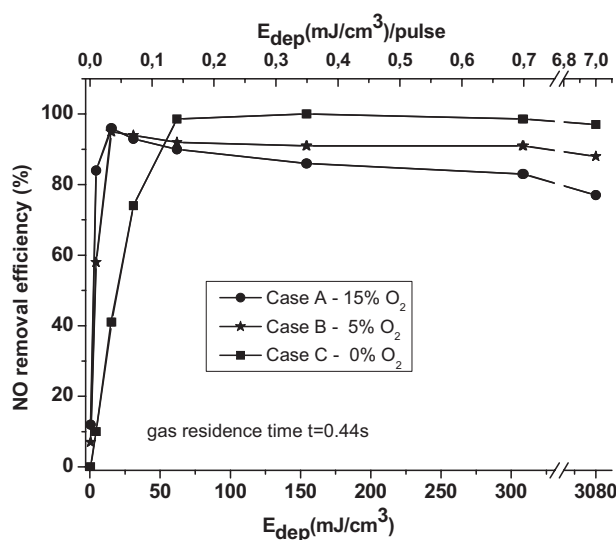


Figure 13. Calculated NO removal efficiency after 440 pulses, as a function of input energy per pulse (top axis) and total input energy (bottom axis) for a gas residence time of 0.44 s.

In case C, on the other hand, a maximum NO removal of nearly 100% is reached for 0.35 mJ/cm<sup>3</sup>/pulse, hence corresponding to a total energy cost of 154 mJ cm<sup>-3</sup>.

The NO<sub>2</sub> and N<sub>2</sub>O concentrations obtained in the multi-pulse regime are plotted versus input energy per pulse (top x-axis) and total input energy (bottom x-axis) for the three cases (A, B, and C) in Figure 14 and 15, respectively. After 440 pulses, the lowest NO<sub>2</sub> concentration in cases A and B was obtained for an input energy of 0.035 mJ/cm<sup>3</sup>/pulse (or a total input energy of 15.4 mJ cm<sup>-3</sup>), yielding values of 8 and 4 ppm, respectively (see Figure 14). However, at this energy condition, N<sub>2</sub>O values are still rather high (i.e., 283 ppm in case A and 187 ppm in case B; cf. Figure 15), illustrating that even when the NO remediation is good in these two cases, the conditions are far from optimized. The density of this by-product increases with the applied energy and it reaches the smallest values (i.e., 9 ppm in case A and 5 ppm in case B) at the lowest total input energy investigated of 0.4 mJ cm<sup>-3</sup>, but at this condition the NO removal efficiency is less than 20% (see Figure 13), indicating that this condition is also far from optimized.

In case C, on the other hand, the concentration of these two major by-products lies in the range of 0.006–1.7 ppm for different input energies, and the lowest values (i.e., 0.006 ppm for NO<sub>2</sub> and 0.02 ppm for N<sub>2</sub>O) are reached at an energy of 0.35 mJ/cm<sup>3</sup>/pulse, corresponding to a total energy cost of 154 mJ cm<sup>-3</sup>.

From Figure 13–15 it is clear that for the conditions under study, case C is the best candidate for an optimum NO remediation (100%) with the smallest amount of by-products formed, i.e., less than 0.02 ppm, for a total energy cost of 154 mJ cm<sup>-3</sup>.

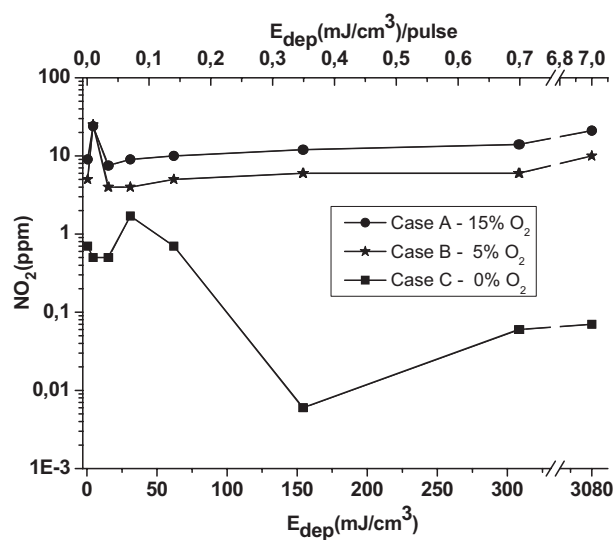


Figure 14. Calculated NO<sub>2</sub> concentration after 440 pulses, as a function of input energy per pulse (top axis) and total input energy (bottom axis) for a gas residence time of 0.44 s.

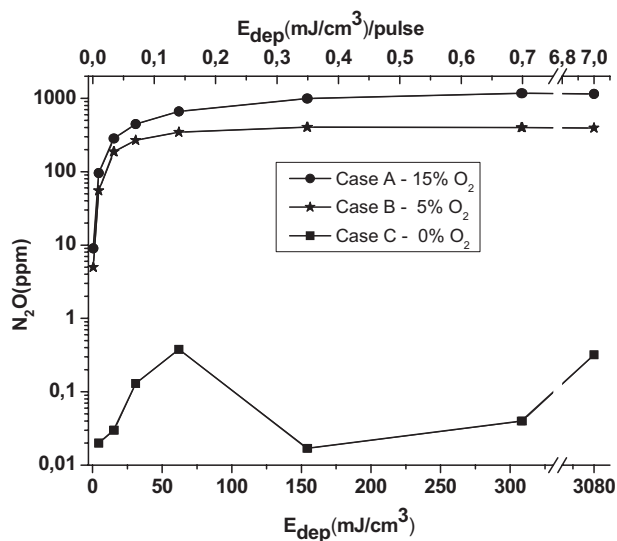


Figure 15. Calculated N<sub>2</sub>O concentration after 440 pulses, as a function of input energy per pulse (top axis) and total input energy (bottom axis) for a gas residence time of 0.44 s.

#### 4. Conclusion

A zero-dimensional chemical kinetics model for the NO remediation process is presented, focusing on a detailed analysis of the reaction mechanisms during one pulse. The gas mixture under study was N<sub>2</sub>/O<sub>2</sub>/H<sub>2</sub>O/NO/NO<sub>2</sub>. The H<sub>2</sub>O, NO and NO<sub>2</sub> concentrations were kept fixed at 25%, 100 and 1 ppm, respectively, while the O<sub>2</sub> concentration was varied from 15% over 5 to 0%.

The major pathway from NO to NO<sub>2</sub> was found to be the reactions with O radicals (i.e., NO + O + M → NO<sub>2</sub> + M). For the N<sub>2</sub>O molecules, however, the most important processes are the reaction of excited N<sub>2</sub>(A) molecules with O<sub>2</sub> (N<sub>2</sub>(A) + O<sub>2</sub> → N<sub>2</sub>O + O) and the reaction of NO<sub>2</sub> molecules with N radicals (NO<sub>2</sub> + N → N<sub>2</sub>O + O).

It has been shown that a better NO removal efficiency can be achieved for lower oxygen concentrations in the feedstock gas. Also, the applied input energy per pulse is

an important parameter when optimizing the NO abatement process.

A maximum removal efficiency of 100% was obtained when no O<sub>2</sub> was present in the carrier gas, for an input energy of 0.35 mJ/cm<sup>3</sup>/pulse, corresponding to a total energy cost of 154 mJ cm<sup>-3</sup>, for a gas residence time of 0.44 s (440 pulses). In this case, very small concentrations of the by-products NO<sub>2</sub> (~0.005 ppm) and N<sub>2</sub>O (~0.02 ppm) were obtained.

When oxygen was present in the gas at concentrations of 15 or 5%, a maximum NO removal of 96% was obtained for an input energy of 0.035 mJ/cm<sup>3</sup>/pulse at an energy cost of 15.4 mJ cm<sup>-3</sup>. These cases are attractive from the point of view of a low energy cost, but the disadvantage is the relatively high NO<sub>2</sub> and N<sub>2</sub>O by-product concentrations, i.e., after 440 pulses, the NO<sub>2</sub> concentration was calculated to be 8 and 4 ppm, for cases A and B, respectively, while the N<sub>2</sub>O concentration was still almost 283 and 187 ppm, for cases A and B, respectively. Lower N<sub>2</sub>O concentrations can be obtained at total energies lower than 15.4 mJ cm<sup>-3</sup>, but the NO removal efficiency then becomes too small (i.e., lower than 20% at 0.44 mJ cm<sup>-3</sup>).

This work suggests that for acquiring a good NO remediation with minimum by-product formation, quite low energies per pulse can be applied, but it also shows that for different O<sub>2</sub> contents in the carrier gas, there is a threshold for the energy, below which a poor NO remediation is achieved. The case without O<sub>2</sub> in the feedstock gas revealed the lowest by-product concentrations for a NO removal efficiency of 100%. Similar results for NO and NO<sub>2</sub> pollutants were predicted by other numerical and experimental works,<sup>[11,12,17]</sup> but N<sub>2</sub>O production was not yet discussed in great detail until now. Nevertheless, our calculations show that it is a more important by-product than NO<sub>2</sub>.

In future work, we will investigate in more detail the chemical kinetics of the multiple-pulses case for the attempt to optimize the conditions for a maximum removal efficiency, minimum energy cost, and low concentrations of by-products.

#### Appendix 1. Chemical reactions included in the model for the gas mixture N<sub>2</sub>/O<sub>2</sub>/H<sub>2</sub>O/NO/NO<sub>2</sub>, as well as the references where the cross-sections or rate coefficients were adopted from

No.	Chemical reaction	Rate coefficient $k$ (cm <sup>3</sup> s <sup>-1</sup> for two body and cm <sup>6</sup> s <sup>-1</sup> for three body reactions) and cross section $\sigma(E)$ [cm <sup>2</sup> ]	Ref.
Electron reactions			
1	e + O → e + O	$\sigma(E)$	[1]
2	e + O → e + O( <sup>1</sup> D)	$\sigma(E)$	[1]

Appendix 1. (Continued)

No.	Chemical reaction	Rate coefficient $k$ ( $\text{cm}^3 \text{s}^{-1}$ for two body and $\text{cm}^6 \text{s}^{-1}$ for three body reactions) cross section $\sigma(E)$ [ $\text{cm}^2$ ]	Ref.
3	$e + O \rightarrow e + O(^1S)$	$\sigma(E)$	[1]
4	$e + O \rightarrow 2e + O^+$	$\sigma(E)$	[1]
5	$e + O + M \rightarrow O^- + M$	$k = 10^{-31}$	[2]
6	$e + O(^1S) \rightarrow e + O(^1S)$	$\sigma(E)$	[1]
7	$e + O(^1D) \rightarrow e + O(^1D)$	$\sigma(E)$	[1]
8	$e + O(^1D) \rightarrow e + O$	$\sigma(E)$	[1]
9	$e + O(^1D) \rightarrow e + e + O^+$	$\sigma(E)$	[1]
10	$e + O^+ + M \rightarrow O + M$	$k = 10^{-26}$	[2]
11	$e + e + O^+ \rightarrow e + O$	$k = 7.1 \times 10^{-27} [T_e(\text{eV})]^{-4.5}$	[3]
12	$e + O^+ \rightarrow O(^1D)$	$k = 5.3 \times 10^{-13} [T_e(\text{eV})]^{-0.5}$	[5]
13	$e + O^- \rightarrow 2e + O$	$k = 2 \times 10^{-7} \exp[-5.5/T_e(\text{eV})]$	[2]
14	$e + O^- \rightarrow e + O^-$	$\sigma(E)$	[1]
15	$e + O_2 \rightarrow e + O + O$	$\sigma(E)$	[1]
16	$e + O_2 \rightarrow e + O_2$	$\sigma(E)$	[1]
17	$e + O_2 \rightarrow e + O_2(a)$	$\sigma(E)$	[1]
18	$e + O_2 \rightarrow e + O_2(b)$	$\sigma(E)$	[1]
19	$e + O_2 \rightarrow 2e + O_2^+$	$\sigma(E)$	[1]
20	$e + O_2 \rightarrow O + O^-$	$\sigma(E)$	[1]
21	$e + O_2 \rightarrow e + O + O(^1D)$	$\sigma(E)$	[1]
22	$e + O_2 \rightarrow 2e + O^+ + O$	$\sigma(E)$	[1]
23	$e + O_2 + M \rightarrow O_2^- + M$	$k = 1.4 \times 10^{-29}$	[5]
24	$e + O_2 \rightarrow e + O_{2v1}$	$\sigma(E)$	[1]
25	$e + O_2 \rightarrow e + O_{2v2}$	$\sigma(E)$	[1]
26	$e + O_2 \rightarrow e + O_{2v3}$	$\sigma(E)$	[1]
27	$e + O_2 \rightarrow e + O_{2v4}$	$\sigma(E)$	[1]
28	$e + O_2 \rightarrow e + O_{2v5}$	$\sigma(E)$	[1]
29	$e + O_2 \rightarrow e + O_{2v6}$	$\sigma(E)$	[1]
30	$e + O_{2v} \rightarrow e + O_{2v}$	$\sigma(E)$	[1]
31	$e + O_{2v} \rightarrow O^- + O$	$\sigma(E)$	[1]
32	$e + O_{2v} \rightarrow e + O_2$	$\sigma(E)$	[1]
33	$e + O_{2v} \rightarrow e + O_2(a)$	$\sigma(E)$	[1]
34	$e + O_{2v} \rightarrow e + O_2(b)$	$\sigma(E)$	[1]
35	$e + O_{2v} \rightarrow e + O + O$	$\sigma(E)$	[1]
36	$e + O_{2v} \rightarrow e + e + O_2^+$	$\sigma(E)$	[1]
37	$e + O_{2v} \rightarrow e + e + O + O^+$	$\sigma(E)$	[1]
38	$e + O_{2v} + M \rightarrow O_2^- + M$	$\sigma(E)$	[1]
39	$e + O_2^+ \rightarrow O + O$	$\sigma(E)$	[1]
40	$e + e + O_2^+ \rightarrow e + O_2$	$k = 7.1 \times 10^{-27} [T_e(\text{eV})]^{-4.5}$	[3]
41	$e + O_2^+ + M \rightarrow O_2 + M$	$k = 2 \times 10^{-26}$	[2]

## Appendix 1. (Continued)

No.	Chemical reaction	Rate coefficient $k$ (cm <sup>3</sup> s <sup>-1</sup> for two body and cm <sup>6</sup> s <sup>-1</sup> for three body reactions) cross section $\sigma(E)$ [cm <sup>2</sup> ]	Ref.
42	$e + O_2^+ \rightarrow O(^1D) + O(^1D)$	$k = 6.87 \times 10^{-9} [T_e(\text{eV})]^{-0.7}$	[5]
43	$e + O_2^+ \rightarrow e + O_2^+$	$\sigma(E)$	[1]
44	$e + O_2^+ \rightarrow O + O(^1D)$	$k = 1.54 \times 10^{-7} [T_e(\text{eV})]^{-0.7}$	[2]
45	$e + O_3 \rightarrow e + O_3$	$\sigma(E)$	[1]
46	$e + O_3 \rightarrow O_2 + O^-$	$\sigma(E)$	[1]
47	$e + O_3 \rightarrow O_2^- + O$	$\sigma(E)$	[1]
48	$e + O_3 \rightarrow e + O + O_2$	$\sigma(E)$	[1]
49	$e + O_3 \rightarrow e + O_3^-$	$\sigma(E)$	[1]
50	$e + N_2 \rightarrow e + N_2$	$\sigma(E)$	[1]
51	$e + N_2 \rightarrow e + N_2(A)$	$\sigma(E)$	[1]
52	$e + N_2 \rightarrow e + N_2(B)$	$\sigma(E)$	[1]
53	$e + N_2 \rightarrow e + N_2(a')$	$\sigma(E)$	[1]
54	$e + N_2 \rightarrow e + N + N$	$\sigma(E)$	[1]
55	$e + N_2 \rightarrow 2e + N_2^+$	$\sigma(E)$	[1]
56	$e + N_2(A) \rightarrow e + N_2$	$\sigma(E)$	[1]
57	$e + N_2^+ \rightarrow e + N_2^+$	$\sigma(E)$	[1]
58	$e + N_2^+ \rightarrow N + N$	$\sigma(E)$	[1]
59	$e + N \rightarrow e + N$	$\sigma(E)$	[1]
60	$e + N \rightarrow 2e + N^+$	$\sigma(E)$	[1]
61	$e + N \rightarrow e + N(^2P)$	$\sigma(E)$	[1]
62	$e + N(^2D) \rightarrow e + N$	$\sigma(E)$	[1]
63	$e + N(^2D) \rightarrow e + N(^2P)$	$\sigma(E)$	[1]
64	$e + N(^2D) \rightarrow 2e + N^+$	$\sigma(E)$	[1]
65	$e + N(^2D) \rightarrow e + N(^2D)$	$\sigma(E)$	[1]
66	$e + N^+ \rightarrow e + N^+$	$\sigma(E)$	[1]
67	$e + N^+ + M \rightarrow N + M$	$\sigma(E)$	[1]
68	$2e + N^+ \rightarrow e + N$	$k = 5.4 \times 10^{-24} [T_e(\text{eV})]^{-4.5}$	[4]
69	$e + N^+ + M \rightarrow N + M$	$k = 2.52 \times 10^{-29} [T_e(\text{eV})]^{-1.5}$	[4]
70	$e + N_4^+ \rightarrow e + N_4^+$	$\sigma(E)$	[1]
71	$e + N_4^+ \rightarrow N_2 + N_2$	$\sigma(E)$	[1]
72	$e + NO \rightarrow e + NO$	$\sigma(E)$	[1]
73	$e + NO \rightarrow e + N + O$	$\sigma(E)$	[1]
74	$e + NO \rightarrow 2e + NO^+$	$\sigma(E)$	[1]
75	$e + NO \rightarrow N + O^-$	$\sigma(E)$	[1]
76	$e + NO \rightarrow 2e + N^+ + O$	$\sigma(E)$	[1]
77	$e + NO \rightarrow 2e + N + O^+$	$\sigma(E)$	[1]
78	$e + NO^+ \rightarrow N + O$	$\sigma(E)$	[1]
79	$e + NO^+ \rightarrow e + NO^+$	$\sigma(E)$	[1]
80	$e + NO^+ \rightarrow N(^2D) + O$	$k = 7.8 \times 10^{-9} [T_e(\text{eV})]^{-1}$	[3]



Appendix 1. (Continued)

No.	Chemical reaction	Rate coefficient $k$ ( $\text{cm}^3 \text{s}^{-1}$ for two body and $\text{cm}^6 \text{s}^{-1}$ for three body reactions) cross section $\sigma(E)$ [ $\text{cm}^2$ ]	Ref.
81	$2e + \text{NO}^+ \rightarrow e + \text{NO}$	$k = 7.1 \times 10^{-27} [T_e(\text{eV})]^{-4.5}$	[3]
82	$e + \text{NO}^+ + \text{M} \rightarrow \text{NO} + \text{M}$	$k = 2.52 \times 10^{-29} [T_e(\text{eV})]^{-1.5}$	[3]
83	$e + \text{NO}_2 \rightarrow \text{NO} + \text{O}^-$	$k = 10^{-11}$	[3]
84	$e + \text{NO}_2 + \text{M} \rightarrow \text{NO}_2^- + \text{M}$	$k = 6 \times 10^{-30}$	[3]
85	$e + \text{N}_2\text{O} \rightarrow e + \text{N}_2\text{O}$	$\sigma(E)$	[1]
86	$e + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}^-$	$\sigma(E)$	[1]
87	$e + \text{N}_2\text{O} \rightarrow \text{N}_2\text{O}^+ + e + e$	$\sigma(E)$	[1]
88	$e + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}^+ + e + e$	$\sigma(E)$	[1]
89	$e + \text{N}_2\text{O} \rightarrow \text{N} + \text{NO}^+ + e + e$	$\sigma(E)$	[1]
90	$e + \text{N}_2\text{O} \rightarrow \text{N}_2^+ + \text{O} + e + e$	$\sigma(E)$	[1]
91	$e + \text{N}_2\text{O}^+ \rightarrow \text{N}_2 + \text{O}$	$\sigma(E)$	[1]
92	$e + \text{H}_2\text{O} \rightarrow e + \text{H}_2\text{O}$	$\sigma(E)$	[1]
93	$e + \text{H}_2\text{O} \rightarrow 2e + \text{H}_2\text{O}^+$	$\sigma(E)$	[1]
94	$e + \text{H}_2\text{O} \rightarrow \text{OH} + \text{H}^-$	$\sigma(E)$	[1]
95	$e + \text{H}_2\text{O} \rightarrow \text{OH}^- + \text{H}$	$\sigma(E)$	[1]
96	$e + \text{H}_2\text{O} \rightarrow e + \text{OH} + \text{H}$	$\sigma(E)$	[1]
97	$e + \text{H}_2 \rightarrow e + \text{H}_2$	$\sigma(E)$	[1]
98	$e + \text{H}_2 \rightarrow 2e + \text{H}_2^+$	$\sigma(E)$	[1]
99	$e + \text{H}_2 \rightarrow e + \text{H} + \text{H}$	$\sigma(E)$	[1]
100	$e + \text{H}_2^+ \rightarrow e + \text{H}^+ + \text{H}$	$\sigma(E)$	[1]
101	$e + \text{H}_2^+ \rightarrow \text{H} + \text{H}$	$\sigma(E)$	[1]
102	$e + \text{OH} \rightarrow 2e + \text{OH}^+$	$\sigma(E)$	[1]
103	$e + \text{OH} \rightarrow e + \text{OH}$	$\sigma(E)$	[1]
104	$e + \text{OH} \rightarrow e + \text{O} + \text{H}$	$k = 2.08 \times 10^{-7} T_e^{-0.76}(\text{eV}) \exp[-6.9/T_e(\text{eV})]$	[5]
105	$e + \text{HO}_2 \rightarrow e + \text{H} + \text{O}_2$	$k = 3.1 \times 10^{-9}$	[5]
106	$e + \text{H}_2\text{O}_2 \rightarrow e + 2\text{OH}$	$k = 2.36 \times 10^{-9}$	[5]
107	$e + \text{H}_2\text{O}_2 \rightarrow e + \text{HO}_2 + \text{H}$	$k = 3 \times 10^{-11}$	[5]
108	$e + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{O}^-$	$k = 1.57 \times 10^{-10} T_e^{-0.55}(\text{eV})$	[5]
109	$e + \text{H}_2\text{O}_2 \rightarrow \text{OH} + \text{OH}^-$	$k = 2.7 \times 10^{-10} T_e^{-0.5}(\text{eV})$	[5]
110	$e + \text{H}_3^+ \rightarrow \text{H}_2 + \text{H}$	$\sigma(E)$	[5]
111	$e + \text{H}_3^+ \rightarrow e + \text{H}_3^+$	$\sigma(E)$	[1]
112	$e + \text{H}_3^+ \rightarrow e + \text{H}^+ + \text{H}_2$	$\sigma(E)$	[1]
113	$e + \text{H}_3^+ \rightarrow e + \text{H}^+ + \text{H} + \text{H}$	$k = 1.8 \times 10^{-8} [T_e(\text{eV})]^{0.95} \exp[-10.5/T_e(\text{eV})]$	[5]
114	$e + \text{H}_3^+ \rightarrow \text{H} + \text{H} + \text{H}$	$k = 4.15 \times 10^{-8} [T_e(\text{eV})]^{-0.4}$	[5]
115	$e + \text{H}_3\text{O}^+ \rightarrow \text{H} + \text{H} + \text{OH}$	$k = 1 \times 10^{-7} [T_e(\text{eV})]^{-0.5}$	[5]
116	$e + \text{H}_3\text{O}^+ \rightarrow \text{H}_2\text{O} + \text{H}$	$k = 5.6 \times 10^{-8} [T_e(\text{eV})]^{-0.5}$	[5]
	Ion reactions		
117	$\text{O}^+ + \text{O}_2 \rightarrow \text{O} + \text{O}_2^+$	$k = 2 \times 10^{-11}$	[2]
118	$\text{O}^+ + \text{O}_2(a) \rightarrow \text{O} + \text{O}_2^+$	$k = 2 \times 10^{-11}$	[2]

## Appendix 1. (Continued)

No.	Chemical reaction	Rate coefficient $k$ (cm <sup>3</sup> s <sup>-1</sup> for two body and cm <sup>6</sup> s <sup>-1</sup> for three body reactions) cross section $\sigma(E)$ [cm <sup>2</sup> ]	Ref.
119	$O^+ + O_2(b) \rightarrow O + O_2^+$	$k = 2 \times 10^{-11}$	[2]
120	$O^+ + O_3 \rightarrow O_2 + O_2^+$	$k = 10^{-10}$	[2]
121	$O^+ + O + M \rightarrow O_2^+ + M$	$k = 10^{-29} [T_g(k)/300]^{0.5}$	[5]
122	$O^+ + O^- \rightarrow O + O$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	e
123	$O^+ + N_2 + M \rightarrow NO^+ + N + M$	$k = 6 \times 10^{-29} [T_g(k)/300]^{-2}$	[3]
124	$O^+ + N + M \rightarrow NO^+ + M$	$k = 10^{-29}$	[3]
125	$O^+ + NO \rightarrow NO^+ + O$	$k = 2.4 \times 10^{-11}$	[3]
126	$O^+ + N(^2D) \rightarrow N^+ + O$	$k = 1.3 \times 10^{-10}$	[3]
127	$O^+ + NO_2 \rightarrow NO_2^+ + O$	$k = 1.6 \times 10^{-9}$	[3]
128	$O^+ + N_2O \rightarrow NO^+ + NO$	$k = 2.3 \times 10^{-10}$	[3]
129	$O^+ + N_2O \rightarrow N_2O^+ + O$	$k = 4 \times 10^{-10}$	[3]
130	$O^+ + N_2O \rightarrow O_2^+ + N_2$	$k = 2 \times 10^{-11}$	[3]
131	$O^+ + H \rightarrow O + H^+$	$k = 6.8 \times 10^{-10}$	[5]
132	$O^+ + H_2 \rightarrow OH^+ + H$	$k = 1.62 \times 10^{-9}$	[5]
133	$O^+ + OH \rightarrow O + OH^+$	$k = 3.3 \times 10^{-10}$	[5]
134	$O^+ + H_2O \rightarrow O + H_2O^+$	$k = 2.6 \times 10^{-9}$	[5]
135	$O^+ + H^- \rightarrow O + H$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	e
136	$O^+ + OH^- \rightarrow HO_2$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	e
137	$O_2^+ + O^- \rightarrow O_2 + O$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	[6]
138	$O_2^+ + O^- \rightarrow 3O$	$k = 1 \times 10^{-7}$	[3]
139	$O_2^+ + O^- + M \rightarrow O_3 + M$	$k = 2 \times 10^{-25} [T_g(k)/300]^{-2.5}$	[2]
140	$O_2^+ + N_2 \rightarrow NO^+ + NO$	$k = 10^{-17}$	[3]
141	$O_2^+ + N \rightarrow NO^+ + O$	$k = 1.2 \times 10^{-10}$	[3]
142	$O_2^+ + NO \rightarrow NO^+ + O_2$	$k = 4.4 \times 10^{-10}$	[3]
143	$O_2^+ + NO_2 \rightarrow NO_2^+ + O_2$	$k = 6.6 \times 10^{-10}$	[3]
144	$O_2^+ + NO_2 \rightarrow O_3 + NO^+$	$k = 10^{-11}$	[3]
145	$O_2^+ + N_2O_5 \rightarrow NO_2^+ + NO_3 + O_2$	$k = 8.8 \times 10^{-10}$	[3]
146	$O_2^+ + H^- \rightarrow O_2 + H$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	e
147	$O_2^+ + OH^- \rightarrow O_2 + OH$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	e
148	$O^- + O_2 \rightarrow e + O_3$	$k = 5 \times 10^{-15}$	[2]
149	$O^- + O_2 + M \rightarrow O_3^- + M$	$k = 1.1 \times 10^{-30} [T_g(k)/300]^{-1}$	[3]
150	$O^- + O_2(a) \rightarrow O_2^- + O$	$k = 10^{-10}$	[3]
151	$O^- + O_2(b) \rightarrow e + O + O_2$	$k = 6.9 \times 10^{-10}$	[2]
152	$O^- + O \rightarrow e + O_2$	$k = 3 \times 10^{-10} [T_g(k)/300]^{-0.5}$	[2]
153	$O^- + H_3O^+ \rightarrow H_2O + OH$	$k = 3 \times 10^{-6} [T_g(k)/300]^{-0.5}$	[6]
154	$O^- + O_3 \rightarrow 2O_2 + e$	$k = 3 \times 10^{-10} [T_g(k)/300]^{0.5}$	[5]
155	$O^- + O_3 \rightarrow O + O_3^-$	$k = 5.3 \times 10^{-10}$	[3]

## Appendix 1. (Continued)

No.	Chemical reaction	Rate coefficient $k$ ( $\text{cm}^3 \text{s}^{-1}$ for two body and $\text{cm}^6 \text{s}^{-1}$ for three body reactions) cross section $\sigma(E)$ [ $\text{cm}^2$ ]	Ref.
156	$\text{O}^- + \text{O}_3 \rightarrow \text{O}_2 + \text{O}_2^-$	$k = 1.02 \times 10^{-11} [T_g(k)/300]^{0.5}$	[5]
157	$\text{O}^- + \text{O}_{2v} \rightarrow \text{O}_3 + \text{e}$	$k = 5 \times 10^{-15} [T_g(k)/300]^{0.5}$	[14]
158	$\text{O}^- + \text{NO} + \text{M} \rightarrow \text{NO}_2^- + \text{M}$	$k = 10^{-29}$	[3]
159	$\text{O}^- + \text{NO}_2 \rightarrow \text{NO}_2^- + \text{O}$	$k = 1.2 \times 10^{-9}$	[3]
160	$\text{O}^- + \text{N}_2\text{O} \rightarrow \text{NO}^- + \text{NO}$	$k = 2 \times 10^{-10}$	[3]
161	$\text{O}^- + \text{H}_2 \rightarrow \text{OH}^- + \text{H}$	$k = 3 \times 10^{-11}$	[5]
162	$\text{O}^- + \text{H} \rightarrow \text{OH} + \text{e}$	$k = 5 \times 10^{-10}$	[5]
163	$\text{O}^- + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{e}$	$k = 6 \times 10^{-10} [T_g(k)/300]^{-0.24}$	[5]
164	$\text{O}^- + \text{H}_2\text{O} \rightarrow \text{OH}^- + \text{OH}$	$k = 1.4 \times 10^{-9}$	[5]
165	$\text{O}^- + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{e}$	$k = 6 \times 10^{-13}$	[5]
166	$\text{O}_2^- + \text{O}^+ \rightarrow \text{O}_2 + \text{O}$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	[6]
167	$\text{O}_2^- + \text{O}_2^+ \rightarrow \text{O}_2 + \text{O}_2$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	[6]
168	$\text{O}_2^- + \text{O}_2^+ \rightarrow \text{O}_2 + \text{O} + \text{O}$	$k = 10^{-7}$	[3]
169	$\text{O}_2^- + \text{N}^+ \rightarrow \text{O}_2 + \text{N}$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	[6]
170	$\text{O}_2^- + \text{N}_2^+ \rightarrow \text{O}_2 + \text{N}_2$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	[6]
171	$\text{O}_2^- + \text{N}_4^+ \rightarrow \text{O}_2 + \text{N}_2 + \text{N}_2$	$k = 10^{-7}$	[3]
172	$\text{O}_2^- + \text{OH}^+ \rightarrow \text{O}_2 + \text{OH}$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	e
173	$\text{O}_2^- + \text{H}_3\text{O}^+ \rightarrow \text{HO}_2 + \text{H}_2\text{O}$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	e
174	$\text{O}_2^- + \text{H}_3\text{O}^+ \rightarrow \text{H} + \text{O}_2 + \text{H}_2\text{O}$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	e
175	$\text{O}_2^- + \text{O}_2(a) \rightarrow \text{O}_2 + \text{O}_2 + \text{e}$	$k = 2 \times 10^{-10}$	[3]
176	$\text{O}_2^- + \text{O}_2(b) \rightarrow \text{O}_2 + \text{O}_2 + \text{e}$	$k = 3.6 \times 10^{-10}$	[3]
177	$\text{O}_2^- + \text{N}_2(A) \rightarrow \text{O}_2 + \text{N}_2 + \text{e}$	$k = 2.1 \times 10^{-9}$	[3]
178	$\text{O}_2^- + \text{N}_2(B) \rightarrow \text{O}_2 + \text{N}_2 + \text{e}$	$k = 2.5 \times 10^{-9}$	[3]
179	$\text{O}_2^- + \text{O} \rightarrow \text{O}_2 + \text{O}^-$	$k = 3.3 \times 10^{-10}$	[3]
180	$\text{O}_2^- + \text{O} \rightarrow \text{O}_3 + \text{e}$	$k = 1.5 \times 10^{-10}$	[3]
181	$\text{O}_2^- + \text{O}_2 \rightarrow \text{e} + \text{O}_2 + \text{O}_2$	$k = 2.7 \times 10^{-10} [T_g(k)/300]^{0.5} \exp[-5590/T_g(k)]$	[3]
182	$\text{O}_2^- + \text{O}_3 \rightarrow \text{O}_2 + \text{O}_3^-$	$k = 4 \times 10^{-10}$	[3]
183	$\text{O}_2^- + \text{N}_2 \rightarrow \text{O}_2 + \text{N}_2 + \text{e}$	$k = 1.9 \times 10^{-12} [T_g(k)/300]^{0.5} \exp[-4990/T_g(k)]$	[3]
184	$\text{O}_2^- + \text{NO}_2 \rightarrow \text{NO}_2^- + \text{O}_2$	$k = 8 \times 10^{-10}$	[3]
185	$\text{O}_2^- + \text{NO}_3 \rightarrow \text{O}_2 + \text{NO}_3^-$	$k = 5 \times 10^{-10}$	[3]
186	$\text{O}_2^- + \text{N}_2\text{O} \rightarrow \text{O}_3^- + \text{N}_2$	$k = 9 \times 10^{-13}$	[3]
187	$\text{O}_2^- + \text{OH} \rightarrow \text{O}_2 + \text{OH}^-$	$k = 10^{-10}$	[5]
188	$\text{O}_2^- + \text{H} \rightarrow \text{HO}_2 + \text{e}$	$k = 1.5 \times 10^{-9}$	[5]
189	$\text{O}_2^- + \text{H}_2\text{O} \rightarrow \text{O}_2 + \text{H}_2\text{O} + \text{e}$	$k = 5 \times 10^{-9} \exp[-5000/T_g(k)]$	[5]
190	$\text{O}_3^- + \text{O}^+ \rightarrow \text{O}_3 + \text{O}$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	e
191	$\text{O}_3^- + \text{O}_2^+ \rightarrow \text{O}_3 + \text{O}_2$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	e
192	$\text{O}_3^- + \text{N}^+ \rightarrow \text{O}_3 + \text{N}$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	e

## Appendix 1. (Continued)

No.	Chemical reaction	Rate coefficient $k$ (cm <sup>3</sup> s <sup>-1</sup> for two body and cm <sup>6</sup> s <sup>-1</sup> for three body reactions) cross section $\sigma(E)$ [cm <sup>2</sup> ]	Ref.
193	$O_3^- + N_2^+ \rightarrow O_3 + N_2$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	e
194	$O_3^- + O \rightarrow O_2^- + O_2$	$k = 3.2 \times 10^{-10}$	[3]
195	$O_3^- + O \rightarrow O_2 + O_2 + e$	$k = 3 \times 10^{-10}$	[3]
196	$O_3^- + NO \rightarrow NO_3^- + O$	$k = 10^{-11}$	[3]
197	$O_3^- + NO \rightarrow NO_2^- + O_2$	$k = 2.6 \times 10^{-12}$	[3]
198	$O_3^- + NO_2 \rightarrow O_3 + NO_2^-$	$k = 7 \times 10^{-10}$	[3]
199	$O_3^- + NO_2 \rightarrow O_2 + NO_3^-$	$k = 2 \times 10^{-11}$	[3]
200	$O_3^- + NO_3 \rightarrow O_3 + NO_3^-$	$k = 5 \times 10^{-10}$	[3]
201	$N^+ + O_2 \rightarrow N + O_2^+$	$k = 2.8 \times 10^{-10}$	[3]
202	$N^+ + O_2 \rightarrow NO^+ + O$	$k = 2.5 \times 10^{-10}$	[3]
203	$N^+ + O_2 \rightarrow NO + O^+$	$k = 2.8 \times 10^{-11}$	[3]
204	$N^+ + O \rightarrow N + O^+$	$k = 10^{-12}$	[3]
205	$N^+ + O_3 \rightarrow NO^+ + O_2$	$k = 5 \times 10^{-10}$	[3]
206	$N^+ + N_2 \rightarrow N + N_2^+$	$k = 4.45 \times 10^{-10}$	[4]
207	$N^+ + N + M \rightarrow N_2^+ + M$	$k = 3 \times 10^{-31} [300/T_g(k)]^{0.75}$	[4]
208	$N^+ + N + M \rightarrow N_2^+ + M$	$k = 10^{-29}$	[4]
209	$N^+ + O + M \rightarrow NO^+ + M$	$k = 10^{-29}$	[3]
210	$N^+ + N + M \rightarrow N_2^+ + M$	$k = 10^{-29}$	[3]
211	$N^+ + NO \rightarrow N + NO^+$	$k = 8 \times 10^{-10}$	[3]
212	$N^+ + NO \rightarrow N_2^+ + O$	$k = 3 \times 10^{-12}$	[3]
213	$N^+ + NO \rightarrow O^+ + N_2$	$k = 10^{-12}$	[3]
214	$N^+ + N_2O \rightarrow N_2 + NO^+$	$k = 5.5 \times 10^{-10}$	[3]
215	$N_2^+ + O_2 \rightarrow O_2^+ + N_2$	$k = 6 \times 10^{-11} [300/T_g(k)]^{0.5}$	[3]
216	$N_2^+ + O \rightarrow NO^+ + N$	$k = 1.3 \times 10^{-10} [300/T_g(k)]^{0.5}$	[3]
217	$N_2^+ + O \rightarrow O^+ + N_2$	$k = 10^{-11} [300/T_g(k)]^{0.2}$	[3]
218	$N_2^+ + O_3 \rightarrow O_2^+ + O + N_2$	$k = 10^{-10}$	[3]
219	$N_2^+ + N \rightarrow N_2 + N^+$	$k = 2.4 \times 10^{-15} T_g(K)$	[4]
220	$N_2^+ + N_2 + M \rightarrow N_4^+ + M$	$k = 6.8 \times 10^{-29} [300/T_g(k)]^{1.64}$	[4]
221	$N_2^+ + NO \rightarrow N_2 + NO^+$	$k = 3.3 \times 10^{-10}$	[3]
222	$N_2^+ + N_2O \rightarrow N_2 + NO^+ + N$	$k = 4 \times 10^{-10}$	[3]
223	$N_2^+ + N_2O \rightarrow N_2 + N_2O^+$	$k = 5 \times 10^{-10}$	[3]
224	$N_4^+ + O_2 \rightarrow 2N_2 + O_2^+$	$k = 2.5 \times 10^{-10}$	[3]
225	$N_4^+ + O \rightarrow O^+ + 2N_2$	$k = 2.5 \times 10^{-10}$	[3]
226	$N_4^+ + N \rightarrow 2N_2 + N^+$	$k = 10^{-11}$	[3]
227	$N_4^+ + NO \rightarrow 2N_2 + NO^+$	$k = 4 \times 10^{-10}$	[3]
228	$NO^+ + O^- \rightarrow NO + O$	$k = 3 \times 10^{-6} [T_g(k)/300]^{-0.5}$	[6]
229	$NO^+ + O^- \rightarrow N + O + O$	$k = 10^{-7}$	[3]
230	$NO^+ + O^- + M \rightarrow NO_2 + M$	$k = 2 \times 10^{-25} [T_g(k)/300]^{-2.5}$	[3]

## Appendix 1. (Continued)

No.	Chemical reaction	Rate coefficient $k$ ( $\text{cm}^3 \text{s}^{-1}$ for two body and $\text{cm}^6 \text{s}^{-1}$ for three body reactions) cross section $\sigma(E)$ [ $\text{cm}^2$ ]	Ref.
231	$\text{NO}^+ + \text{O}_2^- \rightarrow \text{NO} + \text{O}_2$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	[6]
232	$\text{NO}^+ + \text{O}_2^- + \text{M} \rightarrow \text{NO}_3 + \text{M}$	$k = 2 \times 10^{-25} [T_g(k)/300]^{-2.5}$	[3]
233	$\text{NO}^+ + \text{O}_2^- \rightarrow \text{N} + \text{O} + \text{O}_2$	$k = 10^{-7}$	[3]
234	$\text{NO}^+ + \text{O}_3^- \rightarrow \text{NO} + \text{O}_3$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	e
235	$\text{NO}^+ + \text{O}_3^- \rightarrow \text{N} + \text{O} + \text{O}_3$	$k = 10^{-7}$	[3]
236	$\text{NO}^+ + \text{H}^- \rightarrow \text{NO} + \text{H}$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	e
237	$\text{NO}^+ + \text{H}^- + \text{M} \rightarrow \text{HNO} + \text{M}$	$k = 10^{-25}$	[6]
238	$\text{NO}^+ + \text{OH}^- \rightarrow \text{NO} + \text{OH}$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	e
239	$\text{NO}^+ + \text{NO}^- \rightarrow \text{NO} + \text{NO}$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	e
240	$\text{NO}^+ + \text{NO}^- \rightarrow \text{N} + \text{O} + \text{NO}$	$k = 10^{-7}$	[3]
241	$\text{NO}^+ + \text{NO}_2^- \rightarrow \text{NO} + \text{NO}_2$	$k = 3 \times 10^{-6} [T_g(k)/300]^{-0.5}$	e
242	$\text{NO}^+ + \text{NO}_2^- \rightarrow \text{N} + \text{O} + \text{NO}_2$	$k = 10^{-7}$	[3]
243	$\text{NO}^+ + \text{NO}_3^- \rightarrow \text{NO} + \text{NO}_3$	$k = 3 \times 10^{-6} [T_g(k)/300]^{-0.5}$	e
244	$\text{NO}^+ + \text{NO}_3^- \rightarrow \text{N} + \text{O} + \text{NO}_3$	$k = 10^{-7}$	[3]
245	$\text{NO}^+ + \text{O}_3 \rightarrow \text{NO}_2^+ + \text{O}_2$	$k = 10^{-15}$	[3]
246	$\text{NO}^+ + \text{N}_2\text{O}_5 \rightarrow \text{NO}_2^+ + 2\text{NO}_2$	$k = 5.9 \times 10^{-10}$	[3]
247	$\text{NO}_2^+ + \text{O}^- \rightarrow \text{N} + \text{O} + \text{O}_2$	$k = 10^{-7}$	[3]
248	$\text{NO}_2^+ + \text{O}_2^- \rightarrow \text{N} + \text{O}_2 + \text{O}_2$	$k = 10^{-7}$	[3]
249	$\text{NO}_2^+ + \text{O}_3^- \rightarrow \text{NO}_2 + \text{O}_3$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	e
250	$\text{NO}_2^+ + \text{O}_3^- \rightarrow \text{N} + \text{O}_2 + \text{O}_3$	$k = 10^{-7}$	[3]
251	$\text{NO}_2^+ + \text{H}^- \rightarrow \text{NO}_2 + \text{H}$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	e
252	$\text{NO}_2^+ + \text{OH}^- \rightarrow \text{NO}_2 + \text{OH}$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	e
253	$\text{NO}_2^+ + \text{NO}^- \rightarrow \text{NO}_2 + \text{NO}$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	e
254	$\text{NO}_2^+ + \text{NO} \rightarrow \text{NO}^+ + \text{NO}_2$	$k = 2.9 \times 10^{-10}$	[3]
255	$\text{N}_2\text{O}^+ + \text{NO} \rightarrow \text{NO}^+ + \text{N}_2\text{O}$	$k = 2.9 \times 10^{-10}$	[3]
256	$\text{NO}^- + \text{O}_2 \rightarrow \text{NO} + \text{O}_2^-$	$k = 5 \times 10^{-10}$	[3]
257	$\text{NO}^- + \text{NO}_2 \rightarrow \text{NO}_2^- + \text{NO}$	$k = 7.4 \times 10^{-16}$	[3]
258	$\text{NO}^- + \text{N}_2\text{O} \rightarrow \text{NO}_2^- + \text{N}_2$	$k = 2.8 \times 10^{-14}$	[3]
259	$\text{NO}_2^- + \text{O}^+ \rightarrow \text{NO}_2 + \text{O}$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	[6]
260	$\text{NO}_2^- + \text{O}_2^+ \rightarrow \text{NO}_2 + \text{O}_2$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	[6]
261	$\text{NO}_2^- + \text{N}^+ \rightarrow \text{NO}_2 + \text{N}$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	[6]
262	$\text{NO}_2^- + \text{N}_2^+ \rightarrow \text{NO}_2 + \text{N}_2$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	e
263	$\text{NO}_2^- + \text{N}_4^+ \rightarrow \text{NO}_2 + \text{N}_2 + \text{N}_2$	$k = 3 \times 10^{-6} [T_g(k)/300]^{-0.5}$	[6]
264	$\text{NO}_2^- + \text{NO}_2^+ \rightarrow \text{NO}_2 + \text{NO}_2$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	e
265	$\text{NO}_2^- + \text{N}_2\text{O}^+ \rightarrow \text{NO}_2 + \text{N}_2\text{O}$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	[6]
266	$\text{NO}_2^- + \text{H}^+ \rightarrow \text{NO}_2 + \text{H}$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	e

## Appendix 1. (Continued)

No.	Chemical reaction	Rate coefficient $k$ (cm <sup>3</sup> s <sup>-1</sup> for two body and cm <sup>6</sup> s <sup>-1</sup> for three body reactions) cross section $\sigma(E)$ [cm <sup>2</sup> ]	Ref.
267	$\text{NO}_2^- + \text{H}_2^+ \rightarrow \text{NO}_2 + \text{H}_2$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	e
268	$\text{NO}_2^- + \text{OH}^+ \rightarrow \text{NO}_2 + \text{OH}$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	e
269	$\text{NO}_2^- + \text{H}_2\text{O}^+ \rightarrow \text{NO}_2 + \text{H}_2\text{O}$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	[6]
270	$\text{NO}_2^- + \text{H}_3\text{O}^+ \rightarrow \text{NO}_2 + \text{H}_2\text{O} + \text{H}$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	[6]
271	$\text{NO}_2^- + \text{O}_3 \rightarrow \text{NO}_3^- + \text{O}_2$	$k = 1.8 \times 10^{-11}$	[3]
272	$\text{NO}_2^- + \text{NO}_2 \rightarrow \text{NO}_3^- + \text{NO}$	$k = 4 \times 10^{-12}$	[3]
273	$\text{NO}_2^- + \text{NO}_3 \rightarrow \text{NO}_3^- + \text{NO}_2$	$k = 5 \times 10^{-10}$	[3]
274	$\text{NO}_2^- + \text{N}_2\text{O} \rightarrow \text{NO}_3^- + \text{N}_2$	$k = 5 \times 10^{-13}$	[6]
275	$\text{NO}_2^- + \text{N}_2\text{O}_5 \rightarrow \text{NO}_3^- + \text{NO}_3 + \text{NO}$	$k = 7 \times 10^{-10}$	[3]
276	$\text{NO}_2^- + \text{HNO}_3 \rightarrow \text{NO}_3^- + \text{HNO}_2$	$k = 1.6 \times 10^{-9}$	[6]
277	$\text{NO}_3^- + \text{O}^+ \rightarrow \text{NO}_3 + \text{O}$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	[6]
278	$\text{NO}_3^- + \text{O}_2^+ \rightarrow \text{NO}_3 + \text{O}_2$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	[6]
279	$\text{NO}_3^- + \text{N}^+ \rightarrow \text{NO}_3 + \text{N}$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	[6]
280	$\text{NO}_3^- + \text{N}_2^+ \rightarrow \text{NO}_3 + \text{N}_2$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	[6]
281	$\text{NO}_3^- + \text{N}_4^+ \rightarrow \text{NO}_3 + \text{N}_2 + \text{N}_2$	$k = 3 \times 10^{-6} [T_g(k)/300]^{-0.5}$	[6]
282	$\text{NO}_3^- + \text{NO}_2^+ \rightarrow \text{NO}_3 + \text{NO}_2$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	e
283	$\text{NO}_3^- + \text{N}_2\text{O}^+ \rightarrow \text{NO}_3 + \text{N}_2\text{O}$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	e
284	$\text{NO}_3^- + \text{H}^+ \rightarrow \text{NO}_3 + \text{H}$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	e
285	$\text{NO}_3^- + \text{H}_2^+ \rightarrow \text{NO}_3 + \text{H}_2$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	e
286	$\text{NO}_3^- + \text{OH}^+ \rightarrow \text{NO}_3 + \text{OH}$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	e
287	$\text{NO}_3^- + \text{H}_2\text{O}^+ \rightarrow \text{NO}_3 + \text{H}_2\text{O}$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	[6]
288	$\text{NO}_3^- + \text{H}_3\text{O}^+ \rightarrow \text{NO}_3 + \text{H}_2\text{O} + \text{H}$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	[6]
289	$\text{NO}_3^- + \text{NO} \rightarrow \text{NO}_2^- + \text{NO}_2$	$k = 3 \times 10^{-15}$	[3]
290	$\text{H}^- + \text{H} \rightarrow \text{e} + \text{H}_2$	$k = 1.3 \times 10^{-9}$	[7]
291	$\text{H}^- + \text{O}(^1D) \rightarrow \text{OH} + \text{e}$	$k = 10^{-9}$	[5]
292	$\text{H}^- + \text{O} \rightarrow \text{e} + \text{OH}$	$k = 10^{-9}$	[5]
293	$\text{H}^- + \text{O}_2 \rightarrow \text{HO}_2 + \text{e}$	$k = 1.2 \times 10^{-9}$	[5]
294	$\text{H}^- + \text{OH} \rightarrow \text{H}_2\text{O} + \text{e}$	$k = 10^{-10}$	[5]
295	$\text{H}^- + \text{H}_2\text{O} \rightarrow \text{OH}^- + \text{H}_2$	$k = 3.8 \times 10^{-9}$	[5]
296	$\text{H}^+ + \text{H} + \text{M} \rightarrow \text{H}_2^+ + \text{M}$	$k = 10^{-34}$	[5]
297	$\text{H}^+ + \text{O} \rightarrow \text{H} + \text{O}^+$	$k = 7 \times 10^{-10} \exp[-232/T_g(k)]$	[5]
298	$\text{H}^+ + \text{O}_2 \rightarrow \text{H} + \text{O}_2^+$	$k = 2 \times 10^{-9}$	[5]
299	$\text{H}^+ + \text{OH} \rightarrow \text{H} + \text{OH}^+$	$k = 2 \times 10^{-9}$	[5]
300	$\text{H}^+ + \text{H}_2\text{O} \rightarrow \text{H} + \text{H}_2\text{O}^+$	$k = 6.9 \times 10^{-9}$	[5]
301	$\text{H}^+ + \text{H}_2 + \text{M} \rightarrow \text{H}_3^+ + \text{M}$	$k = 3.1 \times 10^{-29} [T_g(k)/300]^{-0.5}$	[5]
302	$\text{H}^+ + \text{O}^- \rightarrow \text{H} + \text{O}$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	e
303	$\text{H}^+ + \text{O}_2^- \rightarrow \text{HO}_2$	$k = 2 \times 10^{-7} [T_g(k)/300]^{-0.5}$	[5]

## Appendix 1. (Continued)

No.	Chemical reaction	Rate coefficient $k$ ( $\text{cm}^3 \text{s}^{-1}$ for two body and $\text{cm}^6 \text{s}^{-1}$ for three body reactions) cross section $\sigma(E)$ [ $\text{cm}^2$ ]	Ref.
304	$\text{H}^+ + \text{OH}^- + \text{M} \rightarrow \text{H}_2\text{O} + \text{M}$	$k = 2 \times 10^{-25} [T_g(k)/300]^{-2.5}$	[5]
305	$\text{H}_2^+ + \text{H} \rightarrow \text{H}^+ + \text{H}_2$	$k = 6.39 \times 10^{-10}$	[5]
306	$\text{H}_2^+ + \text{O} \rightarrow \text{OH}^+ + \text{H}$	$k = 1.5 \times 10^{-9}$	[5]
307	$\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}$	$k = 2.1 \times 10^{-9}$	[5]
308	$\text{H}_2^+ + \text{O}_2 \rightarrow \text{O}_2^+ + \text{H}_2$	$k = 8 \times 10^{-10}$	[5]
309	$\text{H}_2^+ + \text{OH} \rightarrow \text{H}_2 + \text{OH}^+$	$k = 7.6 \times 10^{-10}$	[5]
310	$\text{H}_2^+ + \text{OH} \rightarrow \text{H}_2\text{O}^+ + \text{H}$	$k = 7.6 \times 10^{-10}$	[5]
311	$\text{H}_2^+ + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{H}_2\text{O}^+$	$k = 3.9 \times 10^{-9}$	[5]
312	$\text{H}_2^+ + \text{H}_2\text{O} \rightarrow \text{H} + \text{H}_3\text{O}^+$	$k = 3.4 \times 10^{-9}$	[5]
313	$\text{H}_2^+ + \text{H}^- \rightarrow \text{H} + \text{H}_2$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	e
314	$\text{H}_2^+ + \text{O}^- \rightarrow \text{H}_2\text{O}$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	e
315	$\text{H}_2^+ + \text{O}_2^- \rightarrow \text{H}_2 + \text{O}_2$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	e
316	$\text{H}_2^+ + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{H}$	$k = 10^{-7}$	[5]
317	$\text{H}_2^+ + \text{OH}^- \rightarrow \text{H}_2 + \text{OH}$	$k = 10^{-7}$	[5]
318	$\text{H}_3^+ + \text{O} \rightarrow \text{OH}^+ + \text{H}_2$	$k = 8 \times 10^{-10}$	[5]
319	$\text{H}_3^+ + \text{OH} \rightarrow \text{H}_2\text{O}^+ + \text{H}_2$	$k = 1.3 \times 10^{-9}$	[5]
320	$\text{H}_3^+ + \text{H}^- \rightarrow \text{H}_2 + \text{H}_2$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	e
321	$\text{H}_3^+ + \text{O}^- \rightarrow \text{OH} + \text{H}_2$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	e
322	$\text{H}_3^+ + \text{O}_2^- \rightarrow \text{OH} + \text{H}_2\text{O}$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	e
323	$\text{H}_3^+ + \text{OH}^- \rightarrow \text{H}_2 + \text{H}_2\text{O}$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	e
324	$\text{H}_3^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{H}_2$	$k = 5.9 \times 10^{-9}$	[5]
325	$\text{OH}^+ + \text{H}_2 \rightarrow \text{H}_2\text{O}^+ + \text{H}$	$k = 1.3 \times 10^{-9}$	[5]
326	$\text{OH}^+ + \text{O} \rightarrow \text{O}_2^+ + \text{H}$	$k = 7 \times 10^{-10}$	[5]
327	$\text{OH}^+ + \text{O}_2 \rightarrow \text{OH} + \text{O}_2^+$	$k = 3.8 \times 10^{-10}$	[5]
328	$\text{OH}^+ + \text{OH} \rightarrow \text{H}_2\text{O}^+ + \text{O}$	$k = 7 \times 10^{-10}$	[5]
329	$\text{OH}^+ + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^+ + \text{OH}$	$k = 1.5 \times 10^{-9}$	[5]
330	$\text{OH}^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{O}$	$k = 1.3 \times 10^{-9}$	[5]
331	$\text{OH}^+ + \text{H}^- \rightarrow \text{H}_2\text{O}$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	e
332	$\text{OH}^+ + \text{O}^- \rightarrow \text{HO}_2$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	e
333	$\text{OH}^+ + \text{O}_2^- \rightarrow \text{OH} + \text{O}_2$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	e
334	$\text{OH}^+ + \text{OH}^- \rightarrow \text{OH} + \text{OH}$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	e
335	$\text{OH}^- + \text{H} \rightarrow \text{H}_2\text{O} + \text{e}$	$k = 1.8 \times 10^{-9}$	[5]
336	$\text{OH}^- + \text{O} \rightarrow \text{HO}_2 + \text{e}$	$k = 2 \times 10^{-10}$	[5]
337	$\text{OH}^- + \text{O}^+ \rightarrow \text{OH} + \text{O}$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	e
338	$\text{OH}^- + \text{N}^+ \rightarrow \text{OH} + \text{N}$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	e
339	$\text{OH}^- + \text{N}_2^+ \rightarrow \text{OH} + \text{N}_2$	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	e
340	$\text{OH}^- + \text{N}_4^+ \rightarrow \text{OH} + \text{N}_2 + \text{N}_2$	$k = 10^{-7}$	e

## Appendix 1. (Continued)

No.	Chemical reaction	Rate coefficient $k$ (cm <sup>3</sup> s <sup>-1</sup> for two body and cm <sup>6</sup> s <sup>-1</sup> for three body reactions) cross section $\sigma(E)$ [cm <sup>2</sup> ]	Ref.
341	OH <sup>-</sup> + N <sub>2</sub> O <sup>+</sup> → OH + N <sub>2</sub> O	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	e
342	OH <sup>-</sup> + H <sub>3</sub> <sup>+</sup> → OH + H + H <sub>2</sub>	$k = 10^{-7}$	e
343	OH <sup>-</sup> + H <sub>3</sub> O <sup>+</sup> → H <sub>2</sub> O + H <sub>2</sub> O	$k = 10^{-7}$	e
344	H <sub>2</sub> O <sup>+</sup> + H <sup>-</sup> → H <sub>2</sub> O + H	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	e
345	H <sub>2</sub> O <sup>+</sup> + O <sup>-</sup> + M → H <sub>2</sub> O + O + M	$k = 2 \times 10^{-25} [T_g(k)/300]^{-2.5}$	[5]
346	H <sub>2</sub> O <sup>+</sup> + O <sub>2</sub> <sup>-</sup> → H <sub>2</sub> O + O <sub>2</sub>	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	e
347	H <sub>2</sub> O <sup>+</sup> + OH <sup>-</sup> → H <sub>2</sub> O + OH	$k = 2 \times 10^{-6} [T_g(k)/300]^{-0.5}$	e
348	H <sub>2</sub> O <sup>+</sup> + O → H <sub>2</sub> + O <sub>2</sub> <sup>+</sup>	$k = 5.5 \times 10^{-11}$	[5]
349	H <sub>2</sub> O <sup>+</sup> + O <sub>2</sub> → H <sub>2</sub> O + O <sub>2</sub> <sup>+</sup>	$k = 3.3 \times 10^{-10}$	[5]
350	H <sub>2</sub> O <sup>+</sup> + H <sub>2</sub> → H <sub>3</sub> O <sup>+</sup> + H	$k = 1.3 \times 10^{-9}$	[5]
351	H <sub>2</sub> O <sup>+</sup> + OH → H <sub>3</sub> O <sup>+</sup> + O	$k = 6.9 \times 10^{-10}$	[5]
352	H <sub>2</sub> O <sup>+</sup> + H <sub>2</sub> O → H <sub>3</sub> O <sup>+</sup> + OH	$k = 1.7 \times 10^{-9}$	[5]
Excited species reactions			
353	O <sub>2</sub> (a) + O → O <sub>2</sub> + O	$k = 10^{-16}$	[8]
354	O <sub>2</sub> (a) + O <sub>2</sub> → O <sub>2</sub> + O <sub>2</sub>	$k = 3 \times 10^{-18} \exp[-200/T_g(k)]$	[9]
355	O <sub>2</sub> (a) + O <sub>2v</sub> → O <sub>2v</sub> + O <sub>2</sub>	$k = 3 \times 10^{-18} \exp[-200/T_g(k)]$	[14]
356	O <sub>2</sub> (a) + O <sub>2v</sub> → O + O <sub>3</sub>	$k = 5 \times 10^{-20} [T_g(K)/300]^{0.5}$	[14]
357	O <sub>2</sub> (a) + O <sub>3</sub> → O <sub>2</sub> + O <sub>2</sub> + O	$k = 5.2 \times 10^{-11} \exp[-2840/T_g(k)]$	[9]
358	O <sub>2</sub> (a) + O <sub>3</sub> → O <sub>2</sub> + O <sub>3</sub>	$k = 4.6 \times 10^{-11} \exp[-2810/T_g(k)]$	[2]
359	O <sub>2</sub> (a) + O <sub>2</sub> (a) → O <sub>2</sub> (b) + O <sub>2</sub>	$k = 1.8 \times 10^{-19} [T_g(k)/300]^{3.8} \exp[700/T_g(k)]$	[4]
360	O <sub>2</sub> (a) + N → O + NO	$k = 2 \times 10^{-14} \exp[-600/T_g(k)]$	[3]
361	O <sub>2</sub> (a) + N <sub>2</sub> → O <sub>2</sub> + N <sub>2</sub>	$k = 1.4 \times 10^{-19}$	[8]
362	O <sub>2</sub> (a) + NO → O <sub>2</sub> + NO	$k = 2.5 \times 10^{-11}$	[3]
363	O <sub>2</sub> (a) + H → OH + O	$k = 1.8 \times 10^{-13} \exp[-1550/T_g(k)]$	[5]
364	O <sub>2</sub> (a) + HO <sub>2</sub> → OH + O + O <sub>2</sub>	$k = 1.6 \times 10^{-11}$	[5]
365	O <sub>2</sub> (b) + O → O <sub>2</sub> + O( <sup>1</sup> D)	$k = 3.39 \times 10^{-11} \exp[-4201/T_g(k)]$	[2]
366	O <sub>2</sub> (b) + O → O <sub>2</sub> (a) + O	$k = 8 \times 10^{-14}$	[8]
367	O <sub>2</sub> (b) + O <sub>2</sub> → O <sub>2</sub> (a) + O <sub>2</sub>	$k = 4.3 \times 10^{-22} \exp[-241/T_g(k)]$	[2]
368	O <sub>2</sub> (b) + O <sub>2</sub> → O <sub>2</sub> + O <sub>2</sub>	$k = 4 \times 10^{-17}$	[9]
369	O <sub>2</sub> (b) + O <sub>2v</sub> → O <sub>2v</sub> + O <sub>2</sub> (a)	$k = 6.23 \times 10^{-16} [T_g(K)/300]^{0.5}$	[14]
370	O <sub>2</sub> (b) + O <sub>2v</sub> → O <sub>2v</sub> + O <sub>2</sub>	$k = 6.93 \times 10^{-16} [T_g(K)/300]^{0.5}$	[14]
371	O <sub>2</sub> (b) + O <sub>3</sub> → O <sub>2</sub> + O <sub>2</sub> + O	$k = 2.2 \times 10^{-11}$	[8]
372	O <sub>2</sub> (b) + O <sub>3</sub> → O <sub>2</sub> (a) + O <sub>3</sub>	$k = 2.2 \times 10^{-11}$	[8]
373	O <sub>2</sub> (b) + O <sub>3</sub> → O <sub>2</sub> + O <sub>3</sub>	$k = 2.2 \times 10^{-11}$	[8]
374	O <sub>2</sub> (b) + N <sub>2</sub> → O <sub>2</sub> (a) + N <sub>2</sub>	$k = 4.9 \times 10^{-15} \exp[-253/T_g(k)]$	[3]
375	O <sub>2</sub> (b) + H <sub>2</sub> O → O <sub>2</sub> (a) + H <sub>2</sub> O	$k = 4.5 \times 10^{-12} \exp[89/T_g(k)]$	[5]
376	O <sub>2v</sub> + O <sub>2</sub> → O <sub>2</sub> + O <sub>2</sub>	$k = 1.73 \times 10^{-13} [T_g(K)/300]^{0.5}$	[14]



## Appendix 1. (Continued)

No.	Chemical reaction	Rate coefficient $k$ ( $\text{cm}^3 \text{s}^{-1}$ for two body and $\text{cm}^6 \text{s}^{-1}$ for three body reactions) cross section $\sigma(E)$ [ $\text{cm}^2$ ]	Ref.
377	$\text{O}(^1D) + \text{O} \rightarrow \text{O} + \text{O}$	$k = 8 \times 10^{-12}$	[2]
378	$\text{O}(^1D) + \text{O}_2 \rightarrow \text{O}_2(b) + \text{O}$	$k = 2.56 \times 10^{-11} \exp[67/T_g(k)]$	[2]
379	$\text{O}(^1D) + \text{O}_2 \rightarrow \text{O}_2(a) + \text{O}$	$k = 10^{-12}$	[2]
380	$\text{O}(^1D) + \text{O}_2 \rightarrow \text{O}_2 + \text{O}$	$k = 3.2 \times 10^{-11} \exp[67/T_g(k)]$	[9]
381	$\text{O}(^1D) + \text{O}_3 \rightarrow \text{O}_2 + \text{O} + \text{O}$	$k = 2.4 \times 10^{-10}$	[9]
382	$\text{O}(^1D) + \text{O}_3 \rightarrow \text{O}_2(a) + \text{O}_2(a)$	$k = 2.4 \times 10^{-10}$	[9]
383	$\text{O}(^1D) + \text{O}_3 \rightarrow \text{O}_2(b) + \text{O}_2$	$k = 2.4 \times 10^{-10}$	[9]
384	$\text{O}(^1D) + \text{O}_3 \rightarrow \text{O}_3 + \text{O}$	$k = 2.4 \times 10^{-10}$	[9]
385	$\text{O}(^1D) + \text{O}_3 \rightarrow \text{O}_2 + \text{O}_2$	$k = 2.4 \times 10^{-10}$	[9]
386	$\text{O}(^1D) + \text{N}_2 \rightarrow \text{O} + \text{N}_2$	$k = 1.8 \times 10^{-11} \exp[107/T_g(k)]$	[9]
387	$\text{O}(^1D) + \text{NO} \rightarrow \text{O} + \text{NO}$	$k = 4 \times 10^{-11}$	[8]
388	$\text{O}(^1D) + \text{NO} \rightarrow \text{O}_2 + \text{N}$	$k = 1.7 \times 10^{-10}$	[3]
389	$\text{O}(^1D) + \text{N}_2\text{O} \rightarrow \text{NO} + \text{NO}$	$k = 7.2 \times 10^{-11}$	[9]
390	$\text{O}(^1D) + \text{N}_2\text{O} \rightarrow \text{O}_2 + \text{N}_2$	$k = 4.4 \times 10^{-11}$	[9]
391	$\text{O}(^1D) + \text{N}_2 + \text{M} \rightarrow \text{N}_2\text{O} + \text{M}$	$k = 2.8 \times 10^{-36}$	[9]
392	$\text{O}(^1D) + \text{NO}_2 \rightarrow \text{O}_2 + \text{NO}$	$k = 1.4 \times 10^{-10}$	[8]
393	$\text{O}(^1D) + \text{HO}_2 \rightarrow \text{OH} + \text{O}_2$	$k = 2.9 \times 10^{-11} \exp[200/T_g(k)]$	[5]
394	$\text{O}(^1D) + \text{H}_2\text{O} \rightarrow \text{OH} + \text{OH}$	$k = 1.6 \times 10^{-10} \exp[64/T_g(k)]$	[5]
395	$\text{O}(^1D) + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{O}_2$	$k = 2.2 \times 10^{-12}$	[5]
396	$\text{O}(^1D) + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O} + \text{O}$	$k = 1.2 \times 10^{-11}$	[5]
397	$\text{O}(^1D) + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$	$k = 5.2 \times 10^{-10}$	[5]
398	$\text{O}(^1S) + \text{O}_2 \rightarrow \text{O} + \text{O}_2$	$k = 4.8 \times 10^{-12} \exp[-850/T_g(k)]$	[8]
399	$\text{O}(^1S) + \text{O}_2 \rightarrow \text{O}(^1D) + \text{O}_2$	$k = 3.2 \times 10^{-12} \exp[-850/T_g(k)]$	[5]
400	$\text{O}(^1S) + \text{O}_3 \rightarrow \text{O}(^1D) + \text{O} + \text{O}_2$	$k = 2.9 \times 10^{-10}$	[3]
401	$\text{O}(^1S) + \text{O}_3 \rightarrow \text{O}_2 + \text{O}_2$	$k = 2.9 \times 10^{-10}$	[3]
402	$\text{O}(^1S) + \text{O} \rightarrow \text{O} + \text{O}$	$k = 5 \times 10^{-11} \exp[-300/T_g(k)]$	[8]
403	$\text{O}(^1S) + \text{O} \rightarrow \text{O}(^1D) + \text{O}$	$k = 5 \times 10^{-11} \exp[-300/T_g(k)]$	[8]
404	$\text{O}(^1S) + \text{O}_2(a) \rightarrow \text{O}(^1D) + \text{O}_2(b)$	$k = 3.6 \times 10^{-11}$	[3]
405	$\text{O}(^1S) + \text{O}_2(a) \rightarrow \text{O} + \text{O} + \text{O}$	$k = 3.4 \times 10^{-11}$	[3]
406	$\text{O}(^1S) + \text{N}_2 \rightarrow \text{O} + \text{N}_2$	$k = 4 \times 10^{-17}$	[8]
407	$\text{O}(^1S) + \text{NO} \rightarrow \text{O} + \text{NO}$	$k = 8.3 \times 10^{-10} \exp[-110/T_g(k)]$	[8]
408	$\text{O}(^1S) + \text{NO} \rightarrow \text{O}(^1D) + \text{NO}$	$k = 8.3 \times 10^{-10} \exp[-110/T_g(k)]$	[8]
409	$\text{O}(^1S) + \text{N}_2\text{O} \rightarrow \text{O}(^1D) + \text{N}_2\text{O}$	$k = 3.8 \times 10^{-11} \exp[-420/T_g(k)]$	[8]
410	$\text{O}(^1S) + \text{N}_2\text{O} \rightarrow \text{O} + \text{N}_2\text{O}$	$k = 3.8 \times 10^{-11} \exp[-420/T_g(k)]$	[8]
411	$\text{O}(^1S) + \text{HO}_2 \rightarrow \text{OH} + \text{O}_2$	$k = 2.9 \times 10^{-11} \exp[200/T_g(k)]$	[5]
412	$\text{O}(^1S) + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O} + \text{O}(^1D)$	$k = 1.5 \times 10^{-10}$	[5]
413	$\text{O}(^1S) + \text{H}_2\text{O} \rightarrow \text{OH} + \text{OH}$	$k = 3 \times 10^{-10}$	[5]
414	$\text{O}(^1S) + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{O}_2$	$k = 2.2 \times 10^{-12}$	[5]

## Appendix 1. (Continued)

No.	Chemical reaction	Rate coefficient $k$ (cm <sup>3</sup> s <sup>-1</sup> for two body and cm <sup>6</sup> s <sup>-1</sup> for three body reactions) cross section $\sigma(E)$ [cm <sup>2</sup> ]	Ref.
415	O( <sup>1</sup> S) + H <sub>2</sub> O → H <sub>2</sub> O + O	$k = 4.5 \times 10^{-11}$	[5]
416	N( <sup>2</sup> P) + O <sub>2</sub> → NO + O	$k = 2.5 \times 10^{-12} \exp[-60/T_g(k)]$	[8]
417	N( <sup>2</sup> P) + O <sub>2</sub> → NO + O( <sup>1</sup> D)	$k = 2.5 \times 10^{-12} \exp[-60/T_g(k)]$	[8]
418	N( <sup>2</sup> P) + O <sub>2</sub> → NO + O( <sup>1</sup> S)	$k = 2.5 \times 10^{-12} \exp[-60/T_g(k)]$	[8]
419	N( <sup>2</sup> P) + NO → N <sub>2</sub> (A) + O	$k = 3.4 \times 10^{-11}$	[3]
420	N( <sup>2</sup> P) + NO → N + NO	$k = 2.8 \times 10^{-11}$	[10]
421	N( <sup>2</sup> P) + N → N( <sup>2</sup> D) + N	$k = 1.8 \times 10^{-12}$	[3]
422	N( <sup>2</sup> D) + H <sub>2</sub> → NH + H	$k = 4.6 \times 10^{-11} \exp[-880/T_g(k)]$	[8]
423	N( <sup>2</sup> D) + O <sub>2</sub> → NO + O	$k = 1.5 \times 10^{-12} [T_g(k)/300]^{0.5}$	[3]
424	N( <sup>2</sup> D) + O <sub>2</sub> → NO + O( <sup>1</sup> D)	$k = 6 \times 10^{-12} [T_g(K)/300]^{0.5}$	[3]
425	N( <sup>2</sup> D) + NO → N <sub>2</sub> O	$k = 6 \times 10^{-11}$	[3]
426	N( <sup>2</sup> D) + N <sub>2</sub> O → NO + N <sub>2</sub>	$k = 1.5 \times 10^{-11} \exp[-570/T_g(k)]$	[8]
427	N( <sup>2</sup> D) + N <sub>2</sub> → N + N <sub>2</sub>	$k = 5 \times 10^{-12} \exp[-1620/T_g(k)]$	[8]
428	N( <sup>2</sup> D) + O <sub>3</sub> → NO + O <sub>2</sub>	$k = 10^{-10}$	[8]
429	N( <sup>2</sup> D) + NO → N <sub>2</sub> + O	$k = 4.5 \times 10^{-11}$	[8]
430	N( <sup>2</sup> D) + NO → N <sub>2</sub> + O( <sup>1</sup> D)	$k = 4.5 \times 10^{-11}$	[8]
431	N( <sup>2</sup> D) + NO → N <sub>2</sub> + O( <sup>1</sup> S)	$k = 4.5 \times 10^{-11}$	[8]
432	N( <sup>2</sup> D) + H <sub>2</sub> O → OH + NH	$k = 2.5 \times 10^{-10}$	[8]
433	N <sub>2</sub> + N → N <sub>2</sub> (A) + N	$k = 1.2 \times 10^{-12} T_e^{-1.5}(\text{eV}) \exp[-6.2/T_e(\text{eV})]$	[11]
434	N <sub>2</sub> (A) + O <sub>2</sub> → N <sub>2</sub> O + O	$k = 7.8 \times 10^{-14}$	[3]
435	N <sub>2</sub> (A) + O → N <sub>2</sub> + O( <sup>1</sup> S)	$k = 2 \times 10^{-11}$	[3]
436	N <sub>2</sub> (A) + O → NO + N( <sup>2</sup> D)	$k = 7 \times 10^{-12}$	[3]
437	N <sub>2</sub> (A) + O <sub>3</sub> → N <sub>2</sub> + O <sub>2</sub> + O	$k = 4.2 \times 10^{-11}$	[8]
438	N <sub>2</sub> (A) + O <sub>3</sub> → NO + NO + O	$k = 4.2 \times 10^{-11}$	[8]
439	N <sub>2</sub> (A) + N → N <sub>2</sub> + N( <sup>2</sup> P)	$k = 4 \times 10^{-11}$	[4]
440	N <sub>2</sub> (A) + NO → N <sub>2</sub> + NO	$k = 7 \times 10^{-11}$	[3]
441	N <sub>2</sub> (A) + NO <sub>2</sub> → N <sub>2</sub> + NO + O	$k = 1.3 \times 10^{-11}$	[8]
442	N <sub>2</sub> (A) + N <sub>2</sub> O → N <sub>2</sub> + N + NO	$k = 10^{-11}$	[3]
443	N <sub>2</sub> (A) + N <sub>2</sub> (A) → N <sub>2</sub> (B) + N <sub>2</sub>	$k = 4 \times 10^{-10}$	[8]
444	N <sub>2</sub> (A) + N <sub>2</sub> (A) → N <sub>2</sub> + N <sub>2</sub>	$k = 2 \times 10^{-12}$	[12]
445	N <sub>2</sub> (A) + N <sub>2</sub> (a') → N <sub>4</sub> <sup>+</sup> + e	$k = 9 \times 10^{-12}$	[4]
446	N <sub>2</sub> (A) + N <sub>2</sub> (a') → N <sub>2</sub> <sup>+</sup> + N <sub>2</sub> + e	$k = 10^{-12}$	[4]
447	N <sub>2</sub> (B) + NO → N <sub>2</sub> (A) + NO	$k = 2.4 \times 10^{-10}$	[3]
448	N <sub>2</sub> (B) + N <sub>2</sub> → N <sub>2</sub> (A) + N <sub>2</sub>	$k = 5 \times 10^{-11}$	[3]
449	N <sub>2</sub> (B) + N <sub>2</sub> → N <sub>2</sub> + N <sub>2</sub>	$k = 1.5 \times 10^{-12}$	[4]
450	N <sub>2</sub> (a') + N <sub>2</sub> → N <sub>2</sub> (B) + N <sub>2</sub>	$k = 1.9 \times 10^{-13}$	[4]
451	N <sub>2</sub> (a') + N <sub>2</sub> (a') → N <sub>4</sub> <sup>+</sup> + e	$k = 4.5 \times 10^{-11}$	[4]
452	N <sub>2</sub> (a') + N <sub>2</sub> (a') → N <sub>2</sub> <sup>+</sup> + N <sub>2</sub> + e	$k = 5 \times 10^{-12}$	[4]

## Appendix 1. (Continued)

No.	Chemical reaction	Rate coefficient $k$ ( $\text{cm}^3 \text{s}^{-1}$ for two body and $\text{cm}^6 \text{s}^{-1}$ for three body reactions) cross section $\sigma(E)$ [ $\text{cm}^2$ ]	Ref.
Neutral-neutral reactions			
453	$\text{O} + \text{O} + \text{M} \rightarrow \text{O}_2 + \text{M}$	$k = 6.61 \times 10^{-33} [T_g(k)/300]^{-0.63}$	[3]
454	$\text{O} + \text{O} + \text{M} \rightarrow \text{O}_2(a) + \text{M}$	$k = 6.61 \times 10^{-33} [T_g(k)/300]^{-0.63}$	[3]
455	$\text{O} + \text{O} + \text{M} \rightarrow \text{O}_2(b) + \text{M}$	$k = 6.61 \times 10^{-33} [T_g(k)/300]^{-0.63}$	[3]
456	$\text{O} + \text{O} + \text{O}_2 \rightarrow \text{O}_3 + \text{O}$	$k = 2.15 \times 10^{-34} \exp[345/T_g(k)]$	[2]
457	$\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}$	$k = 6 \times 10^{-34} \exp[T_g(k)/300]^{-2.6}$	[9]
458	$\text{O} + \text{O}_3 \rightarrow \text{O}_2(a) + \text{O}_2$	$k = 10^{-11} \exp[-2300/T_g(k)]$	[2]
459	$\text{O} + \text{O}_3 \rightarrow \text{O}_2 + \text{O}_2$	$k = 8 \times 10^{-12} \exp[-2060/T_g(k)]$	[9]
460	$\text{O}_3 + \text{O}_2 \rightarrow \text{O} + \text{O}_2 + \text{O}_2$	$k = 7.3 \times 10^{-10} \exp[-11400/T_g(k)]$	[2]
461	$\text{N} + \text{N} + \text{M} \rightarrow \text{N}_2(B) + \text{M}$	$k = 8.27 \times 10^{-34} \exp[500/T_g(K)]$	[4]
462	$\text{N} + \text{O}_2 \rightarrow \text{NO} + \text{O}$	$k = 3 \times 10^{-12} [T_g(K)/300] \exp[-3150/T_g(k)]$	[3]
463	$\text{N} + \text{O}_3 \rightarrow \text{NO} + \text{O}_2$	$k = 10^{-16}$	[8]
464	$\text{N} + \text{O} + \text{M} \rightarrow \text{NO} + \text{M}$	$k = 10^{-32} [T_g(K)/300]^{-0.5}$	[3]
465	$\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$	$k = 4.3 \times 10^{-12} \exp[-1560/T_g(k)]$	[3]
466	$\text{NO} + \text{O} + \text{M} \rightarrow \text{NO}_2 + \text{M}$	$k_\infty = 3 \times 10^{-11} [T_g(K)/300]^{0.3}$	[8]
467	$\text{NO} + \text{N} \rightarrow \text{N}_2 + \text{O}$	$k = 1.7 \times 10^{-11} [T_g(K)/300]^{0.5}$	[3]
468	$\text{NO} + \text{NO}_2 + \text{M} \rightarrow \text{N}_2\text{O}_3 + \text{M}$	$k_\infty = 8 \times 10^{-12} [T_g(K)/300]^{1.4}$	[9]
469	$\text{NO} + \text{NO}_3 \rightarrow \text{NO}_2 + \text{NO}_2$	$k = 1.8 \times 10^{-11} \exp[110/T_g(k)]$	[8]
470	$\text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2$	$k = 8 \times 10^{-12} [T_g(K)/300]^{0.18}$	[3]
471	$\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2$	$k = 1.4 \times 10^{-13} \exp[-2470/T_g(k)]$	[8]
472	$\text{NO}_2 + \text{O} + \text{M} \rightarrow \text{NO}_3 + \text{M}$	$k_\infty = 2.2 \times 10^{-11}$	[8]
473	$\text{NO}_2 + \text{N} \rightarrow \text{N}_2 + \text{O}_2$	$k = 7 \times 10^{-13}$	[3]
474	$\text{NO}_2 + \text{N} \rightarrow \text{N}_2 + \text{O} + \text{O}$	$k = 9 \times 10^{-13}$	[3]
475	$\text{NO}_2 + \text{N} \rightarrow \text{NO} + \text{NO}$	$k = 2.3 \times 10^{-12}$	[3]
476	$\text{NO}_2 + \text{N} \rightarrow \text{N}_2\text{O} + \text{O}$	$k = 5.8 \times 10^{-12} \exp[220/T_g(k)]$	[8]
477	$\text{NO}_2 + \text{NO}_2 + \text{M} \rightarrow \text{N}_2\text{O}_4 + \text{M}$	$k_\infty = 10^{-12}$	[9]
478	$\text{NO}_2 + \text{NO}_3 \rightarrow \text{NO} + \text{NO}_2 + \text{O}_2$	$k = 5.4 \times 10^{-14} \exp[-1490/T_g(K)]$	[13]
479	$\text{NO}_2 + \text{NO}_3 + \text{M} \rightarrow \text{N}_2\text{O}_5 + \text{M}$	$k_\infty = 1.9 \times 10^{-12} [T_g(K)/300]^{0.2}$	[9]
480	$\text{NO}_3 + \text{O} \rightarrow \text{NO}_2 + \text{O}_2$	$k = 1.7 \times 10^{-11}$	[9]
481	$\text{NO}_3 + \text{O}_2 \rightarrow \text{NO}_2 + \text{O}_3$	$k = 10^{-17}$	[8]
482	$\text{NO}_3 + \text{NO}_3 \rightarrow \text{NO}_2 + \text{NO}_2 + \text{O}_2$	$k = 8.5 \times 10^{-13} \exp[-2450/T_g(k)]$	[8]
483	$\text{NO}_3 + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 + \text{O}_2$	$k = 10^{-17}$	[13]
484	$\text{N}_2\text{O}_5 + \text{M} \rightarrow \text{NO}_2 + \text{NO}_3 + \text{M}$	$k = 1.3 \times 10^{-3} [T_g(K)/300]^{-3.5} \exp[-11000/T_g(K)]$	[9]
485	$\text{N}_2\text{O}_4 + \text{M} \rightarrow \text{NO}_2 + \text{NO}_2 + \text{M}$	$k = 1.3 \times 10^{-5} [T_g(K)/300]^{-3.8} \exp[-6460/T_g(K)]$	[9]
486	$\text{N}_2\text{O}_3 + \text{M} \rightarrow \text{NO} + \text{NO}_2 + \text{M}$	$k = 1.9 \times 10^{-7} [T_g(K)/300]^{-8.7} \exp[-4880/T_g(K)]$	[9]
487	$\text{H} + \text{O} + \text{M} \rightarrow \text{OH} + \text{M}$	$k = 4.36 \times 10^{-32} [T_g(K)/300]^{-1}$	[5]

## Appendix 1. (Continued)

No.	Chemical reaction	Rate coefficient $k$ (cm <sup>3</sup> s <sup>-1</sup> for two body and cm <sup>6</sup> s <sup>-1</sup> for three body reactions) and cross section $\sigma(E)$ [cm <sup>2</sup> ]	Ref.
488	H + O <sub>2</sub> → OH + O	$k = 1.6 \times 10^{-10} \exp[-7470/T_g(k)]$	[5]
489	H + O <sub>2</sub> + M → HO <sub>2</sub> + M	$k_\infty = 7.5 \times 10^{-11}$	[8]
490	H + O <sub>2</sub> (a) → OH + O	$k = 1.8 \times 10^{-13} \exp[-1550/T_g(k)]$	[5]
491	H + O <sub>3</sub> → OH + O <sub>2</sub>	$k = 2.7 \times 10^{-11} [-1550/T_g(k)]^{0.75}$	[5]
492	H + O <sub>3</sub> → HO <sub>2</sub> + O	$k = 7.5 \times 10^{-13}$	[5]
493	H + HO <sub>2</sub> → H <sub>2</sub> + O <sub>2</sub>	$k = 10^{-12} [T_g(k)/300]^{0.56} \exp[-346/T_g(k)]$	[5]
494	H + HO <sub>2</sub> → OH + OH	$k = 2.35 \times 10^{-10} \exp[-373.7/T_g(k)]$	[5]
495	H + HO <sub>2</sub> → H <sub>2</sub> O + O	$k = 2.4 \times 10^{-12}$	[9]
496	H + NO <sub>2</sub> → OH + NO	$k = 4 \times 10^{-10} \exp[-340/T_g(k)]$	[8]
497	H <sub>2</sub> + O → OH + H	$k = 9 \times 10^{-12} [T_g(k)/300] \exp[-4480/T_g(k)]$	[5]
498	H <sub>2</sub> + N( <sup>2</sup> D) → NH + H	$k = 4.6 \times 10^{-11} \exp[-880/T_g(k)]$	[8]
499	NH + O → H + NO	$k = 6.6 \times 10^{-11}$	[8]
500	NH + O <sub>2</sub> → OH + NO	$k = 9.8 \times 10^{-15}$	[8]
501	NH + N → H + N <sub>2</sub>	$k = 2.5 \times 10^{-11}$	[8]
502	NH + NO → H + N <sub>2</sub> O	$k = 5 \times 10^{-11}$	[8]
503	NH + NO <sub>2</sub> → OH + N <sub>2</sub> O	$k = 3.5 \times 10^{-13} \exp[1140/T_g(k)]$	[8]
504	NH + NO <sub>2</sub> → HO <sub>2</sub> + N <sub>2</sub>	$k = 3.5 \times 10^{-13} \exp[1140/T_g(k)]$	[8]
505	NH + NO <sub>2</sub> → HNO + NO	$k = 3.5 \times 10^{-13} \exp[1140/T_g(k)]$	[8]
506	NH + H → H <sub>2</sub> + N	$k = 1.7 \times 10^{-11}$	[8]
507	NH + OH → H <sub>2</sub> + NO	$k = 8 \times 10^{-11}$	[8]
508	HNO + O → OH + NO	$k = 6 \times 10^{-11}$	[8]
509	HNO + NO <sub>2</sub> → HNO <sub>2</sub> + NO	$k = 10^{-12} \exp[-200/T_g(k)]$	[8]
510	HNO + H → H <sub>2</sub> + NO	$k = 3 \times 10^{-11} \exp[-500/T_g(k)]$	[8]
511	HNO + OH → H <sub>2</sub> O + NO	$k = 8 \times 10^{-11} \exp[-500/T_g(k)]$	[8]
512	HNO <sub>2</sub> + O → OH + NO <sub>2</sub>	$k = 2 \times 10^{-11} \exp[-3000/T_g(k)]$	[8]
513	HNO <sub>2</sub> + H → H <sub>2</sub> + NO <sub>2</sub>	$k = 2 \times 10^{-11} \exp[-3700/T_g(k)]$	[8]
514	HNO <sub>2</sub> + OH → H <sub>2</sub> O + NO <sub>2</sub>	$k = 2.7 \times 10^{-12} \exp[260/T_g(k)]$	[8]
515	HNO <sub>3</sub> + OH → H <sub>2</sub> O + NO <sub>3</sub>	$k = 1.5 \times 10^{-13}$	[8]
516	HNO <sub>4</sub> + OH → H <sub>2</sub> O + NO <sub>2</sub> + O <sub>2</sub>	$k = 1.9 \times 10^{-12} \exp[270/T_g(k)]$	[9]
517	HNO <sub>4</sub> + OH → H <sub>2</sub> O <sub>2</sub> + NO <sub>3</sub>	$k = 1.9 \times 10^{-12} \exp[270/T_g(k)]$	[9]
518	OH + O → H + O <sub>2</sub>	$k = 2 \times 10^{-11} [T_g(k)/300]^{-0.186} \exp[-154/T_g(k)]$	[5]
519	OH + O <sub>3</sub> → HO <sub>2</sub> + O <sub>2</sub>	$k = 1.7 \times 10^{-12} \exp[-941/T_g(k)]$	[5]
520	OH + H <sub>2</sub> → H <sub>2</sub> O + H	$k = 7.7 \times 10^{-12} \exp[-2100/T_g(k)]$	[8]
521	OH + OH → H <sub>2</sub> O + O	$k = 1.6 \times 10^{-12} [T_g(k)/300]^{1.14} \exp[-50/T_g(k)]$	[5]
522	OH + OH → H <sub>2</sub> O <sub>2</sub>	$k = 1.5 \times 10^{-11} [T_g(K)/300]^{-0.37}$	[5]
523	OH + HO <sub>2</sub> → H <sub>2</sub> O + O <sub>2</sub>	$k = 4.38 \times 10^{-11} \exp[110.9/T_g(k)]$	[5]
524	OH + H <sub>2</sub> O <sub>2</sub> → H <sub>2</sub> O + HO <sub>2</sub>	$k = 4.53 \times 10^{-12} \exp[-288.9/T_g(k)]$	[5]

## Appendix 1. (Continued)

No.	Chemical reaction	Rate coefficient $k$ ( $\text{cm}^3 \text{s}^{-1}$ for two body and $\text{cm}^6 \text{s}^{-1}$ for three body reactions) and cross section $\sigma(E)$ [ $\text{cm}^2$ ]	Ref.
525	$\text{OH} + \text{N} \rightarrow \text{H} + \text{NO}$	$k = 4.7 \times 10^{-11}$	[8]
526	$\text{OH} + \text{NO} + \text{M} \rightarrow \text{HNO}_2 + \text{M}$	$k_\infty = 3.3 \times 10^{-11}$	[8]
527	$\text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M}$	$k_\infty = 7.5 \times 10^{-11} [T_g(K)/300]^{-0.6}$	[8]
528	$\text{OH} + \text{NO}_3 \rightarrow \text{HO}_2 + \text{NO}_2$	$k = 2 \times 10^{-11}$	[8]
529	$\text{HO}_2 + \text{O} \rightarrow \text{OH} + \text{O}_2$	$k = 2.9 \times 10^{-11} \exp[200/T_g(k)]$	[5]
530	$\text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + \text{O}_2 + \text{O}_2$	$k = 1.97 \times 10^{-16} [T_g(k)/300]^{4.57} \exp[693/T_g(k)]$	[5]
531	$\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	$k = 8 \times 10^{-11} [T_g(K)/300]^{-1}$	[5]
532	$\text{HO}_2 + \text{N} \rightarrow \text{OH} + \text{NO}$	$k = 2.2 \times 10^{-11}$	[8]
533	$\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2$	$k = 3.6 \times 10^{-12} \exp[270/T_g(k)]$	[9]
534	$\text{HO}_2 + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_4 + \text{M}$	$k_\infty = 4.7 \times 10^{-12}$	[9]
535	$\text{HO}_2 + \text{NO}_3 \rightarrow \text{OH} + \text{NO}_2 + \text{O}_2$	$k = 4 \times 10^{-12}$	[8]
536	$\text{H}_2\text{O}_2 + \text{H} \rightarrow \text{HO}_2 + \text{H}_2$	$k = 8 \times 10^{-11} \exp[-4000/T_g(k)]$	[5]
537	$\text{H}_2\text{O}_2 + \text{H} \rightarrow \text{H}_2\text{O} + \text{OH}$	$k = 4 \times 10^{-11} \exp[-2000/T_g(k)]$	[5]
538	$\text{H}_2\text{O} + \text{H} \rightarrow \text{OH} + \text{H}_2$	$k = 6.8 \times 10^{-12} [T_g(k)/300]^{1.6} \exp[-9720/T_g(k)]$	[5]
539	$\text{H}_2\text{O} + \text{O} \rightarrow \text{OH} + \text{OH}$	$k = 1.66 \times 10^{-11} [T_g(k)/300]^{1.14} \exp[-8624/T_g(k)]$	[5]
540	$\text{H}_2\text{O} + \text{N}_2\text{O}_5 \rightarrow \text{HNO}_3 + \text{HNO}_3$	$k = 2.5 \times 10^{-22}$	[9]

“M” stands for a gas molecule, acting as “third body.” In our model, we take the sum of the  $\text{N}_2$ ,  $\text{O}_2$  and  $\text{H}_2\text{O}$  molecule densities;

“e” denotes that the rate coefficients of these ion-ion recombination reactions are estimated according to the work of Gentile;<sup>[6]</sup>

For the three-body collisions, the rate coefficient is normally  $\text{cm}^6 \text{s}^{-1}$ , but in some cases, the data were found in literature as the “high pressure limit” ( $k_\infty$  in the table) with units of  $\text{cm}^3 \text{s}^{-1}$ . In this case, the rate coefficient should not be multiplied anymore with the third body [M].

The low limit pressure was considered for reactions 484–486 because no data were found for high pressure limit at  $T_g = 350 \text{ K}$ .

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**Appendix 2: Detailed overview of production and loss processes of the various species**

Here the reaction mechanisms responsible for production and loss of several plasma species are presented, at different moments in time, i.e.,  $t_1 = 2.43$  ns, when the pulse (and hence the electron density) reaches its maximum value,  $t_2 = 5.25$  ns, i.e., at the end of the pulse,  $t_3 = 10$  ns, i.e., in the early afterglow,  $t_4 = 4$   $\mu$ s, i.e., when the N<sub>x</sub>O<sub>y</sub> pollutant concentrations in the afterglow vary strongly in time,  $t_5 = 30$   $\mu$ s, i.e., in the late afterglow, and  $t_6 = 1$  ms, i.e., at the end of the afterglow, just before the next pulse would start (Figure A1–A8).

The electron and OH<sup>−</sup> ion production/loss processes are calculated in the time interval ( $t_1, t_4$ ), because these species are depleted around  $t_4$ .

The reaction mechanism of the OH, HO<sub>2</sub> and NH radicals is evaluated in the time interval ( $t_1, t_6$ ). For these radicals the

production/loss processes at  $t_2$  and  $t_3$  are similar, hence it will not be shown for  $t_2$ .

The NO, NO<sub>2</sub> and N<sub>2</sub>O pollutants do not change in time during the pulse and in the early afterglow, therefore the reaction mechanism is estimated starting with  $t_3$  to the end of the afterglow  $t_6$ .

The absolute ( $C_{AP}$ ) and relative contributions to production/loss ( $C_{RP}/C_{RL}$ ) of a species from a reaction  $j$  whose reactants are A and B, and a rate coefficient  $k$ , are calculated by the following formulas:

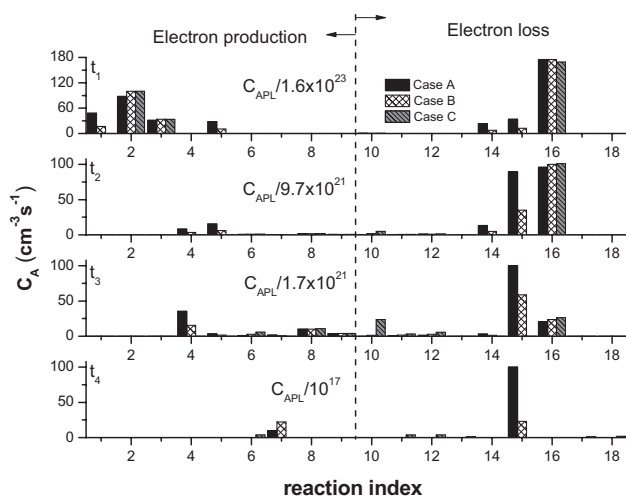
$$C_{AP} = k[A] \cdot [B]$$

$$C_{RP}^j = \frac{C_A^j}{\sum_{i=1}^N C_{AP}^i} \text{ or } C_{RL}^j = \frac{C_A^j}{\sum_{i=1}^N C_{AL}^i}$$

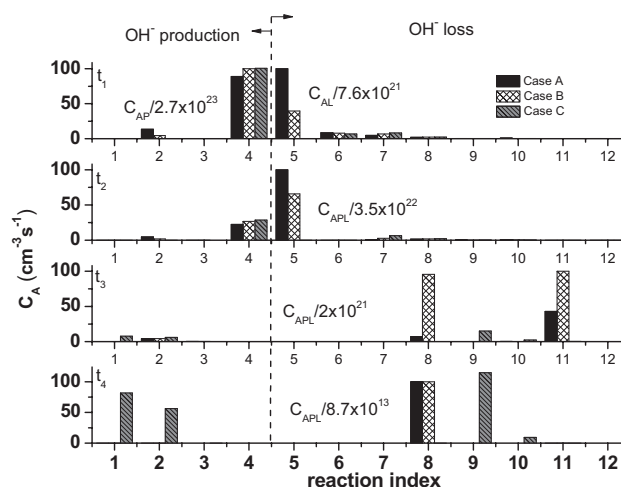
where  $N$  is the number of reactions which contribute to the production/loss process (Table A1–A8).

**Table A1.** Overview of the most important reactions which contribute to the formation and loss of electrons, with their relative contributions for cases A, B and C, at different moments in time.

No.	Electron production	Relative contribution [%]											
		Case A				Case B				Case C			
		$t_1$	$t_2$	$t_3$	$t_4$	$t_1$	$t_2$	$t_3$	$t_4$	$t_1$	$t_2$	$t_3$	$t_4$
1	$e + O_2 \rightarrow 2e + O_2^+$	24	–	–	–	10	–	–	–	–	–	–	–
2	$e + N_2 \rightarrow 2e + N_2^+$	45	–	–	–	62	–	–	–	76	–	–	–
3	$e + H_2O \rightarrow 2e + H_2O^+$	16	–	–	–	21	–	–	–	24	–	–	–
4	$O_2^- + N_2(A) \rightarrow O_2 + N_2 + e$	–	29	62	–	–	24	42	–	–	–	–	–
5	$H^- + O_2 \rightarrow HO_2 + e$	14	54	6	–	7	44	4	–	–	–	–	–
6	$OH^- + H \rightarrow H_2O + e$	–	–	1	–	–	7	7	–	–	30	29	97
7	$OH^- + O \rightarrow HO_2 + e$	–	–	3	91	–	–	2	96	–	–	–	2
8	$N_2(A) + N_2(a') \rightarrow N_4^+ + e$	–	6	17	–	–	12	29	–	–	45	46	–
9	$N_2(a') + N_2(a') \rightarrow N_4^+ + e$	–	2	7	–	–	5	11	–	–	19	18	–
Electron loss													
10	$e + N_4^+ \rightarrow N_2 + N_2$	–	–	–	–	–	1	1	–	–	5	41	–
11	$e + H_3O^+ \rightarrow H + H + OH$	–	–	–	–	–	–	1	–	–	–	5	29
12	$e + H_3O^+ \rightarrow H_2O + H$	–	–	–	–	–	–	3	–	–	1	9	29
13	$e + NO^+ \rightarrow N(^2D) + O$	–	–	–	–	–	–	–	–	–	–	–	10
14	$e + O_2 \rightarrow O + O^-$	10	7	2	–	4	3	1	–	–	–	–	–
15	$e + O_2 + H_2O \rightarrow O_2^- + H_2O$	14	44	78	100	6	24	65	99	–	–	–	–
16	$e + H_2O \rightarrow OH + H^-$	75	47	16	–	90	67	23	–	100	94	44	–
17	$e + H_2O_2 \rightarrow H_2O + O^-$	–	–	–	–	–	–	–	–	–	–	–	11
18	$e + H_2O_2 \rightarrow OH + OH^-$	–	–	–	–	–	–	–	–	–	–	–	15



**Figure A1.** Absolute reaction rates of the most important production and loss processes for the electrons, for cases A, B and C, at different moments in time. The numbers on the x-axis of the figure correspond to the reaction numbers in Table A1;  $C_{APL}$  means that the absolute contributions to production and loss are normalized to the same number.



**Figure A2.** Absolute reaction rates of the most important production and loss processes for the  $\text{OH}^-$  ions, for cases A, B and C, at different moments in time. The numbers on the x-axis of the figure correspond to the reaction numbers in Table A2;  $C_{APL}$  means that the absolute contributions to production and loss are normalized to the same number.

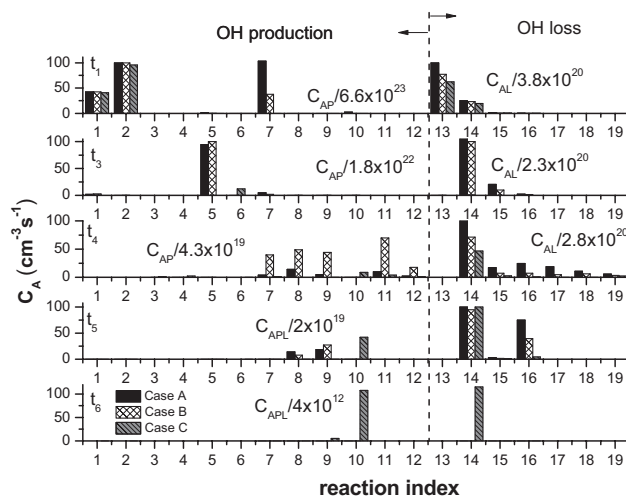
**Table A2.** Overview of the most important reactions which contribute to the formation and loss of the  $\text{OH}^-$  ions, with their relative contributions for cases A, B and C, at different moments in time.

No.	$\text{OH}^-$ production	Relative contribution [%]											
		Case A				Case B				Case C			
		$t_1$	$t_2$	$t_3$	$t_4$	$t_1$	$t_2$	$t_3$	$t_4$	$t_1$	$t_2$	$t_3$	$t_4$
1	$e + \text{H}_2\text{O}_2 \rightarrow \text{OH} + \text{OH}^-$	–	–	–	–	–	–	–	–	–	–	–	57
2	$\text{H}_2\text{O} + \text{O}^- \rightarrow \text{OH} + \text{OH}^-$	13	6	17	93	4	17	5	91	–	–	–	43
3	$\text{O}_2^- + \text{OH} \rightarrow \text{OH}^- + \text{O}_2$	–	–	–	7	–	–	–	8	–	–	–	–
4	$\text{H}^- + \text{H}_2\text{O} \rightarrow \text{OH}^- + \text{H}_2$	87	94	82	–	96	83	94	–	100	100	100	–
	$\text{OH}^-$ loss												
5	$\text{O}_2^+ + \text{OH}^- \rightarrow \text{O}_2 + \text{OH}$	86	93	97	–	70	97	96	–	–	–	–	–
6	$\text{N}_2^+ + \text{OH}^- \rightarrow \text{N}_2 + \text{OH}$	7	–	–	–	13	–	–	–	38	–	–	–
7	$\text{N}_4^+ + \text{OH}^- \rightarrow 2\text{N}_2 + \text{OH}$	4	4	–	–	12	–	–	–	45	70	68	–
8	$\text{H}_3\text{O}^+ + \text{OH}^- \rightarrow 2\text{H}_2\text{O}$	2	3	2	15	4	1	2	49	13	21	21	–
9	$\text{H} + \text{OH}^- \rightarrow \text{H}_2\text{O} + e$	–	–	–	–	–	–	–	–	2	4	4	85
10	$\text{NO}^+ + \text{OH}^- \rightarrow \text{NO} + \text{OH}$	–	–	1	–	–	–	–	–	1	4	8	13
11	$\text{O} + \text{OH}^- \rightarrow \text{HO}_2 + e$	–	–	–	85	–	–	–	51	–	–	–	–

**Table A3.** Overview of the most important reactions which contribute to the formation and loss of the OH radicals, with their relative contributions for cases A, B and C, at different moments in time.

No	OH production	Relative contribution [%]														
		Case A					Case B					Case C				
		t <sub>1</sub>	t <sub>3</sub>	t <sub>4</sub>	t <sub>5</sub>	t <sub>6</sub>	t <sub>1</sub>	t <sub>3</sub>	t <sub>4</sub>	t <sub>5</sub>	t <sub>6</sub>	t <sub>1</sub>	t <sub>3</sub>	t <sub>4</sub>	t <sub>5</sub>	t <sub>6</sub>
1	e + H <sub>2</sub> O → OH + H <sup>-</sup>	17	2	-	-	-	22	2	-	-	-	28	15	-	-	-
2	e + H <sub>2</sub> O → e + OH + H	38	-	-	-	-	52	-	-	-	-	65	1	-	-	-
3	e + H <sub>3</sub> O <sup>+</sup> → H + OH + H	-	-	-	-	-	-	-	-	-	-	2	6	-	-	-
4	NO <sup>+</sup> + OH <sup>-</sup> → NO + OH	-	-	-	-	-	1	-	-	-	-	9	12	-	-	-
5	O <sub>2</sub> <sup>+</sup> + OH <sup>-</sup> → O <sub>2</sub> + OH	-	89	-	-	-	-	93	-	-	-	-	-	-	-	-
6	N <sub>4</sub> <sup>+</sup> + OH <sup>-</sup> → N <sub>2</sub> + N <sub>2</sub> + OH	-	-	-	-	-	-	-	-	-	-	73	-	-	-	-
7	H <sub>2</sub> O + O( <sup>1</sup> D) → OH + OH	39	4	10	-	-	19	2	15	-	-	-	7	-	-	-
8	HO <sub>2</sub> + O → OH + O <sub>2</sub>	-	-	38	40	-	-	-	22	22	-	-	-	-	-	-
9	HO <sub>2</sub> + NO → OH + NO <sub>2</sub>	-	-	12	51	100	-	-	20	73	100	-	-	-	-	5
10	H + NO <sub>2</sub> → OH + NO	-	-	-	-	-	-	-	-	-	-	-	47	99	93	-
11	H <sub>2</sub> O + O( <sup>1</sup> S) → OH + OH	-	2	27	-	-	-	-	31	-	-	-	20	-	-	-
12	H <sub>2</sub> O + N( <sup>2</sup> D) → OH + NH	-	-	7	-	-	-	-	8	-	-	-	7	-	-	-
OH loss																
13	e + OH → e + O + H	77	3	-	-	-	75	-	-	-	-	74	-	-	-	-
14	OH + NO + M → HNO <sub>2</sub> + M	20	65	52	49	50	23	76	66	63	64	24	86	88	91	97
15	OH + OH → H <sub>2</sub> O <sub>2</sub>	1	10	9	2	-	1	8	7	1	-	-	6	5	1	-
16	OH + NO <sub>2</sub> + M → HNO <sub>3</sub> + M	-	1	13	37	47	-	1	7	26	33	-	2	2	4	-
17	OH + O → H + O <sub>2</sub>	-	4	10	2	-	-	2	4	1	-	-	-	-	-	-
18	OH + HO <sub>2</sub> → H <sub>2</sub> O + O <sub>2</sub>	-	6	6	3	-	-	4	6	3	-	-	-	-	-	-
19	OH + N → H + NO	-	4	3	2	-	-	5	3	1	-	-	6	4	-	-

“M” stands for a gas molecule, acting as “third body.” In our model, we take the sum of the N<sub>2</sub>, O<sub>2</sub>, and H<sub>2</sub>O molecule densities.

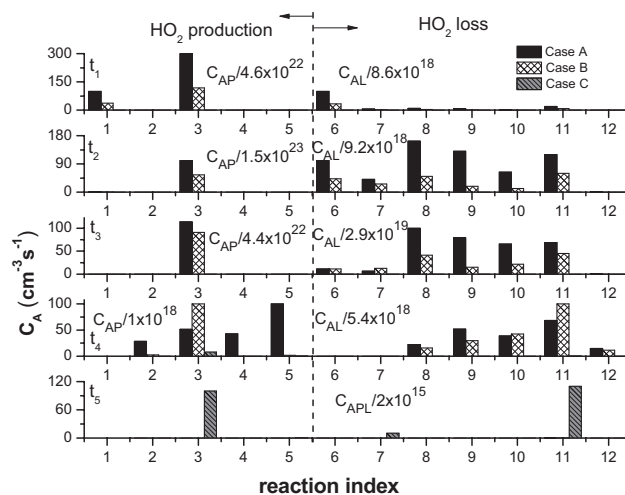


**Figure A3.** Absolute reaction rates of the most important production and loss processes for the OH radicals, for cases A, B and C, at different moments in time. The numbers on the x-axis of the figure correspond to the reaction numbers in Table A3; C<sub>APL</sub> means that the absolute contributions to production and loss are normalized to the same number.



**Table A4.** Overview of the most important reactions which contribute to the formation and loss of the HO<sub>2</sub> radicals, with their relative contributions for cases A, B and C, at different moments in time.

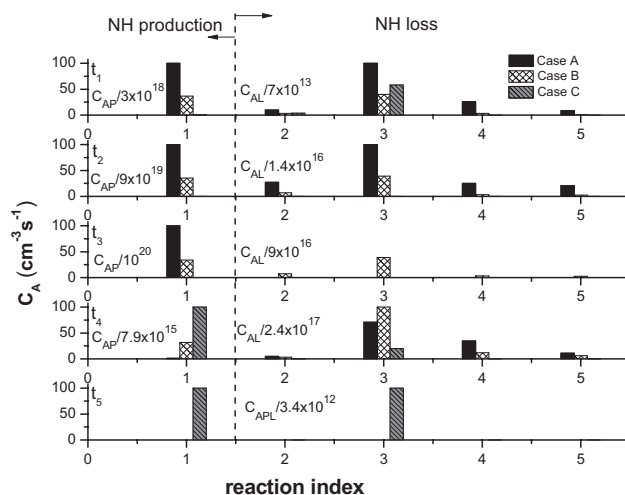
No.	HO <sub>2</sub> production	Relative contribution [%]														
		Case A					Case B					Case C				
		t <sub>1</sub>	t <sub>3</sub>	t <sub>4</sub>	t <sub>5</sub>	t <sub>6</sub>	t <sub>1</sub>	t <sub>3</sub>	t <sub>4</sub>	t <sub>5</sub>	t <sub>6</sub>	t <sub>1</sub>	t <sub>3</sub>	t <sub>4</sub>	t <sub>5</sub>	t <sub>6</sub>
1	H <sup>-</sup> + O <sub>2</sub> → HO <sub>2</sub> + e	25	-	-	-	-	24	-	-	-	-	-	-	-	-	-
2	OH <sup>-</sup> + O → HO <sub>2</sub> + e	-	-	-	-	-	-	-	2	2	-	100	100	44	-	-
3	H + O <sub>2</sub> + M → HO <sub>2</sub> + M	75	98	98	96	-	76	99	97	95	4	-	-	33	97	100
4	OH + O <sub>3</sub> → HO <sub>2</sub> + O <sub>2</sub>	-	-	-	-	30	-	-	-	-	9	-	-	-	-	-
5	OH + H <sub>2</sub> O <sub>2</sub> → H <sub>2</sub> O + HO <sub>2</sub>	-	-	-	2	69	-	-	-	2	87	-	-	21	3	-
HO <sub>2</sub> loss																
6	e + HO <sub>2</sub> → e + H + O <sub>2</sub>	63	3	-	-	-	64	6	-	-	-	66	13	-	-	-
7	H + HO <sub>2</sub> → OH + OH	4	2	-	-	-	5	6	-	-	-	5	16	20	29	9
8	OH + HO <sub>2</sub> → H <sub>2</sub> O + O <sub>2</sub>	12	44	36	19	-	11	42	37	14	-	10	37	38	11	-
9	HO <sub>2</sub> + O → OH + O <sub>2</sub>	5	17	36	23	-	2	8	22	14	-	-	-	2	4	-
10	HO <sub>2</sub> + HO <sub>2</sub> → H <sub>2</sub> O <sub>2</sub> + O <sub>2</sub>	1	15	12	17	-	-	11	17	19	-	-	-	-	-	-
11	HO <sub>2</sub> + NO → OH + NO <sub>2</sub>	13	16	12	30	78	15	23	20	45	87	17	30	35	52	91
12	HO <sub>2</sub> + NO <sub>2</sub> → HNO <sub>4</sub>	-	-	-	7	21	-	-	-	5	13	-	-	-	-	-



**Figure A4.** Absolute reaction rates of the most important production and loss processes for the HO<sub>2</sub> radicals, for cases A, B and C, at different moments in time. The numbers on the x-axis of the figure correspond to the reaction numbers in Table A4; C<sub>APL</sub> means that the absolute contributions to production and loss are normalized to the same number.

**Table A5.** Overview of the most important reactions which contribute to the formation and loss of the NH radicals, with their relative contributions for cases A, B and C, at different moments in time.

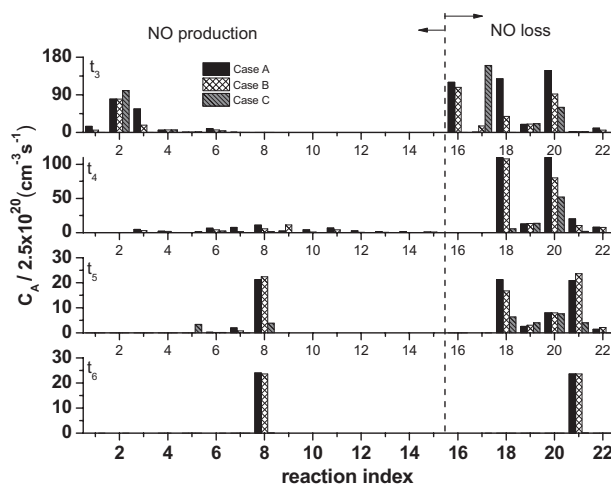
No.	NH production	Relative contribution [%]														
		Case A					Case B					Case C				
		t <sub>1</sub>	t <sub>3</sub>	t <sub>4</sub>	t <sub>5</sub>	t <sub>6</sub>	t <sub>1</sub>	t <sub>3</sub>	t <sub>4</sub>	t <sub>5</sub>	t <sub>6</sub>	t <sub>1</sub>	t <sub>3</sub>	t <sub>4</sub>	t <sub>5</sub>	t <sub>6</sub>
1	H <sub>2</sub> O + N( <sup>2</sup> D) → HO + NH	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
NH loss																
2	NH + OH → H <sub>2</sub> + NO	7	16	14	4	–	6	14	12	2	–	6	11	10	2	–
3	NH + NO → H + N <sub>2</sub> O	68	56	43	53	56	82	73	65	75	80	91	85	86	93	100
4	NH + O <sub>2</sub> → OH + NO	17	14	13	25	31	7	6	6	9	11	–	–	–	–	–
5	NH + O → H + NO	6	12	26	8	–	2	5	14	5	–	–	–	–	1	–



**Figure A5.** Absolute reaction rates of the most important production and loss processes for the NH radicals, for cases A, B and C, at different moments in time. The numbers on the x-axis of the figure correspond to the reaction numbers in Table A5; C<sub>APL</sub> means that the absolute contributions to production and loss are normalized to the same number.

**Table A6.** Overview of the most important reactions which contribute to the formation and loss of the NO molecules, with their relative contributions for cases A, B and C, at different moments in time.

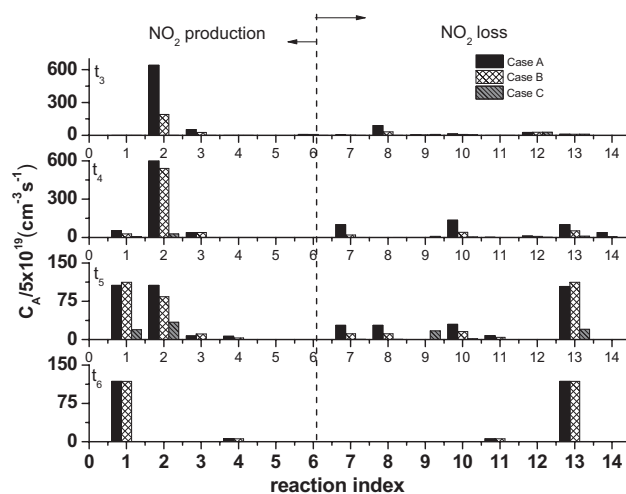
No.	NO production	Relative contribution [%]											
		Case A				Case B				Case C			
		$t_3$	$t_4$	$t_5$	$t_6$	$t_3$	$t_4$	$t_5$	$t_6$	$t_3$	$t_4$	$t_5$	$t_6$
1	$\text{NO}^+ + \text{O}_2^- \rightarrow \text{NO} + \text{O}_2$	8	–	–	–	–	–	–	–	–	–	–	–
2	$\text{NO}^+ + \text{OH}^- \rightarrow \text{NO} + \text{OH}$	44	–	–	–	66	–	–	–	90	6	–	–
3	$\text{N}_2(\text{A}) + \text{O} \rightarrow \text{NO} + \text{N}(^2\text{D})$	31	9	–	–	14	12	–	–	–	3	–	–
4	$\text{N}_2(\text{A}) + \text{NO}_2 \rightarrow \text{N}_2 + \text{NO} + \text{O}$	3	4	–	–	4	6	–	–	5	6	–	–
5	$\text{H} + \text{NO}_2 \rightarrow \text{OH} + \text{NO}$	–	–	–	–	1	–	–	–	1	23	45	13
6	$\text{OH} + \text{N} \rightarrow \text{H} + \text{NO}$	5	12	1	–	5	15	1	–	4	38	2	–
7	$\text{O} + \text{NO}_2 \rightarrow \text{O}_2 + \text{NO}$	–	14	8	–	–	5	4	–	–	–	–	–
8	$\text{N}_2\text{O}_3 + \text{M} \rightarrow \text{NO} + \text{NO}_2 + \text{M}$	–	21	88	100	–	20	94	100	–	22	52	88
9	$\text{N}(^2\text{P}) + \text{O}_2 \rightarrow \text{NO} + \text{O}(^3\text{P}, ^1\text{S}, ^1\text{D})$	–	5	–	–	–	14	–	–	–	–	–	–
10	$\text{N}_2(\text{A}) + \text{O}_3 \rightarrow \text{NO} + \text{NO} + \text{O}$	–	9	–	–	–	3	–	–	–	–	–	–
11	$\text{N}_2(\text{A}) + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{NO} + \text{N}$	–	13	–	–	–	16	–	–	–	–	–	–
12	$\text{NH} + \text{O} \rightarrow \text{H} + \text{NO}$	–	5	–	–	–	2	–	–	–	–	–	–
13	$\text{NH} + \text{OH} \rightarrow \text{H}_2 + \text{NO}$	–	3	–	–	–	2	–	–	–	–	–	–
14	$\text{NH} + \text{O}_2 \rightarrow \text{OH} + \text{NO}$	–	3	–	–	–	2	–	–	–	–	–	–
15	$\text{HO}_2 + \text{N} \rightarrow \text{OH} + \text{NO}$	–	2	–	–	–	3	–	–	–	–	–	–
NO loss													
16	$\text{O}_2^+ + \text{NO} \rightarrow \text{NO}^+ + \text{O}_2$	31	–	–	–	39	–	–	–	–	–	–	–
17	$\text{N}_4^+ + \text{NO} \rightarrow \text{N}_2 + \text{N}_2 + \text{NO}^+$	–	–	–	–	5	–	–	–	66	–	–	–
18	$\text{NO} + \text{O} + \text{M} \rightarrow \text{NO}_2 + \text{M}$	29	61	39	–	13	48	32	–	–	7	29	–
19	$\text{NO} + \text{N} \rightarrow \text{N}_2 + \text{O}$	5	3	5	–	7	6	6	–	8	18	18	–
20	$\text{OH} + \text{NO} + \text{M} \rightarrow \text{HNO}_2 + \text{M}$	33	28	14	–	32	36	15	–	25	67	34	13
21	$\text{NO} + \text{NO}_2 + \text{M} \rightarrow \text{N}_2\text{O}_3 + \text{M}$	–	5	38	100	1	5	43	100	1	3	18	86
22	$\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2$	2	2	3	–	2	3	4	–	–	–	–	–



**Figure A6.** Absolute reaction rates of the most important production and loss processes for the NO molecules, for cases A, B and C, at different moments in time as in Table A1. The numbers on the x-axis of the figure correspond to the reaction numbers in Table A6.

**Table A7.** Overview of the most important reactions which contribute to the formation and loss of the NO<sub>2</sub> molecules, with their relative contributions for cases A, B and C, at different moments in time.

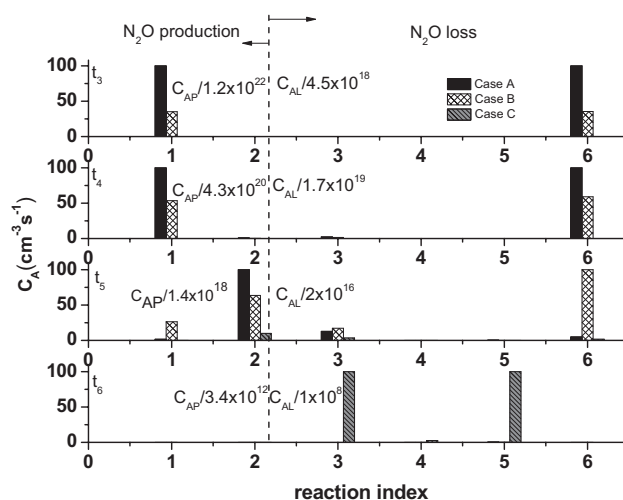
No.	NO <sub>2</sub> production	Relative contribution [%]											
		Case A				Case B				Case C			
		t <sub>3</sub>	t <sub>4</sub>	t <sub>5</sub>	t <sub>6</sub>	t <sub>3</sub>	t <sub>4</sub>	t <sub>5</sub>	t <sub>6</sub>	t <sub>3</sub>	t <sub>4</sub>	t <sub>5</sub>	t <sub>6</sub>
1	N <sub>2</sub> O <sub>3</sub> + M → NO + NO <sub>2</sub> + M	–	4	46	91	–	5	53	95	8	20	36	99
2	NO + O + M → NO <sub>2</sub> + M	92	92	47	–	86	89	40	–	82	77	62	–
3	HO <sub>2</sub> + NO → OH + NO <sub>2</sub>	7	3	3	–	12	6	5	–	–	–	–	–
4	N <sub>2</sub> O <sub>4</sub> + M → NO <sub>2</sub> + NO <sub>2</sub> + M	–	–	3	8	–	–	–	–	–	–	–	–
5	NO <sub>2</sub> <sup>–</sup> + N <sub>4</sub> <sup>+</sup> → NO <sub>2</sub> + N <sub>2</sub> + N <sub>2</sub>	–	–	–	–	–	–	–	–	8	–	–	–
	NO <sub>2</sub> loss												
6	O <sub>2</sub> <sup>+</sup> + NO <sub>2</sub> → NO <sub>2</sub> <sup>+</sup> + O <sub>2</sub>	5	–	–	–	8	–	–	–	–	–	–	–
7	NO <sub>2</sub> + O → NO <sub>3</sub>	2	25	13	–	1	15	7	–	–	–	1	–
8	NO <sub>2</sub> + NO <sub>3</sub> + M → N <sub>2</sub> O <sub>5</sub> + M	58	–	13	–	34	–	7	–	–	–	–	–
9	H + NO <sub>2</sub> → OH + NO	1	–	–	–	4	–	–	–	15	32	41	13
10	OH + NO <sub>2</sub> + M → HNO <sub>3</sub> + M	7	34	14	–	9	31	10	–	10	19	4	–
11	NO <sub>2</sub> + NO <sub>2</sub> + M → N <sub>2</sub> O <sub>4</sub> + M	–	–	4	8	–	–	3	5	–	–	–	–
12	N <sub>2</sub> (A) + NO <sub>2</sub> → N <sub>2</sub> + NO + O	17	3	–	–	30	7	–	–	54	8	–	–
13	NO + NO <sub>2</sub> + M → N <sub>2</sub> O <sub>3</sub> + M	6	25	49	92	11	39	69	95	19	39	50	87
14	NO <sub>2</sub> + O → NO + O <sub>2</sub>	–	9	–	–	–	5	–	–	–	–	–	–



**Figure A7.** Absolute reaction rates of the most important production and loss processes for the NO<sub>2</sub> molecules, for cases A, B and C, at different moments in time. The numbers on the x-axis of the figure correspond to the reaction numbers in Table A7.

**Table A8.** Overview of the most important reactions which contribute to the formation and loss of the N<sub>2</sub>O molecules, with their relative contributions for cases A, B and C, at different moments in time.

No.	N <sub>2</sub> O production	Relative contribution [%]											
		Case A				Case B				Case C			
		t <sub>3</sub>	t <sub>4</sub>	t <sub>5</sub>	t <sub>6</sub>	t <sub>3</sub>	t <sub>4</sub>	t <sub>5</sub>	t <sub>6</sub>	t <sub>3</sub>	t <sub>4</sub>	t <sub>5</sub>	t <sub>6</sub>
1	N <sub>2</sub> (A) + O <sub>2</sub> → N <sub>2</sub> O + O	100	97	1	29	100	97	24	29	–	–	–	–
2	NO <sub>2</sub> + N → N <sub>2</sub> O + O	–	–	87	100	–	–	59	71	100	39	74	–
3	NH + NO → H + N <sub>2</sub> O	–	3	16	–	–	3	11	–	–	61	26	100
	N <sub>2</sub> O loss												
4	O <sub>2</sub> <sup>-</sup> + N <sub>2</sub> O → O <sub>3</sub> <sup>-</sup> + N <sub>2</sub>	–	–	1	27	–	–	–	21	–	–	–	2
5	NO <sub>2</sub> <sup>-</sup> + N <sub>2</sub> O → NO <sub>3</sub> <sup>-</sup> + N <sub>2</sub>	–	–	3	73	–	–	–	79	–	–	–	97
6	N <sub>2</sub> (A) + N <sub>2</sub> O → N <sub>2</sub> + N + NO	100	100	96	–	100	100	100	–	99	100	100	–



**Figure A8.** Absolute reaction rates of the most important production and loss processes for the N<sub>2</sub>O molecules, for cases A, B and C, at different moments in time. The numbers on the x-axis of the figure correspond to the reaction numbers in Table A8.

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