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THE INFLUENCE OF RADICAL N, O AND O_3 IN THE REDUCTION OF NITROGEN OXIDES IN A CORONA DISCHARGE

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ABSTRACT

This work presents a chemical kinetic analysis of different species involved in nitrogen-oxygen mixed gas by a Corona Discharge (CD) at room temperature and atmospheric pressure. This study takes into account 20 different chemical species reacting following 150 selected chemicals reactions. The reaction rate coefficients are taken from the literature and the density is analyzed by the continuity equation without the diffusion term. Many works have study removal NO_x and they have showing the role of N, O and O_3 radicals. So the aim of this simulation is to complete these studies by analyse of various plasma species under different reduced electric field: 100–200 Td. We analyse especially, the temporal depopulation rate evolution (10^{-9} – 10^{-3} s) of NO_x. We have found that the rate depopulation of NO and NO_2 is substantially affected by the reduced electric field rise from the initial value of 100 Td up to 200 Td. Thus, we have obtained in our simulation 2% of NO removal for 100 Td against 96% for 200 Td. This allows us the important role played by the reduced electric field.

Keywords: Chemical Kinetic, Corona discharge, Nitrogen oxide, Reduced electric field

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1. INTRODUCTION

It is well known that gas discharge plasmas are able to initiate chemical reactions in normally inert gas mixtures. A corona discharge is widely used in many applications such as the decomposition of gaseous pollutants [1,2], water treatment [3], ozone production [4–6] surface treatment [7,8] and medical applications [9].

In plasma discharges, the electrons gain energy through an external electric field, and lose via elastic and inelastic collisions with gas molecules [10]. The large difference of mass between electrons and gas species makes elastic collisions inefficient, and the rate of transfer of electron energy to translational degrees of freedom of the gas is slow. On the other hand, inelastic collisions of high energy electrons with gas molecules cause rapid excitation of internal energy modes as well as dissociation and ionization. The reduced electric field, *E*/*N* (ratio of electric field to gas number density) is a critical parameter governing the electron energy. Depending on the *E*/*N* value, the plasma physics and chemistry can be vastly different [11].

For plasma part, which aims at characterizing plasma phenomena ionization, recombination, evolution of electric field, etc, a large number of experimental and modelling papers describing the kinetics and characteristics of plasma have been published. Kossyi *et al.* developed in 1992 a zero-dimensional physical based model which considers 46 species and 450 reactions to research gas discharge in N_2–O_2 mixtures in all time scales [12].

Recently, with the help of sensitivity analysis, Poggie *et al.* filtered 16 species and 51 reactions suitable for nanosecond pulse discharge and built a one-dimensional kinetic model in low pressure [13,14]. As demonstrated in previous researches, it is the heating effect rather than tiny body force generated by nanosecond plasma actuator that plays a dominate role. Thus, revealing the mechanism for rapid gas heating in nanosecond pulse discharges is an important issue.

Popov [15] has made a detailed investigation on the heating effect of nitrogen–oxygen mixtures excited by microwave discharges and concluded that the gas is heated mainly in the reactions of preliminary dissociation of highly excited electronic states of oxygen molecules. Flitti *et al.* introduced a state-specific plasma-chemical model and an energy conservation

equation to analyse the dynamics of gas heating in fast-pulsed discharges in nitrogen–oxygen mixtures and found that higher electron density, electric field or partial pressure of oxygen leads to a faster gas heating [16].

In this technique, the process of eliminating pollutants passes through two main phases. The phase of discharge which lasts few tens of nanoseconds, on the formation of excited species and ionized radical species (such as O, N, and O_3) these radicals are created by the electron-molecule interaction then by ion-molecule interaction [17-19].

Although the asymptotical study has been done using the simplified model given by Lowke [20], one can suppose that it carries through to more complex ionization kinetics.

The phase of post-discharge induced chemical reactivity which able to transform the toxic molecule into inoffensive particles (such as N_2, O or N) or created acids (such as the nitric acid) to the plasma inside, which can be transformed in turn to salt (by addition of a base).

In this study we simulate, for different values of reduced electric field (100 Td, 200 Td), the evolution of neutral species (molecules N_2, O_2, O_3 atoms N, O, and nitrogen oxides NO, NO_2, N_2O, N_2O_5, NO_3,), ions positive (NO^+, N^+_2, O^+_2), ion negative (O^-_4, O^-_3, NO^-_3, NO^-_2, O^-, O^-_2) metastable species ($N(^2D)$, $O(^1D)$, $N_2(A3)$, $O_2(B1)$,$O_2(A1)$) and electron in a mixture (N_2 85% and O_2 15%). This simulation must consider the various effects induced by the passage of a DC in a gas. However, and for the sake of simplification, we assume that the gas has no convective gradients movement and the pressure is non-existent.

2. MATHEMATICAL MODEL

The mathematical model used consists of a system of equations that takes into account the variation of the density and the chemical kinetics of the environment.

To model the nonthermal plasma, we have developed a zero-order kinetic model for solving neutral, radical and ion equations. It is based on the numerical integration of the system of coupled differential equations accounting for the time evolution of the various species to the study state.

2.1 The Conservation Equations of The Density of Each Species

The equation for the density of species j in the mixture can be written:

$$\frac{\partial n_i}{\partial t} = S_j(T) \quad (1)$$

n_i : the density of species i, $\frac{\partial n_i}{\partial t}$: the time rate of change of density, $S_j(T)$: sources term.

n: the total density of the gas is given by the classical equation of a perfect gas:

$$P = n k_B T \quad (2)$$

Where P represents the pressure in Pascal, k_B Boltzmann constant and T the absolute temperature (in Kelvin).

2.2 Modelling of Chemical Kinetics

The reactivity of the gas is taken into account in the source term of each equation $S_j(T)$ conservation density (equation (1)).

In the case where chemical reactions where two body $S_j(T)$ are given a time by the relation:

$$S_j(T) = \sum_\alpha \pm K_\alpha(T)(n_q n_p)_\alpha \quad (3)$$

$K_\alpha(T)$ is the coefficient of the chemical reaction number a and (n_q n_p) the product of densities of species p and q interacting in response to the reaction a, positive and negative signs that are similar to the reactions of formation or disappearance of specie j.

And if we have three bodies so the term source is given by the product of the density of the former.

The coefficients of reactions are made under the form of Arrhénus:

$$K_\alpha(T) = K T^\eta \exp(-\theta/T) \quad (4)$$

K, η, θ, are three coefficients of adjustment, θ is the activation of the T is the absolute temperature of the species involved in the warm rain that has left the chemical reaction α.

2.3 Basic Condition

We have developed zero-dimensional time-dependent kinetic model to describe the NO_x processing in exhaust synthetic gases containing N_2 /O_2. It allows us to consider the evolution of a large number of species (electrons, ions, excited states, radicals, neutrals, etc...).

The mixture studied is synthetic air, considered at atmospheric pressure and room temperature. Gas chemistry considers 20 neutral species (molecules N_2, O_2, O_3 atoms N, O, and oxides NO, NO_2, N_2O, N_2O_5, NO_3), positive ions (NO^+, N^+_2, O^+_2), negative ions (O^-_4, O^-_3, NO^-_3)

metastable species ($N(^2D)$, $O(^1D)$,$N_2(A3)$) and electron responsive there between following 150 chemical reaction selected.

Table 1. The main plasma reactions to generate the main radical to remove NO_x and their rate constants

	Reactions	Rate constants	References
R_1	$NO + NO_3 \rightarrow NO_2 + NO_2$	$k_1= 2.0 \times 10^{-11}$	[12]
R_2	$NO + O_3 \rightarrow O_2 + NO_2$	$k_2 = 1.8 \times 10^{-12}$	[11]
R_3	$NO + O^-_3 \rightarrow NO^-_2 + O_2$	$k_3= 2.0 \times 10^{-12}$	[12]
R_4	$NO + O^-_3 \rightarrow NO^-_3 + O$	$k_4= 1.0 \times 10^{-10}$	[12]
R_5	$NO + O^-_4 \rightarrow NO^-_3 + O_2$	$k_5= 2.5 \times 10^{-10}$	[12]
R_6	$NO + HO_2 \rightarrow NO_2 + OH$	$k_6= 13.5 \times 10^{-11}$	[12]
R_7	$NO_2 + O^-_2 \rightarrow NO^-_2 + O_2$	$k_7= 7.0 \times 10^{-10}$	[11]
R_8	$NO_2 + OH \rightarrow HNO_3$	$k_8= 13.5 \times 10^{-11}$	[11]
R_9	$NO_2 + O^-_3 \rightarrow NO^-_2 + O_3$	$k_9 = 7.0 \times 10^{-10}$	[11]
R_{10}	$NO_2 + N \rightarrow NO + NO$	$k_{10} = 2.3 \times 10^{-12}$	[11]
R_{11}	$NO_3 + OH \rightarrow HO_2 + NO_2$	$k_{11}= 2.35 \times 10^{-11}$	[11]
R_{12}	$NO_3 + HO_2 \rightarrow HNO_3 + O_2$	$k_{12}= 4.05 \times 10^{-12}$	[11]
R_{13}	$NO_3 + NO_3 \rightarrow O_2 + NO_2 + NO_2$	$k_{13}= 1.2 \times 10^{-15}$	[21]
R_{14}	$NO_3 + O \rightarrow O_2 + NO_2$	$k_{14}= 1.7 \times 10^{-11}$	[21]
R_{15}	$N + O_2 \rightarrow O + NO$	$k_{15} = 8.9 \times 10^{-17}$	[12]
R_{16}	$N + NO_2 \rightarrow N_2 + O_2$	$k_{16}= 7.0 \times 10^{-13}$	[12]
R_{17}	$N + NO^-_3 \rightarrow NO + NO_2 + e$	$k_{17}= 5.0 \times 10^{-10}$	[12]
R_{18}	$NO_2 + NO_3 + O_2 \rightarrow N_2O_5 + O_2$	$k_{18} = 3.7 \times 10^{-30}$	[12]
R_{19}	$O_3 + H \rightarrow OH + O_2$	$k_{19}= 2.8 \times 10^{-11}$	[18]

The 20 species and 150 reactions between these species were chosen because of their relative importance, more particularly nitrogen oxides (Table1).

3. RESULTS AND DISCUSSION

In this section we will calculate the rate of depopulation given by equation $(N_0\text{-}N)/N_0$ for species NO, NO_2, NO_3, N_2O_5, N, O, O_3 and to see their variation over time (10^{-9}– 10^{-3} s) will facilitate this analysis we study the evolution of nitrogen oxides for 6 values of the reduced

field (100 , 120, 140, 160, 180, 200 Td) and see how they react with each other for different values of the applied field, and for a better understanding of the chemical kinetics of NO_x. Under these conditions were added primary radicals (O, N and O_3) that affect significantly the reduction of oxides. 100 Td is noted for the creation of NO_2 between 10^{-9} and 10^{-7} s which can reach 40% and NO_3 creation is between 10^{-7} and 10^{-5} s, which will reach 64%. We respect the NO reduction of 50% is from 10^{-8} s. Radicals for it will be consumed in the creation of oxides NO_2, NO_3 and N_2O_5 following reactions:

Creating oxides NO_2, NO_3 and N_2O_5 to 120 Td:

NO_3 reached 86% at $t = 3.10^{-7}$s .

The N_2O_5 equal to 97% from 10^{-6} s. we also note that the ozone created from 10^{-7} s, it reaches 97% from 10^{-6} s. 140 Td nitrogen mono-oxide reached 25% from 10^{-8}s followed by a 74% reduction from 10^{-5} s.

For 160, 180 and 200 Td is always a creation for N_2O_5 which occurs faster with increasing the reduced field. The same goes for other oxides and NO_2 NO_3 followed by reduction revenue is that 10% of NO_2. Regarding NO reduction is faster to reach 200 Td is 56% from 2×10^{-7}s.

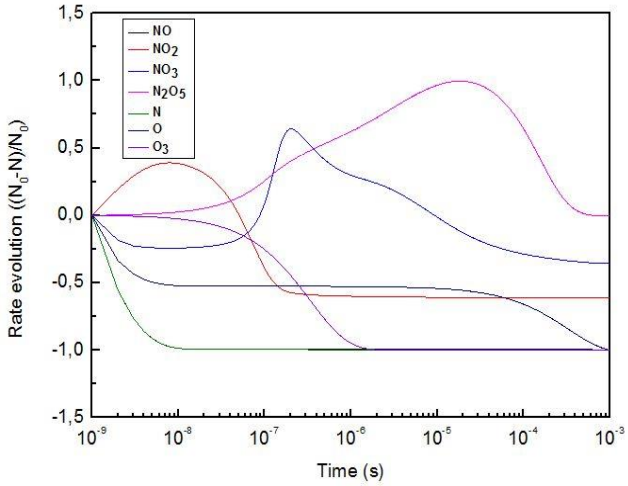

Fig.1. Depopulation of NO, NO_2, NO_3, N_2O_5, N, O, O_3 species in dry air at atmospheric pressure under corona discharge and constant room temperature for the 100 Td reduced electric field

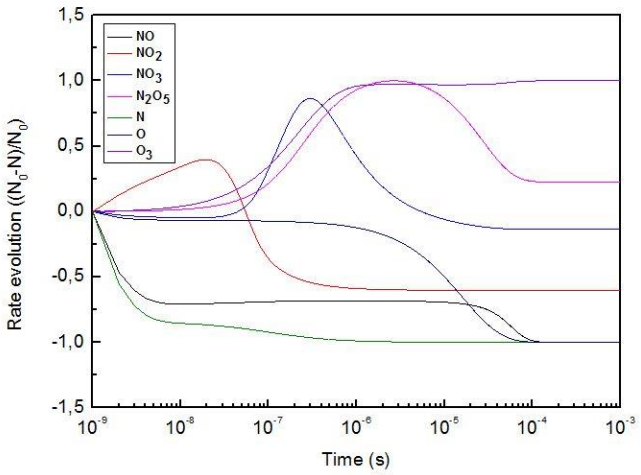

Fig.2. Depopulation of NO, NO_2, NO_3, N_2O_5, N, O, O_3, species in dry air at atmospheric pressure under corona discharge and constant room temperature for the 120 Td reduced electric field

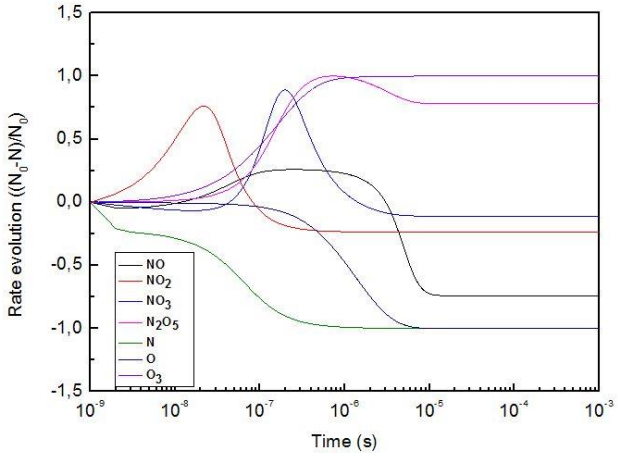

Fig.3. Depopulation of NO, NO_2, NO_3, N_2O_5, N, O, O_3 species in dry air at atmospheric pressure under corona discharge and constant room temperature for the 140 Td reduced electric field

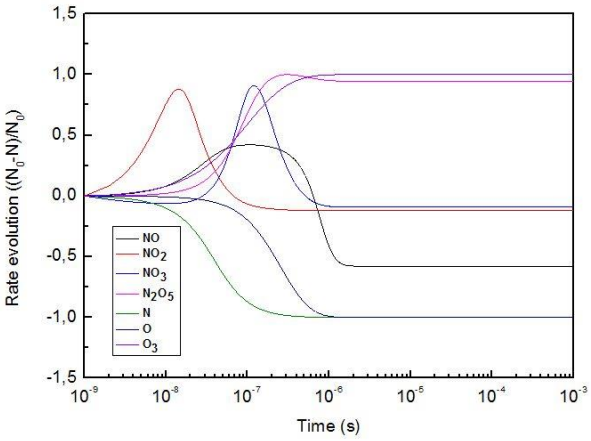

Fig.4. Depopulation of NO, NO_2, NO_3, N_2O_5, N, O, O_3 species in dry air at atmospheric pressure under corona discharge and constant room temperature for the 160 Td reduced electric field

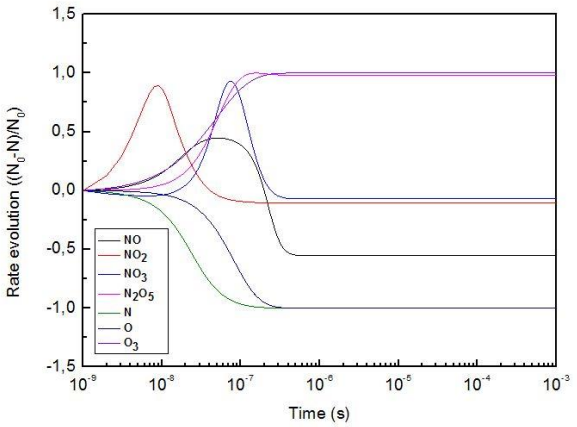

Fig.5. Depopulation of NO, NO_2, NO_3, N_2O_5, N, O, O_3 species in dry air at atmospheric pressure under corona discharge and constant room temperature for the 180 Td reduced electric field

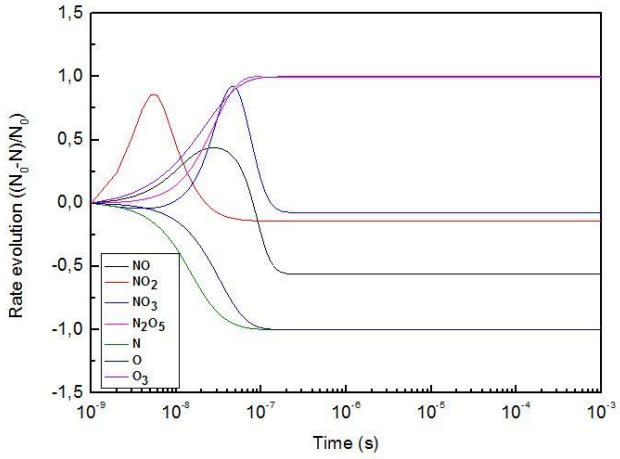

Fig.6. Depopulation of NO, NO_2, NO_3, N_2O_5, N, O, O_3 species in dry air at atmospheric pressure under corona discharge and constant room temperature for the 200 Td reduced electric field

4. CONCLUSION

In general, in the literature It has been emphasized that certain radicals influences the NO or NO_2 removal. In this work, the results obtained show the significance role played by the high reduced electric field.

- ✓ The time evolution of (NO, NO_2, NO_3, N_2O_5, N, O, O_3) species, two types of evolution strongly dependent increase of reduced electric field:

  - creation for O_3, N_2O_5.

  -reduction for NO, NO_2, NO_3, N, O.

- ✓ This reaction contrebalances by reaction of creation Against by the formation of NO is provided by the radicals O and N was crossing the following reaction:

  $O_3^- + N \rightarrow NO + O_2 + E$ and $N + O_2 \rightarrow O + NO$.

In fact, the simulation results demonstrated that the reduced electric field influences the NO_x removal. We obtained 23% for 100 Td at t=10^{-4}s against 56% for 200Td at t= 10^{-6}s.

5. REFERENCES

[1] Hammer T. Non-thermal plasma application to the abatement of noxious emissions in automotive exhaust gases. Plasma Sources Sci. Technol., 2002,11 A,196–201

[2] Chang J S. Physics and chemistry of plasma pollution control technology., Plasma Sources

Sci. Technol., 2008,17, 045004

[3] Locke B R, Sato M, Sunka P, Hoffmann M R and Chang J S. Electrohydraulic discharge and nonthermal plasma for water treatment., Indust. Eng. Chem. Res**.**, 2006, 45, 882–905

[4] Simek M and Clupek M. Efficiency of ozone production by pulsed positive corona discharge in synthetic air., J. Phys. D: Appl. Phys., 2002, 35, 1171–1175

[5] Eliasson B and Kogelschatz U. Nonequilibrium volume plasma chemical processing., *IEEE Trans. Plasma Sci.* ,1991, 19 ,1063–1077

[6] Chen J and Davidson J H. Ozone production in the positive DC corona discharge: Model and comparison to experiments., Plasma Chem. Plasma Process., 2002, 22 ,495–522

[7] Schram D C, Mullen J A. and M Sanden. Plasma processing and chemistry Plasma., Phys. Control. Fusion., 1994, 36 B, 65–78

[8] Miao L, Tanemura S, Watanabe H, Mori Y, Kaneko K. The improvement of optical reactivity for TiO_2–H_2 plasma surface-treatment., J. Crystal Growth, 2004, 260, 118–124

[9] Fridman G, Friedman G, Gutsol A, Shekhter A B, Vasilets V N and Fridman A. Applied plasma medicine., Plasma.Process. Polym., 2008, 5, 503–533

[10] Starikovskiy A and Aleksandrov N. Plasma-assisted ignition and combustion., Science., 2013,39, 61–110

[11] Eichwald O, Guntoro N A, Yousfi M and Benhenni M. Chemical kinetics with electrical and gas dynamics modelization for NOx removal in an air corona discharge., J. Phys. D: Appl. Phys., 2002, 35 ,439–450

[12] Kossyi I A, Kostinsky A Y, Matveyev A A and Silakov V P. Kinetic scheme of the nonequilibrium discharge in nitrogen–oxygen mixtures., Plasma Sources Sci. Technol., 1992, 1, 207–220

[13] Poggie J and Bisek N. Numerical simulation of nanosecond-pulse electrical discharges., AIAA Paper., 2012, 2012-1025

[14] Poggie J, Adamovich I, Bisek N and Nishihara M. Numerical simulation of nanosecond-pulse electrical discharges., Plasma Sources Sci. Technol., 2013, 22, 015001

[15] Popov N A. Investigation of the mechanism for rapid heating of nitrogen and air in gas discharges., Low-Temp. Plasma., 2001, 27, 940–950

[16] Flitti A and Pancheshnyi S. Gas heating in fast pulsed discharges in N_2 –O_2 mixtures Eur., Phys. J. Appl. Phys., 2009, 45, 21001

[17] Atsushi Komuro, Ryo Ono and Tetsuji Oda. Numerical simulation for production of O and N radicals in an atmospheric-pressure streamer discharge., J. Phys. D: Appl. Phys., 2012 45, 265201

[18] Eichwald O, Ducasse O, Dubois D, Abahazem A, Merbahi N, Benhenni M and Yousfi M. Experimental analysis and modelling of positive streamer in air: towards an estimation of O and N radical production., J. Phys. D: Appl. Phys., 2008, 41 ,234002

[19] Duten X, Redolfi M, Aggadi N, Vega A and Hassouni K. Spatial and temporal evolutions of ozone in a nanosecond pulse corona discharge at atmospheric pressure., J. Phys. D: Appl. Phys., 2011, 44 ,415202

[20] Lowke J J. Theory of electrical breakdown in air—the role of metastable oxygen molecules., J. Phys. D: Appl. Phys., 1992 ,25 202–210

[21] Eichwald O., Guntoro N.A., Yousfi M. and Benhenni M., proc XII Int Conf. On Gaz Discharge and their Application, Glasgow, UK., 2000, 732-735

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