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NUMERICAL SIMULATION OF THE REDUCED FIELD INFLUENCE ON THE EVOLUTION OF NITROGEN OXIDES PRESENT IN THE MIXTURE $N_2/O_2/H_2O/CO_2$ BATHED IN AN OUT-OF- EQUILIBRIUM PLASMA

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Abstract. The industrial and technological development of the last century has led to increasing energy consumption, which has led to an increasing increase in the discharge of gaseous pollutants into the atmosphere. In these discharges, nitrogen oxides account for a large part of the environmental pollutants and are there fore directly or indirectly responsible for certain diseases when their concentration in the air is high. In this work, we propose to numerically simulate the evolution of the density of NO_x nitrogen oxides present in the gas mixture $N_2/O_2/H_2O/CO_2$ which is subjected to different values of the reduced electric field: 100 to 200 Td ($1\text{Td} = 10^{-17}$ V.cm^2). We are particularly interested in the NO, NO_2 and NO_3 species that are the main components of nitrogen oxides. The simulation runs from 10^{-9} to 10^{-3} s. The model takes into account twenty species reacting with each other following two hundred chemical reactions. The results obtained clearly show the effectiveness of the reduced electric field in the destruction of nitrogen oxides.

1. Introduction

Generally, the reduced electric field (E/n ratio) is considered a critical parameter controlling the electron energy in plasma discharges. The chemistry of plasma can be different based on the value of E/n ratio (where E is the electric field and n is the gas density). For several years, the common catalytic and thermal methods used to eliminate or at least to reduce the level of NO_x that existed in industrial flue gas and/or generated by the vehicles will not permit us to respect the limits of gases emission [1]. There are several important parameters for the decomposition of NO: initial NO concentration, composition and temperature of the carrier gas and the value of the reduced electric field (E/n). In order to choose the optimal

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operating conditions for a non-thermal plasma process, it is of great importance to understand the chemical mechanisms responsible for the decomposition of pollutant molecules in a plasma. In the past few years, simulation of plasma processing using detailed chemistry has become an important tool for investigating this problem. The influence of different parameters (concentration, gas, temperature...) has been examined theoretically and experimentally [2].

Discharges and post-discharges in pure N_2 and O_2 or in their mixtures with inert gases are receiving increasing attention, due to their importance for understanding atmospheric and ionospheric physics and to their use as active laser media and as sources of active species (N and O atoms, metastable atoms and molecules, ions) for applications in plasma chemistry. Such applications include surface treatments, coating processes, metal nitriding, TiN deposition, oxidation and etching of polymers and semiconductors [3].

During the past decade, the removal of NO, (including NO and NO_2) and SO_2 has become a central scientific concern because of its key role in many global environmental problems such as acid rain or photochemical smog formation. There are also adverse effects on human health: In higher concentrations these chemical species may cause bronchitis or pneumonia [4]. In addition, SO_2 and NO contribute to the degradation of visibility since they form accumulation-mode aerosol particles containing sulfates and nitrates [5]. While the emission of SO_2 can be limited by using low-sulphur fuels, NOx, remains a serious hazard to the human health, is an ozone precursor, and is one of the most difficult air pollutants to suppress [6]. A major source of NO_x, emissions are exhaust gases of motor vehicle, especially from diesel engines. Diesel engines have much better fuel economy than cars with gasoline engines. They also have lower emissions of hydrocarbons and carbon-monoxide, but NO_x, and partliculate, emissions are much higher [7].

In this work, we simulate the time behavior of different species and their reaction rates model based on chemical kinetics equations. The analyze concerns twenty chemical species (molecules i.e. N_2, O_2, H_2O, CO_2, OH, HO_2, HNO_3 and O_3, atoms i.e. N, O and H, nitric oxides i.e. NO, NO_2, NO_3 and N_2O_5, and negative ions i.e. O_2^-, O_3^-, O_4^-, NO_2^- and NO_3^-), in the mixture (i.e. N_2: 70%, O_2: 20%, H_2O: 5% and CO_2: 5%). These different species react following 100 selected chemical reactions and the analyze concerns six values of the reduced electric field (100, 120, 140, 160, 180, 200 Td). In this numerical simulation we suppose various effects induced by the passage of a corona discharge [8] in a mixed gas. For the sake of simplification, we assume that the gas has no convective movement gradients and the pressure remains constant.

2. Basic formulae

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

We developed a zero order numerical code to resolve the transport equations for neutral and charged particles. The algorithm is based on the time integration of the system of equations under consideration [9].

$$\frac{dn_i}{dt} = \sum_{j=1}^{j_{\max}} F_{ij},\ j \in [1, ..., j_{\max}] \tag{2.1}$$

where

$$F_{ij} = \varphi_{ij} - \chi_{ij} \tag{2.2}$$

n_i means the species densities vector, and F_{ij} mean the source term vector depending on the rate coefficient and corresponding to the contributions from different processes. φ_{ij} and χ_{ij} represent respectively the gain and loss of species i due to the chemical reactions. The solution of such a system requires the knowledge of the initial concentrations.

The total density n component is expressed in terms of pressure p equation can be written as (ideal gas law):

$$p = n\, k_\beta\, T \tag{2.3}$$

where T the absolute temperature (is in Kelvins) and k_β is Boltzmann constant (is in J/K). However, the reactivity of the gas were taken into account to the source term F_{ij} (density conservation) Eq (2.1).

$$\varphi_{ij} = \sum_{\gamma} K_\gamma(T)(n_i\, n_j)_\gamma \tag{2.4}$$

and

$$\chi_{ij} = \sum_{\eta} K_\eta(T)(n_i\, n_j)_\eta \tag{2.5}$$

$K_\gamma(T)$ and $K_\eta(T)$ are the coefficients of the chemical reaction number γ or η, $(n_i\, n_j)$ means the product of densities of species i and j.

These coefficients satisfy Arrhenius formula:

$$K_\gamma(T) = \kappa_1 \exp\left(\frac{\theta_\gamma}{T}\right) \tag{2.6}$$

and

$$K_\eta(T) = \kappa_2 \exp\left(\frac{\theta_\eta}{T}\right) \tag{2.7}$$

where κ_1 and κ_2 are the constant factors and θ_γ and θ_η are the activation energy of the chemical reaction.

In table 1, we present the chemical reactions considered in this paper.

Table 1. The main plasma reactions to generate the main radical to remove NO_x and their rate constants. $x[y]$ denotes $x \times 10^y$.

	Reaction	Rate constants	References
R_1	$NO + NO_3 \rightarrow NO_2 + NO_2$	K_1=2.00[-11]	[10]
R_2	$NO + O_3 \rightarrow O_2 + NO_2$	K_2=1.80[-12]	[10]
R_3	$NO + O_3^- \rightarrow NO_2^- + O_2$	K_3=2.00[-12]	[10]
R_4	$NO + O_3^- \rightarrow NO_3^- + O$	K_4=1.00[-10]	[10]
R_5	$NO + O_4^- \rightarrow NO_3^- + O_2$	K_5=2.50[-10]	[10]
R_6	$NO + HO_2 \rightarrow NO_2 + OH$	K_6=13.5[-11]	[10]
R_7	$NO_2 + O_2^- \rightarrow NO_2^- + O_2$	K_7=7.00[-10]	[9]
R_8	$NO_2 + OH \rightarrow HNO_3$	K_8=13.5[-11]	[9]
R_9	$NO_2 + O_3^- \rightarrow NO_2^- + O_3$	K_9=7.00[-10]	[9]
R_{10}	$NO_2 + N \rightarrow NO + NO$	K_{10}=2.30[-12]	[9]
R_{11}	$NO_3 + OH \rightarrow HO_2 + NO_2$	K_{11}=2.35[-11]	[9]
R_{12}	$NO_3 + HO_2 \rightarrow HNO_3 + O_2$	K_{12}=4.05[-12]	[9]
R_{13}	$NO_3 + NO_3 \rightarrow NO_2 + NO_2 + O_2$	K_{13}=1.20[-15]	[11]
R_{14}	$NO_3 + O \rightarrow NO_2 + O_2$	K_{14}=1.70[-11]	[11]
R_{15}	$N + O_2 \rightarrow O + NO$	K_{15}=8.90[-17]	[10]
R_{16}	$N + NO_2 \rightarrow N_2 + O_2$	K_{16}=7.00[-13]	[10]
R_{17}	$N + NO_3^- \rightarrow NO + NO_2 + e^-$	K_{17}=5.00[-10]	[10]
R_{18}	$NO_2 + NO_3 + O_2 \rightarrow N_2O_5 + O_2$	K_{18}=3.70[-30]	[11]
R_{19}	$O_3 + H \rightarrow OH + O_2$	K_{19}=2.80[-11]	[12]
R_{20}	$OH + H_2 \rightarrow H_2O + H$	K_{20}=6.70[-15]	[12]
R_{21}	$OH + O_3 \rightarrow HO_2 + O_2$	K_{21}=6.50[-14]	[12]
R_{22}	$OH + HO_2 \rightarrow H_2O + O_2$	K_{22}=1.10[-10]	[12]
R_{23}	$OH + HNO_3 \rightarrow NO_3 + H_2O$	K_{23}=1.30[-13]	[12]
R_{24}	$H_2O + e^- \rightarrow OH + H + e^-$	K_{24}=2.60[-12]	[12]
R_{25}	$CO_2 + e^- \rightarrow CO + O + e^-$	K_{25}=8.70[-10]	[12]

3. NUMERICAL RESULTS AND DISCUSSION

In figures 1, we have showing the time evolution of rate coefficient of these reactions at various values of reduced electric fields (100, 120, 140, 160, 180 and 200 Td). We notice that NO can react with the oxidizing radicals such as O_3, O_3^-, O_4^- and HO_2 to form especially NO_2^-, NO_3^- and OH. We note firstly that the effectiveness of these reactions is higher at the beginning than at the end. Secondly, plus the value of the reduced electric field is more important reaction is effective. For example, at 100 Td the rate coefficient does not vary significantly, but at 200 Td we have a significant reduction. We notice to all of these curves that the reactions become less effective after $t = 4 \times 10^{-4}$ s.

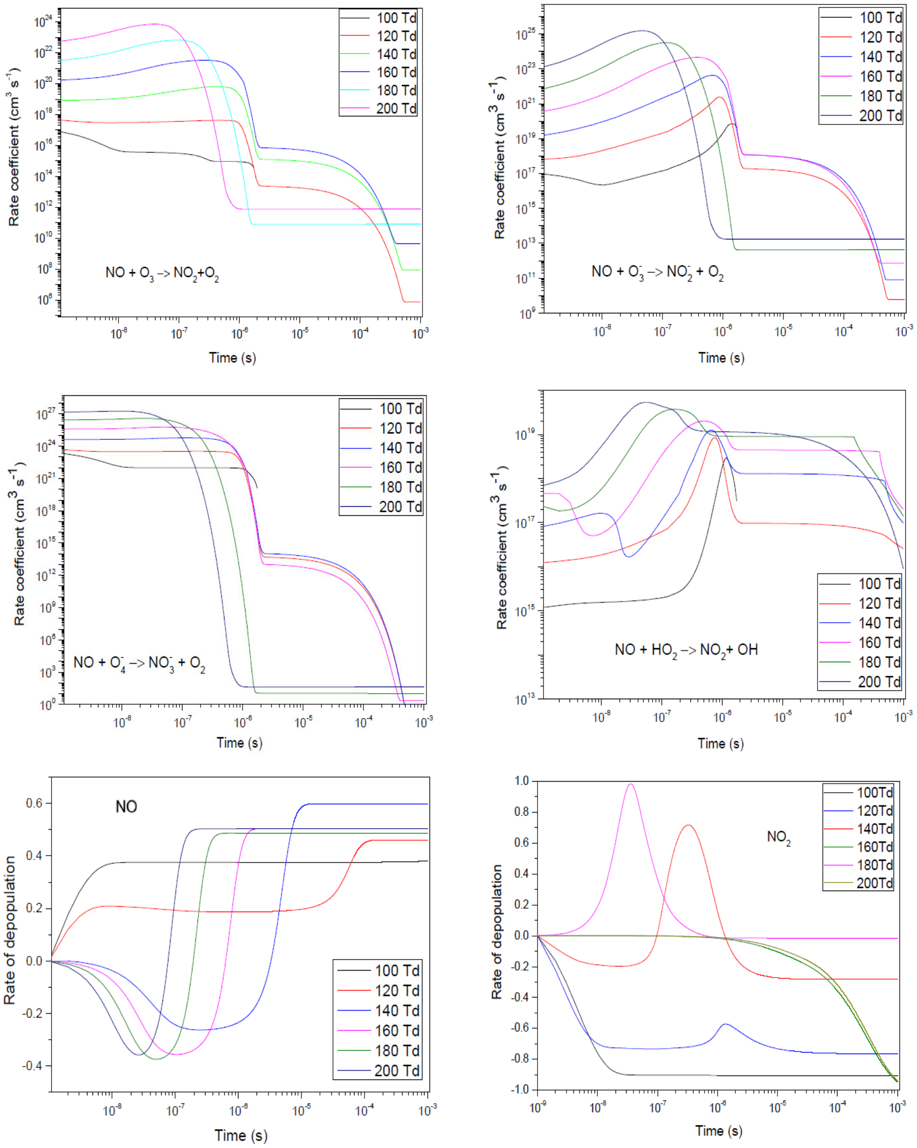

Fig 1: Time evolution of rate coefficient for four reaction selected as a function of the time. Also we presented at the end the time evolution of depopulation rate specie in mixture specie in mixture $N_2/O_2/H_2O/CO_2$ as a function of the time, shown for different reduced E in the range of 100−200 Td. At the end of this figure we presented: *left* is NO and to the *right* NO_2.

In end figure 1 and left, we plot the time evolution of depopulation rate $(n_0 - n)/n_0$, where n_0 means the initial density of NO specie in mixture $N_2/O_2/H_2O/CO_2$

for different values reduced E in the range of $100 - 200$ Td. We presented in this figure the results of the competition between all inherent reactions to oxide nitrogen reduction. We clearly observe the influence of the reduced E on NO reduction, we presented also in this figure the results of the competition between all inherent reactions to oxide nitrogen reduction. What we could notice for low values of the reduced E in the range of $100 - 130$ Td an average reduction of $\sim$ 15% which explains by the overall reaction, while for high value 180 Td, we also observed that the rate coefficient of reduction reached $\sim$ 70%. Finally, NO reduction largely depends on the radical concentration of O_3, O_3^-, O_4^- and HO_2. In the beginning, the NO consumption is not significant because the O_3^-, O_4^- and HO_2 radicals generated react mostly with NO_x and their concentration remains low. In the right shows the time evolution of depopulation rate of NO_2 for various values of reduced E (100−200 Td). Unlike the previous result for oxide nitrogen, we observe for NO_2 a different behavior. Firstly, we notice in the beginning from 10^{-9} s to 10^{-8} s, a significant reduction ($\sim$ 85 % an average) especially for 100 and 140 Td which stabilizes at this value until the end. Secondly at 160 and 200 Td there is a different behavior, for example when the reduced $E \simeq 160$ Td the depopulation rate decreases and reaches approximately $\sim$ 30 % at $t \simeq 5 \times 10^{-8}$ s. Then there is an increase that reaches $\sim$ 65 % at the moment $t \simeq 5 \times 10^{-8}$ s followed by a reduction $\sim$ 30 % till the end.

4. Conclusion

The objective of this work is to contribute to the understanding of the reaction mechanisms that compete in the creation and consumption of nitrogen oxides present in the $N_2/O_2/H_2O/CO_2$ gas mixture at atmospheric pressure. In particular, we were interested in studying:

The main pollutants that are present in most industrial and automotive gaseous effluents (nitrogen monoxide NO, nitrogen dioxide NO_2...).

The influence of the most important reactions that are effective in the temporal evolution of these species.

the results obtained enabled us to highlight the influence of chemical reactivity on the spatio-temporal evolution of these species. In particular, we have shown, on the one hand, the predominant role of certain chemical reactions in the conversion of nitrogen oxides, and on the other hand, the difference in the contribution of these reactions between the different species. Indeed, if we compare the participation of the different chemical reactions on the conversion of the three species we can summarize the results obtained as follows:

For nitrogen monoxide is the reaction:

$NO + O_4^- \rightarrow NO_3^- + O_2$.

containing the radical O_4^- which dominates all other reactions.

For nitrogen dioxide, these are the two reactions: $NO_2 + O_2^- \rightarrow NO_2^- + O_2$ and $NO_2 + O_3^- \rightarrow NO_2^- + O_3$.

containing O_2^- and O_3^- radicals that play a significant role in conversion. For nitrogen trioxide, this is mainly the reaction: $NO_3 + OH \rightarrow HO_2 + NO_2$.

containing the OH radical which gives a better conversion.

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