INFLUENCE OF EXCITED MOLECULES $N_2(A^3\Sigma_u^+)$, $N_2(B^3\Pi_g)$, $O_2(^1\Delta_g)$ AND $O_2(b^1\Sigma_g^+)$ ON OZONE AND HYDROXYLS (H_2O_2, OH, HO_2) KINETICS IN THE PLASMA OF BARRIER DISCHARGE IN AIR AT ATMOSPHERIC PRESSURE

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The kinetics of the $N_2(A^3\Sigma_u^+)$, $N_2(B^3\Pi_g)$, $O_2(^1\Delta_g)$, and $O_2(b^1\Sigma_g^+)$ excited states in the barrier-discharge plasma in atmospheric air is calculated and their effect on the concentrations of derivative products – ozone and hydroxyls OH, HO_2, and H_2O_2 is analyzed. It is shown that the largest deviations in the concentrations obtained with and without taking into account the excited states are observed for H_2O_2 (≈60%) and O_3 (≈ 40%) at a relative humidity of 20%. The variation of the air humidity from 20…80% does not result in qualitative changes in the behavior of the ozone and hydroxyl concentrations in the barrier discharge.

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INTRODUCTION

An interest in the study of a barrier discharge in atmospheric pressure air is stipulated by a wide range of its practical application, such as purification of exhaust gases, sterilization of medical instruments, surface modification, etc. Simulation of plasma kinetics in barrier discharges opens the way to understanding the nature of kinetic processes in its active media and the relationship between their input parameters and the concentrations of secondary products – hydroxyls, ozone, acids. Therefore, of great importance is the creation of an adequate model of plasmachemical reactions in a barrier discharge.

Typically, such models take into account the kinetics of the initial discharge components – nitrogen and oxygen – in the ground states. However, the analysis of the cross sections of their inelastic collisions with electrons testifies to the active formation of $N_2(A^3\Sigma_u^+)$, $N_2(B^3\Pi_g)$, and $O_2(^1\Delta_g)$, $O_2(b^1\Sigma_g^+)$ excited molecules in the discharge. In this paper, the kinetics of these excited states in the barrier discharge plasma in atmospheric pressure is calculated. The effect of kinetic processes involving the $N_2(A^3\Sigma_u^+)$, $N_2(B^3\Pi_g)$, $O_2(^1\Delta_g)$, and $O_2(b^1\Sigma_g^+)$ excited molecules on the concentrations of derivative products – ozone as well as OH, HO_2, and H_2O_2 hydroxyls is also investigated.

1. CALCULATION MODEL

The calculations presented in the paper are obtained using the numerical model of plasma kinetics in a homogeneous volume discharge, where the input parameter is the introduced power density. This power is converted to gas heating and inelastic collisions of electrons and particles in the active medium, i.e.

$$W = \sum_j W_{ej} + \sum_j W_j, \tag{1}$$

where W_{ej} and W_j are the specific powers spent for inelastic and elastic collisions, respectively [1]. Given that the energy introduced into the discharge is uniformly distributed over the discharge chamber, the rate of an electron-molecular reaction with the threshold energy ε_{ei} can be presented as

$$S_{ei} = \frac{W}{V}\frac{1}{\varepsilon_{ei}}\frac{W_{ei}}{\sum_j W_{ej} + \sum_j W_j}. \tag{2}$$

Derivative components in the discharge are formed due to both electron processes and plasmachemical reactions. Thus, one obtains the following kinetic equation for the concentration N_i of particles of kind i

$$\frac{dN_i}{dt} = S_{ei} + \sum_j k_{ij} N_j + \sum_{j,l} k_{ijl} N_j N_l + \ldots, \tag{3}$$

where S_{ei} is calculated by Eq.(2), k_{ij}, k_{ijl} stand for the rate constants of two- and three-particle molecular reactions leading to the formation or destruction of the component under study.

The component composition in the discharge was calculated at the following input parameters: electric field in the plasma of 20 kV/cm, embedded power of 1.5 W/cm^3, and two humidity values – 20 and 80%. The time dependences of the excited $N_2(A)$, $N_2(B)$, $O_2(\Delta)$, $O_2(\Sigma)$states were analyzed together with their effect on the densities of O_3, H_2O_2, OH, and HO_2 molecules.

The system of kinetic equations (3) was solved with regard for the elementary processes described in [1]. To analyze the effect of the excited nitrogen and oxygen states on the discharge kinetics, the reactions listed in Tables 1 and 2 were added to the kinetic model.

Table 1. Reactions involving $N_2(A)$ and $N_2(B)$ states

№	Reaction	Rate constant	
1	$N_2(A)+O_2 > N_2+O+O$	2.54e-12	2
2	$N_2(A)+O_2 > N_2O+O$	7.8e-14	2
3	$N_2(A)+N_2O > N_2+N+NO$	1.0e-11	2
4	$N_2(A)+N_2 > N_2+N_2$	3.0e-18	2
5	$N_2(A)+NO > N_2+NO$	7.0e-11	2
6	$N_2(A)+O_2 > N_2+O_2(\Delta)$	6.45e-13	2
7	$N_2(A)+O_2 > N_2+O_2(\Sigma)$	6.45e-13	2
8	$N_2(A)+O_3 > N_2+O_2+O$	4.2e-11	3
9	$N_2(A)+H_2O > N_2+H+OH$	6.0e-14	3
10	$N_2(A)+NO_2 > N_2+NO+O$	1.3e-11	3
11	$N_2(A)+N_2(A) > N_2+N_2(B)$	4.0e-10	3
12	$N_2(B)+N_2 > N_2(A)+N_2$	5.0e-11	2
13	$N_2(B) > N_2(A)$	1.1.5e5	2
14	$N_2(B)+NO > N_2(A)+NO$	2.4e-10	2
15	$N_2(B)+O_2 > N_2+O+O$	3.0e-10	2

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Table 2. Reactions involving $O_2(\Delta)$ and $O_2(\Sigma)$ states

№	Reaction	Rate constant	
1	$O_2(\Delta)+O_3 > O_2+O_2+O$	$9.7e\text{-}13*\exp^{-1564/T}$	2
2	$O_2(\Delta)+N > NO+O$	$2.0e\text{-}14*\exp^{-600/T}$	2
3	$O_2(\Delta)+N_2 > O_2+N_2$	3.0e-21	2
4	$O_2(\Delta)+O_2 > O_2+O_2$	$2.2e\text{-}18(T/300)^{0.8}$	2
5	$O_2(\Delta)+O > O_2+O$	7.0e-16	2
6	$O_2(\Delta)+NO > O_2+NO$	2.5e-11	2
7	$O_2(\Delta)+H_2O > O_2+H_2O$	5.0e-18	3
8	$O_2(\Sigma)+O_3 > O_2+O_2+O$	1.8e-11	2
9	$O_2(\Sigma)+N_2 > O_2(\Delta)+N_2$	$4.9e\text{-}15*\exp^{-253/T}$	2
10	$O_2(\Sigma)+O_2 > O_2(\Delta)+O_2$	$4.3e\text{-}22*T^{2.4}*\exp^{-241/T}$	2
11	$O_2(\Sigma)+O > O_2(\Delta)+O$	8.0e-14	2
12	$O_2(\Sigma)+NO>O_2(\Delta)+NO$	4.0e-14	2

In our calculations, we compared the concentrations of derivative molecules and radicals calculated without reactions involving $N_2(A)$, $N_2(B)$, $O_2(\Delta)$, $O_2(\Sigma)$, taking into account only those with excited $N_2(A)$, $N_2(B)$ and with excited $O_2(\Delta)$, $O_2(\Sigma)$, and with regard for all processes listed in Tables 1,2.

2. CALCULATION RESULTS

The time dependences of the $N_2(A)$, $N_2(B)$ densities obtained for RH = 20 and 80% are presented in Fig. 1.

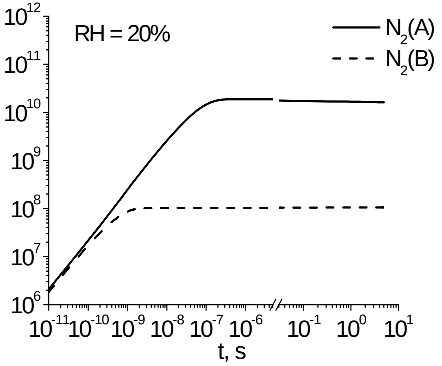

Fig. 1. Time dependences of the $N_2(A)$, $N_2(B)$ densities at air humidity of 20%

One can see that the concentrations of the both molecules are low, yet significantly differing in favor of the former component: the $N_2(A)$ density in the discharge reaches 2e10 cm^3, whereas the $N_2(B)$ concentration does not exceed 1e8 cm^3. Moreover, the both concentrations very quickly reach their stationary values: the concentration of $N_2(A)$ stops changing at t = 5e-7 s, while that of $N_2(B)$ – at t = 5e-9 s.

Such a behavior of the considered dependences is obviously explained by kinetic processes. The $N_2(A)$, $N_2(B)$ excited levels are generated by electronic excitation from the ground state of nitrogen molecules. As concerns their deactivation channels, the dominant processes for $N_2(A)$ are those with participation of oxygen (reaction 1.1) with a rate of 2.54e-12 cm^3/s. The deactivation reaction due to collisions with nitrogen has a much lower rate of 3.0e-18 cm^3/s, while the other reactions with noticeable rates involve derivative molecules such as N_2O and NO_2, whose concentrations in the discharge are much smaller than those of the initial components - nitrogen and oxygen.

$N_2(B)$ molecules are mainly deactivated in collisions with nitrogen (reaction 1.12, k = 5,0e-11 cm^3/s) and oxygen (reaction 3.15, k = 3,0e-10 cm^3/s). It is clear that these values significantly exceed the rates of $N_2(A)$ deactivation.

Thus, analyzing the kinetic processes in Table 1, one can draw the following conclusions:

1. The main decay channels of $N_2(A)$, $N_2(B)$ excited molecules are the reactions involving the major components of the active medium – nitrogen and oxygen in their ground states. Thus, the stationary concentrations of the excited nitrogen states are determined almost exclusively by N_2 and O_2 densities, so that they quickly reach their stationary values.

2. The considerable excess of the deactivation rates of $N_2(B)$ molecules in collisions with N_2, O_2 over the rates of the corresponding processes involving $N_2(A)$ results in a significant gap between the concentrations of the excited nitrogen states in favor of the latter.

3. The humidity value has no significant effect on the $N_2(A)$, $N_2(B)$ concentrations. In the case of $N_2(B)$ molecules, there are no direct interaction channels with water or hydrogen-bearing components, whereas in the case of $N_2(A)$, there is a deactivation reaction in collisions with H_2O, though its rate is comparatively low (6.0e-14 cm^3/s).

The temporal dynamics of the $O_2(\Delta)$, $O_2(\Sigma)$ concentrations presented in Fig. 2 is more complicated.

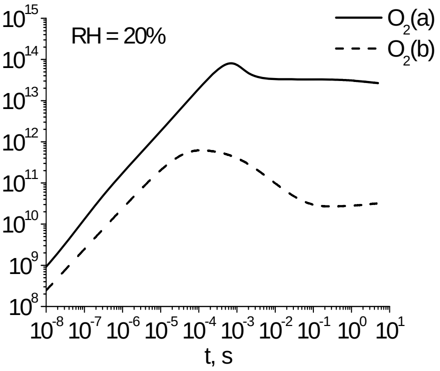

Fig. 2. Time dependences of the $O_2(\Delta)$, $O_2(\Sigma)$ densities at air humidity of 20%

The concentrations of excited oxygen molecules reach significantly higher values than those of excited nitrogen – 8e13 cm^3/s and 6e11 cm^3/s, respectively, and do not come to stationary values in the time range up to 5 s. As follows from Table 2, nitrogen and oxygen in their ground states are involved in the deactivation of excited $O_2(\Delta)$, $O_2(\Sigma)$ molecules, still the rates of the corresponding processes are very small and do not exceed 1e-18 cm^3/s. In this case, of major importance are reactions with participation of derivative products, particularly the main channels of $O_2(\Delta)$ deactivation are collisions with NO (reaction 2.6) and O_3 (reaction 2.1). The same situation is observed in the case of $O_2(\Sigma)$ with the most powerful decay channel being collisions with ozone (reaction 2.8).

Thus, analyzing the kinetic reactions involving excited oxygen states $O_2(\Delta)$, $O_2(\Sigma)$, one can state that:

1. The main deactivation channels of the excited oxygen states are processes involving ozone and NO (for $O_2(\Delta)$ molecules).

2. The insignificant role of deactivation of excited oxygen by the initial mixture components – nitrogen and oxygen in the ground states – provides noticeable values of the $O_2(\Delta)$, $O_2(\Sigma)$ densities in the discharge.

3. The time dependences of excited oxygen have a complicated form determined by the behavior of the O_3 and NO concentrations. For example, the $O_2(\Sigma)$ density grows in the time interval t<1e-4 s, where the ozone concentration in the discharge is insignificant. After that, it decreases due to the rise in the ozone density in this period. At t = 0.5 s, the ozone concentration reaches a maximum and starts falling slowly, which in turn results in a slight increase in the $O_2(\Sigma)$ concentration.

4. The same way as in the case of $N_2(A)$, $N_2(B)$, the humidity has no noticeable effect on the excited oxygen concentration due to the absence of deactivation reactions involving hydrogen-bearing components.

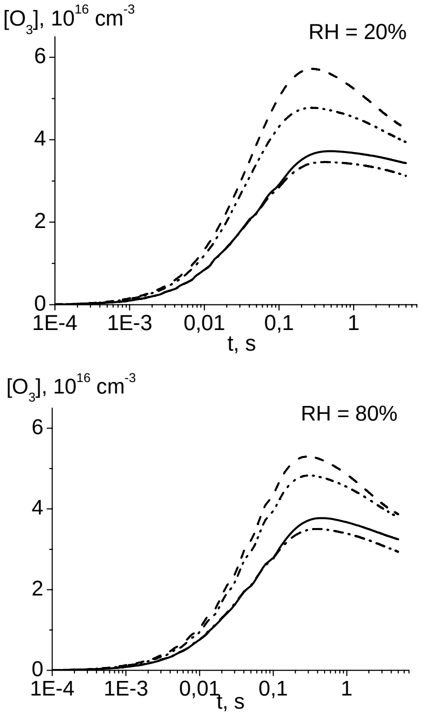

Fig. 3. Time dependences of the ozone concentration at RH =20 and 80% calculated without excited states (——), with $N_2(A)$, $N_2(B)$ (– – –), $O_2(\Delta)$, $O_2(\Sigma)$ (– · – ·) and with all nitrogen and oxygen excited states (– ·· – ··)

The influence of excited nitrogen and oxygen on the ozone density can be traced in Fig. 3. One can see that adding processes involving excited nitrogen molecules to the kinetic model leads to an increase in the ozone concentration, in spite of the process of $N_2(A)$ deactivation in collisions with ozone (reaction 1.8). The observed growth of the O_3 density may be due to the additional channels of formation of atomic oxygen (reaction 1.1, 1.15), which is the main factor in the ozone generation in the discharge.

If adding processes involving excited oxygen $O_2(\Delta)$ and $O_2(\Sigma)$ to the kinetic model, one, on the contrary, observes a decrease of the ozone concentration in the discharge. The deactivation reactions involving excited oxygen molecules do not result in the dissociation of O_2 molecules and, consequently, do not contribute to the efficient ozone formation. Besides, there are processes of direct destruction of ozone due to collisions with excited oxygen molecules (reactions 2.1 and 2.8).

In spite of some compensation of the opposite effects made by excited nitrogen and oxygen, their cumulative influence leads to an increase in the O_3 density. The rise in the humidity to 80% does not change the behavior of the studied dependences.

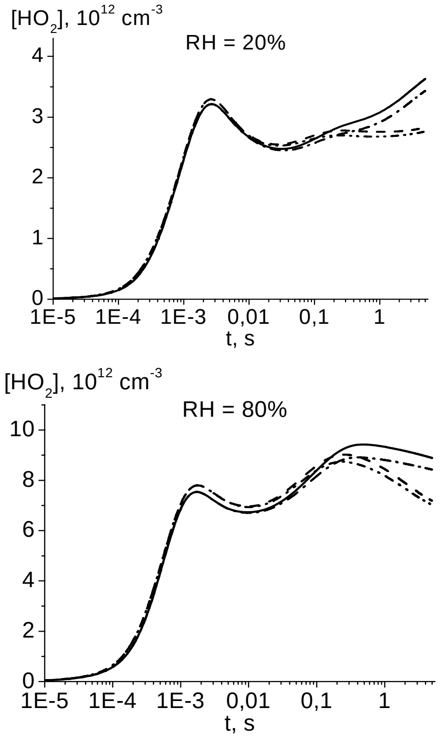

Fig. 4. Time dependences of the HO_2 concentration at RH = 20 and 80% calculated without excited states (——), with $N_2(A)$, $N_2(B)$ (– – –), $O_2(\Delta)$, $O_2(\Sigma)$ (– · – ·) and with all nitrogen and oxygen excited states (– ·· – ··)

The effect of the kinetic reactions involving excited nitrogen and oxygen on the OH concentration is negligible. Taking separately into account either excited nitrogen or oxygen leads to some increase in the OH density, but this tendency is very weak. It is worth noting that the reactions listed in Tables 1, 2 include deactivation processes of excited states in collisions with water molecules (reactions 1.9 and 2.7). Such reactions could result in the decreasing efficiency of OH generation in the discharge, but their rates are too small.

The rise in the air humidity from 20…80% leads to a growth of the absolute OH concentrations, but does not affect the behavior of their time dependence.

Fig. 4 shows the time dependences of the HO_2 concentrations calculated at humidities of 20 and 80%. One can see that taking into account either reactions involving excited nitrogen or oxygen leads to a decrease of the HO_2 concentration, moreover, this effect is more pronounced in the former case. Among the main kinetic reactions, whose competition is responsible for the form of the HO_2 time dependence, one can mark out:

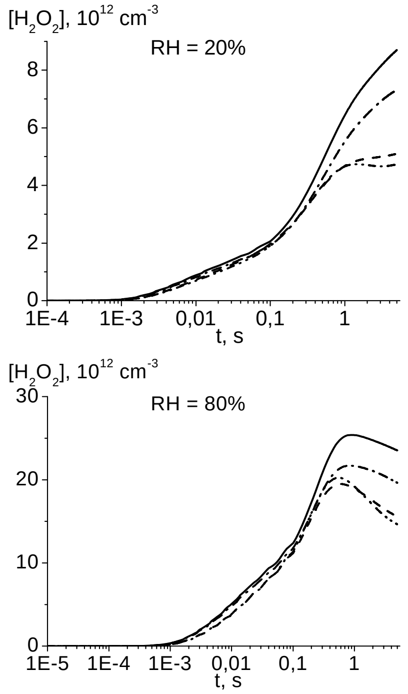

Fig. 5. Time dependences of the H_2O_2 concentration at RH = 20 and 80% calculated without excited states (——), with $N_2(A)$, $N_2(B)$ (– – –), $O_2(\Delta)$, $O_2(\Sigma)$ (– · – ·) and with all nitrogen and oxygen excited states (– ·· – ··)

1. Variations in the ozone concentration, as the most powerful process of HO_2 formation at the late discharge stages is reaction 2.16 ($OH + O_3 \rightarrow HO_2 + O_2$).

2. The influence on the concentrations of atomic oxygen and nitric oxide NO that contribute to the destruction of HO_2 in the discharge.

The form of the dependences obtained for H_2O_2 molecules (Fig. 5) coincides with that of the curves calculated for HO_2, but the quantitative effect is more pronounced as the main channel of H_2O_2 generation is reaction 2.18: $HO_2 + HO_2 + M \rightarrow H_2O_2 + O_2 + M$. The growth of the humidity in the case of both HO_2 and H_2O_2 leads to an increase in the absolute concentrations, though has no effect on the form of the dependences.

CONCLUSIONS

Calculations of the plasma kinetics in a barrier discharge in atmospheric pressure air allowed us to study the effect of excited nitrogen and oxygen states on the basic kinetic processes in the discharge. It is shown that the largest difference in the densities of derivative discharge components calculated with regard for excited states and without them is about 60% for H_2O_2 and 40% for O_3 at 20% humidity. For the rest of the components under study this difference does not exceed 20%. These values are insignificant as compared to the error introduced into calculations by uncertainties in reaction rates and cross sections of electron-molecular processes. This fact allows one to state that the neglect of reactions involving excited nitrogen and oxygen does not lead to a significant inaccuracy in calculations of the kinetics in volume discharges in atmospheric pressure air.

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ВЛИЯНИЕ ВОЗБУЖДЕННЫХ МОЛЕКУЛ $N_2(A^3\Sigma_u^+)$, $N_2(B^3\Pi_g)$, $O_2(^1\Delta_g)$ И $O_2(b^1\Sigma_g^+)$ НА КИНЕТИКУ ОЗОНА И ГИДРОКСИЛОВ (H_2O_2, OH, HO_2) В ПЛАЗМЕ БАРЬЕРНОГО РАЗРЯДА В АТМОСФЕРНОМ ВОЗДУХЕ

А.Г. Калюжная, В.В. Циолко

Рассчитана кинетика возбужденных уровней $N_2(A^3\Sigma_u^+)$, $N_2(B^3\Pi_g)$, $O_2(^1\Delta_g)$ и $O_2(b^1\Sigma_g^+)$ в барьерном разряде в воздухе и проанализировано их влияние на концентрации озона и гидроксилов OH, HO_2 и H_2O_2. Показано, что максимальное расхождение в концентрациях, полученных с учетом возбужденных состояний и без них, составляет около 60% для H_2O_2 и 40% для O_3 при влажности 20%. Варьирование влажности воздуха от 20…80% не приводит к качественному изменению поведения концентраций озона и гидроксилов в разряде.

ВПЛИВ ЗБУДЖЕНИХ МОЛЕКУЛ $N_2(A^3\Sigma_u^+)$, $N_2(B^3\Pi_g)$, $O_2(^1\Delta_g)$, $O_2(b^1\Sigma_g^+)$ НА КІНЕТИКУ ОЗОНУ ТА ГІДРОКСИЛІВ (H_2O_2, OH, HO_2) У ПЛАЗМІ БАР'ЄРНОГО РОЗРЯДУ В ПОВІТРІ АТМОСФЕРНОГО ТИСКУ

Г.Г. Калюжна, В.В. Ціолко

Проведено розрахунки кінетики збуджених станів $N_2(A^3\Sigma_u^+)$, $N_2(B^3\Pi_g)$, $O_2(^1\Delta_g)$ та $O_2(b^1\Sigma_g^+)$ у бар'єрному розряді в повітрі та проаналізовано їх вплив на концентрації озону та гідроксилів OH, HO_2 та H_2O_2. Показано, що максимальне розходження в концентраціях, отриманих із врахуванням збуджених станів та без них, становить близько 60% для H_2O_2 та 40% для O_3 при вологості 20%. Варіювання вологості в межах від 20…80% не призводить до якісної зміни поведінки концентрацій озону та гідроксилів у розряді.