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KINETIC MODEL OF SUPPRESSION OF NITROGEN OXIDES (II) FORMATION DURING COMBUSTION OF GASEOUS FUEL

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One of the common sources of oxygen-containing radicals is ozonated aqueous solutions. During the decomposition of ozone at the first stage, the formation of ozonide ($O_3^{\bullet -}$) or superoxide ($O_2^{\bullet -}$) radicals occurs, which "launch" the entire mechanism of ozone decomposition in the presence of water. Of all the known mechanisms of oxidant chemodestruction, the mechanisms proposed by Razumovsky S.D. [1] (hereinafter the first method) and Stolyarenko G.S. (hereinafter the second method) [2] are of greatest interest. The first of them describes series-parallel reactions that with a sufficient degree of probability occur in the volume of the solution with a constant supply of an ozone-air mixture, i.e. in a mixing reactor, when the primary stage is $O_3^{\bullet -}+HO^{\bullet}$. The second mechanism considered the possibilities of ozone decomposition pathways in the flow, when the solution and the ozone-air mixture move in space, i.e. in a displacement reactor. The purpose of this model, based on literature data and research results on the intensification of combustion processes, was to select from these two mechanisms the one that would correspond to the actual research results.

The yield of radicals was determined by changing the concentration of nitric oxide (II) in the flue gases. By modeling the process of formation of nitric oxide (II) before and after the introduction of radicals into the combustion zone, it is possible to calculate the theoretical values of the radical concentration in the combustion zone. By comparing the results of modeling for both mechanisms with the results of research, it is possible to establish the mechanism of the process.

Description of mathematical models. Ya.B. Zeldovich proposed a chain scheme for nitrogen oxid (II), in which free oxygen and nitrogen atoms play an active role according to reactions (1-4):

$O_2+M \rightarrow O+O+M$—494кДж/моль (chain initiation), (1)

$O+N_2 \rightarrow NO+N$ -314 кДж/ моль, (2)

$N+O_2 \rightarrow NO+0$+134 кДж/ моль, (3)

$O + O + M \rightarrow O_2 + M$ + 494 кДж/ моль (chain break). (4)

The oxygen concentration in combustion products can be determined from the empirical equation [3]:

$$C_{O_2} = 0{,}21\frac{\alpha L_o - L_o}{1+\alpha L_o},$$

where α is the excess air coefficient; L_o is the theoretically required amount of air, m^3/m^3.

The initial concentration of atomic oxygen in the flame during combustion with an excess of oxidant is given by

$$C_o^0 = [K]\sqrt{C_{O_2}},$$

where [K] is the equilibrium constant [1].

Reaction rate for each component taking into account the decomposition reaction of nitric oxide by reaction $2NO \xrightarrow{k_5} N_2 + O_2$

$$\frac{dC_{O2}}{d\tau} = 0, \quad (5)$$

$$\frac{dC_{N_2}}{d\tau} = -k_2 C_{N_2} C_O + k_5 (C_{NO})^2, \quad (6)$$

$$\frac{dC_N}{d\tau} = k_2 C_O C_{N_2} - k_3 C_N C_{O_2}, \quad (7)$$

$$\frac{dC_O}{d\tau} = C_o^0 - k_2 C_{N_2} C_O + k_3 C_N C_{O_2} - k_4 (C_O)^2, \quad (8)$$

$$\frac{dC_{NO}}{d\tau} = k_2 C_O C_{N_2} + k_3 C_{O_2} C_N - k_5 (C_{NO})^2. \quad (9)$$

Reaction rate constants k_2, k_3, k_4, k_5 according to the equations given in [5].

As can be seen from the calculations, the process under study refers to the processes that occur in small heating and industrial boilers. Thus, the ratio of "thermal" nitrogen oxides (II) to "fast" in the combustion products is approximately 1:1. The process of suppressing the formation of nitrogen oxides (II) during the combustion of gaseous fuel is based on the process of binding atomic oxygen with the $HO_2^{\bullet}$ radical by the reaction

$HO_2^{\bullet} + O^{\bullet} \xrightarrow{k_6} HO^{\bullet} + O_2$.(9)

According to the chain scheme of nitrogen oxidation proposed by Ya.B. Zeldovich, with a decrease in the concentration of atomic oxygen, the formation of nitrogen oxide (II) decreases. Then the system of equations (10-14) taking into account the radical $HO_2^{\bullet}$ will take the form

$$\frac{dC_{O2}}{d\tau} = 0, \quad (10)$$

$$\frac{dC_{N_2}}{d\tau} = -k_2 C_{N_2} C_O + k_5 (C_{NO})^2, \quad (11)$$

$$\frac{dC_N}{d\tau} = k_2 C_O C_{N_2} - k_3 C_N C_{O_2}, \quad (12)$$

$$\frac{dC_O}{d\tau} = C_o^0 - k_2 C_{N_2} C_O + k_3 C_N C_{O_2} - k_4 (C_O)^2 - k_6 C_O C_{HO_2^{\bullet}}, \quad (13)$$

$$\frac{dC_{NO}}{d\tau} = k_2 C_O C_{N_2} + k_3 C_{O_2} C_N - k_5 (C_{NO})^2 . \quad (14)$$

Let us consider each mechanism of ozone decomposition in aqueous solutions.

The first mechanism of the process of ozone decomposition in aqueous solutions is represented by the reactions:

$$O_3 + HO^- \xrightarrow{k_7} O_3^{\bullet -} + HO^\bullet, \quad (15)$$

$$O_3^{\bullet -} + H^+ \xrightarrow{k_8} HO_3^\bullet, \quad (16)$$

$$HO_3^\bullet \xrightarrow{k_9} HO^\bullet + O_2 , \quad (17)$$

$$HO^\bullet + O_3 \xrightarrow{k_{10}} HO_2^\bullet + O_2, \quad (18)$$

$$HO^\bullet + HO^- \xrightarrow{k_{11}} H_2O + O^-, \quad (19)$$

$$O^- + O_3 \xrightarrow{k_{12}} O_2^- + O_2. \quad (20)$$

Reaction rate for O_3, OH^-, $HO^\bullet$, H^+, $O_3^{\bullet -}$, $HO_2^\bullet$, $HO_3^\bullet$ taking into account the reaction $H_2O \xrightarrow{k_{13}} H^+ + HO^-$ and assuming that C_{H_2O}=1

$$\frac{dC_{O_3}}{d\tau} = 0, \quad (21)$$

$$\frac{dC_{OH^-}}{d\tau} = -k_7 C_{O_3} C_{OH^-} - k_{11} C_{OH^-} C_{HO^\bullet} - k_{13} , \quad (22)$$

$$\frac{dC_{HO^\bullet}}{d\tau} = k_7 C_{O_3} C_{OH^-} - k_{10} C_{O_3} C_{OH^-} - k_{11} C_{OH^-} C_{HO^\bullet} , \quad (23)$$

$$\frac{dC_{H^+}}{d\tau} = -k_8 C_{O_3^-} C_{H^+} + k_{13} , \quad (24)$$

$$\frac{dC_{O_3^{\bullet -}}}{d\tau} = k_7 C_{O_3} C_{OH^-} - k_8 C_{O_3^{\bullet -}} C_{H^+} , \quad (25)$$

$$\frac{dC_{HO_2^\bullet}}{d\tau} = k_{10} C_{O_3} C_{HO^\bullet} , \quad (26)$$

$$\frac{dC_{HO_3^\bullet}}{d\tau} = k_2 C_{O_3^{\bullet -}} C_{H^+} - k_9 C_{HO_3^\bullet} . \quad (27)$$

The reaction rate constants k_2, k_3, k_4, k_5 according to the equations given in [3]. The ozone concentration at the phase boundary was calculated using the expression:

$$\frac{C_0 - C}{C_0 - C_p} = 11 - \frac{6}{\pi^2} \exp(-4\pi^2 F_0') ,$$

where $F_0' = \frac{D\theta}{d^2}$ - Fourier diffusion criterion; C_0, C - initial concentration and concentration at time θ; C_p - concentration at the phase boundary.

The second mechanism of the process is presented in the reactions

$$O_3 + OH^- \xrightarrow{k_{14}} HO_2^\bullet + O_2^{\bullet -}, \quad (29)$$

$$O_2^{\bullet -} + H_2O \xrightarrow{k_{15}} HO_2^\bullet + OH^-, \quad (30)$$

$$O_3 + OH^- \xrightarrow{k_{16}} HO^\bullet + O_3^{\bullet -}, \quad (31)$$

$$HO_2^\bullet + O_3 \xrightarrow{k_{17}} HO^\bullet + 2O_2, \quad (32)$$

$$HO^\bullet + HO^\bullet \xrightarrow{k_{18}} H_2O + O^\bullet, \quad (33)$$

$$HO^\bullet + HO_2^\bullet \xrightarrow{k_{19}} H_2O + O_2, \quad (34)$$

$$HO^\bullet + O_3 \xrightarrow{k_{20}} HO_2^\bullet + O_2, \quad (35)$$

$$O_3^{\bullet -} + H_2O \xrightarrow{k_{21}} HO^- + HO^{\bullet} + O_2. \quad (36)$$

$$O^{\bullet} + HO^{\bullet} \xrightarrow{k_{22}} HO_2^{\bullet} \quad (37)$$

The reaction rate for O_3, OH^-, $HO_2^{\bullet}$, $O_2^{\bullet -}$, $HO^{\bullet}$, $O_3^{\bullet -}$, $O^{\bullet}$ assuming that C_{H_2O}=1:

$$\frac{dC_{O_3}}{d\tau} = 0, \quad (38)$$

$$\frac{dC_{OH^-}}{d\tau} = -k_{14} \cdot C_{OH^-} + k_{15} \cdot C_{O_2^{\bullet -}} - k_{16} \cdot C_{O_3} \cdot C_{OH^-} + k_{21} \cdot C_{O_3^{\bullet -}}, \quad (39)$$

$$\frac{dC_{HO_2^{\bullet}}}{d\tau} = k_{14} \cdot C_{O_3} \cdot C_{OH^-} + k_{15} \cdot C_{O_2^{\bullet -}} - k_{17} \cdot C_{HO_2^{\bullet}} \cdot C_{O_3} - k_{19} \cdot C_{HO^{\bullet}} \cdot C_{HO_2^{\bullet}} + k_{20} \cdot C_{HO^{\bullet}} \cdot C_{O_3} + k_{22} \cdot C_{HO^{\bullet}} C_{O^{\bullet}}, \quad (40)$$

$$\frac{dC_{O_2^{\bullet -}}}{d\tau} = k_{14} \cdot C_{O_3} \cdot C_{OH^-} - k_{15} \cdot C_{O_2^{\bullet -}}, \quad (41)$$

$$\frac{dC_{OH^{\bullet}}}{d\tau} = k_{16} \cdot C_{O_3} \cdot C_{OH^-} + k_{17} \cdot C_{HO_2^{\bullet}} \cdot C_{O_3} - k_{18} \cdot C^2{}_{HO^{\bullet}} - k_{19} \cdot C_{HO^{\bullet}} \cdot C_{HO_2^{\bullet -}} - k_{22} \cdot C_{HO^{\bullet}} \cdot C_{O^{\bullet}}, \quad (42)$$

$$\frac{dC_{O_3^{\bullet -}}}{d\tau} = k_{16} \cdot C_{OH^-} \cdot C_{O_3} - k_{21} \cdot C_{O_3^{\bullet -}}. \quad (43)$$

$$\frac{dC_{O^{\bullet}}}{d\tau} = k_{18} \cdot C_{OH^{\bullet}} \cdot C_{HO^{\bullet}} - k_{22} \cdot C_{O^{\bullet}} \cdot C_{HO^{\bullet}} \quad (44)$$

The reaction rate constants k_2, k_3, k_4, k_5 according to the equations given in [3].

Discussion of the results. Having solved the system of equations (5-9) by the Runge-Kut method at T=1300 K, α=1.18, Lo=8.83 m^3/m^3, C=2.8 mg/dm^3 and pH=11, the dependence of the change in the concentration of nitric oxide (II) on time was obtained, which is presented in Fig. 1. The time for the formation of the equilibrium concentration of nitric oxide (II) was taken to be 0.3 s.

Fig. 2 shows the dependence of the degree of inhibition of nitric oxides (II) formation on time by both mechanisms.

The results of solving the system of equations (5-9) are presented in Fig.3 and the results of solving the system of equations (39-44) are presented in Fig.4, the dependence of the concentration of nitric oxide (II) on time in the process of inhibiting the formation of nitric oxide with the synthesis of the radical $HO_2^{\bullet}$ according to the second mechanism is shown in Fig. 3.

As can be seen from Fig. 2, the inhibition of the formation of nitric oxide (II) with the synthesis of the radical $HO_2^{\bullet}$ by the first mechanism almost does not occur, because the concentration of the radical $HO_2^{\bullet}$ is synthesized from the radical $HO^{\bullet}$. On the other hand, the influence of the radical $HO^{\bullet}$ is impossible due to the relatively low quenching rate $HO^{\bullet} + O^{\bullet}$. In Fig. 1, the curve of the change in the concentration

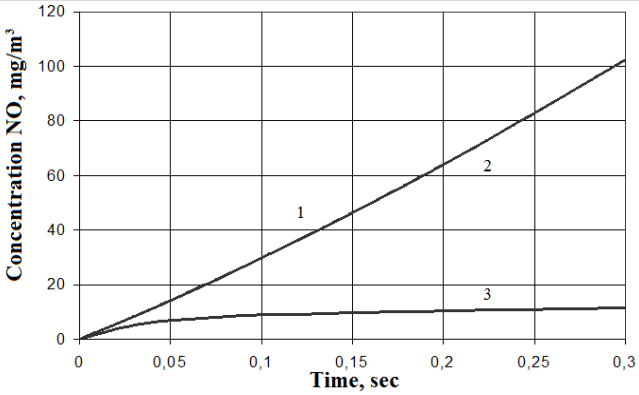

Figure 1. The time for the formation of the equilibrium concentration of nitric oxide (II) was taken to be 0.3 s.
1 – before radical conduction; 2 – according to the first mechanism, 3 – according to the second mechanism

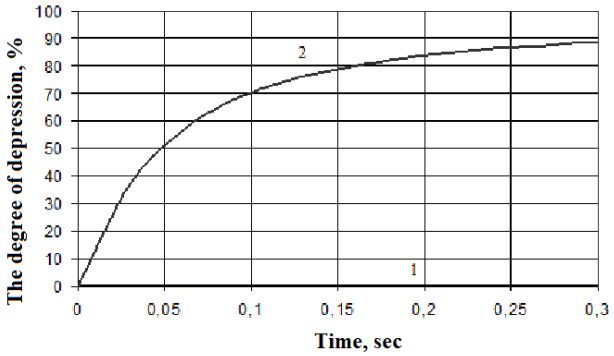

Figure 2. Dependence of the degree of inhibition of the formation of nitric oxide (II) on time.
1 – by the first mechanism; 2 – by the second mechanism

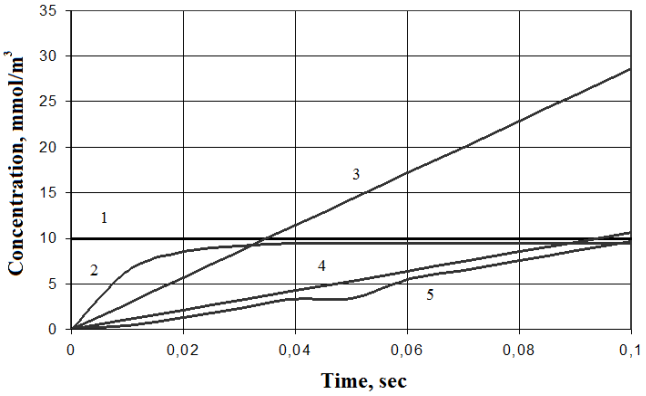

Figure 3. Dependence of changes in concentrations of substances over time according to the first mechanism
1 – $100 \cdot C_{OH^-}$; 2 – $100 \cdot C_{HO^\bullet}$; 3 – $10^6 \cdot C_{H^+}$; 4 – $10 \cdot C_{O_3^{\bullet-}}$; 5 – $1000 \cdot C_{HO_2^\bullet}$

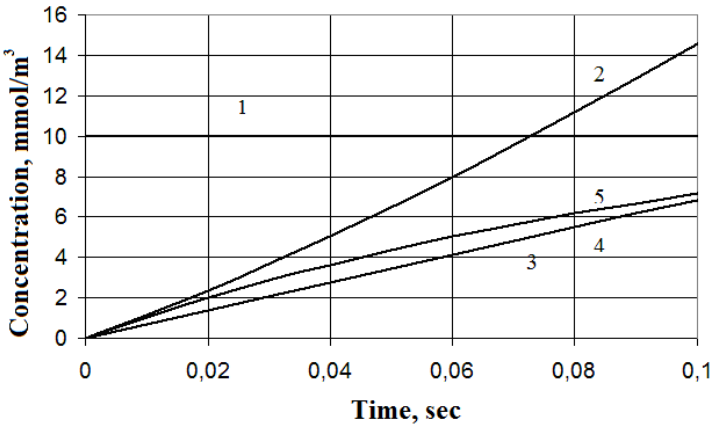

Figure 4. Dependence of changes in concentrations of substances over time according to the second mechanism

1 – 100·C_{OH^-} ; 2 –10·$C_{HO^\bullet}$; 3 – 10^6·$C_{O_2^{\bullet-}}$; 4 –100·$C_{HO_2^\bullet}$ and $C_{O_2^{\bullet-}}$; 5 – 10·$C_{O_3^{\bullet-}}$

of nitric oxides (II) over time when using the inhibition of the formation of nitric oxides (II) with the synthesis of the radical $HO_2^\bullet$ by the first mechanism coincides with the curve of the change in the concentration of nitric oxide (II) before the introduction of radicals, which also indicates a low degree of inhibition of nitric oxides (II). The inhibition of the formation of nitric oxide (II) with the synthesis of the radical $HO_2^\bullet$ by the second mechanism reaches almost 90% of the inhibition of "thermal" nitric oxides.

Comparing Fig. 3 and Fig. 4, it is seen that the yield of the radical $HO_2^\bullet$ by the first mechanism is an order of magnitude lower than the formation by the second mechanism. At the same time, the formation of the radical $HO^\bullet$ by the first mechanism is 20 times lower than by the second mechanism, and several times more ozonide radical is formed than by the second mechanism. In the first mechanism, there is no superoxide radical, which plays a significant role in the formation of oxygen radicals.

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