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## Kinetic models of ozone decomposition mechanisms in aqueous solutions as sources of oxygen-containing HO<sub>2</sub><sup>•</sup> and HO<sup>•</sup> radicals

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**Abstract.** Oxygen-containing HO<sub>2</sub><sup>•</sup> and HO<sup>•</sup> radicals are one of the most effective and environmentally friendly oxidants, one of the sources of which are ozonated aqueous solutions, the mechanism of the processes occurring in them has not yet been precisely established. The purpose of the work is to compare, to confirm or refute, mechanisms proposed by S.D. Razumovsky and H.S. Stolyarenko as the most modern ones based on the processes of suppressing the formation of “thermal” nitrogen(II) oxides during fuel combustion. For this, changes in the concentration of all compounds involved in ozone destruction processes in aqueous solutions and the effect of these compounds on the formation of “thermal” nitrogen oxides have been investigated using a kinetic mathematical model. During the study, kinetic mathematical models of the process of suppressing the formation of “thermal” nitrogen(II) oxides during fuel combustion using the process of ozone destruction in aqueous solutions have been obtained according to mechanisms proposed by S.D. Razumovsky and H.S. Stolyarenko. Based on the results of the comparison of both mechanisms, it can be stated that the mechanism of H.S. Stolyarenko more realistically reflects the process of decomposition of ozone in aqueous solutions. The dependences of changes in the concentration of substances that participate in the process of decomposition of ozone in aqueous solutions on time, as well as the amount of ozone consumed for this process have been determined. Establishing of the mechanism of ozone destruction in the same solutions and the obtained dependencies will make it possible to more freely use oxygen-containing HO<sub>2</sub><sup>•</sup> and HO<sup>•</sup> radicals, which are formed during the destruction of ozone in

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the same solutions, for the processes of gas flows cleaning, especially for their denitrification, as well as for the intensification of oxidation processes in chemical industry, for example, in the production of nitric acid

**Keywords:** hydroxyl radical; peroxide radical; destruction of ozone; nitrogen(II) oxides; oxidiser

## INTRODUCTION

In the case of chemodestruction or removal of toxic impurities from process gas streams or exhaust gases, high reactivity of chemical compounds, as well as the intensification of diffusion processes are of great importance. The use of highly reactive reagents – radicals is the most effective method of accelerating chemical processes. Oxygen-containing  $\text{HO}_2^\cdot$  and  $\text{HO}^\cdot$  radicals are found in various chemical processes: they play a significant role in the combustion of any fuel; are synthesised during the formation of ozone holes; are formed in various chemical processes in which ozone participates. The processes of synthesis of oxygen-containing  $\text{HO}_2^\cdot$  and  $\text{HO}^\cdot$  radicals during the destruction of ozone in aqueous solutions are of great interest. In most cases, the presence and high reactivity of oxygen-containing  $\text{HO}_2^\cdot$  and  $\text{HO}^\cdot$  radicals during the destruction of ozone in aqueous solutions has been experimentally proven. Ozonated aqueous solutions are one of the widespread sources of oxygen-containing radicals. However, there is still no precisely formed mechanism for this process. The decomposition of ozone in water environments has been studied for quite a long time, and already in early works attempts were made to explain its kinetics and mechanism.

The authors A.B. Murphy *et al.* (2023), F.G. Beltrán and F.J. Rivas (2023) studied and described radical mechanism of ozone decomposition in water environments, which was first proposed by D. Weiss in 1935. In the mechanism of D. Weiss, for the first-time the existence of  $\text{H}_2\text{O} - \text{O}_3$  in the system was noted for superoxide radical, the formation of which was explained by the absorption band in the blue region of the spectrum during ozonation of a 40% KOH solution at a temperature of  $-40^\circ\text{C}$ . In this mechanism, ion-radical mechanism of ozone decomposition and spontaneous interaction of radicals after their occurrence in the solution were shown. In this, the main role is given to  $\text{HO}_2^\cdot$  radical. It has been established that the absorption band in the region of 430 nm is due to the formation of  $\text{O}_3^{\cdot-}$  ozonide ion-radical under the same conditions as those used by D. Weiss.

Scientists such as A. Mojiri *et al.* (2019), W. Fan *et al.* (2020) and M. Rodríguez-Peña *et al.* (2021) in their works studied the mechanism of ozone decomposition proposed in 1950 by M. Alder and G. Hill. The scientists noted that this mechanism is more prone to neutral and acidic environments. The rate of ozone decomposition according to this mechanism is determined by the reactions of the formation of  $\text{HO}_3^\cdot$  radical and decomposition of  $\text{HO}^\cdot$  radical. The authors A.B. Murphy *et al.* (2023), as well as F.G. Beltrán and F.J. Rivas (2023), in their works described the mechanism proposed by

E. Abel in 1955. The authors noted that E. Abel tried to take into account all intermediate complex compounds that are formed according to this mechanism and are determined spectrally:  $\text{O}^\cdot-\text{O}^\cdot\text{O}^\cdot\text{OH}^\cdot$ ,  $\text{O}_2^\cdot$ ,  $\text{HO}_2^\cdot$ ,  $\text{O}^\cdot-\text{O}^\cdot\text{O}^\cdot$ ,  $\text{O}^{2-}$ . In the mechanism of E. Abel, the formation of an intermediate  $\text{O}^\cdot\text{O}^\cdot\text{O}^\cdot$  particle, which is essentially a  $\text{O}_3^{\cdot-}$  ion-ozonide radical with an electron localised on a certain oxygen atom, was proposed for the first time.

Researchers A. Mojiri *et al.* (2019) and W. Fan *et al.* (2020) in their studies, among more modern mechanisms, described the mechanism of ozone destruction in aqueous solutions proposed by S.D. Razumovsky, and the mechanism proposed by H.S. Stolyarenko (2021; 2023). However, both of these mechanisms due to short existence time of compounds participating in the process (existence time is  $10^{-4}$ - $10^{-5}$  s) and therefore the impossibility of determining them by analytical methods, have not received exact confirmation or refutation.

The purpose of this study was to theoretically confirm the mechanism of ozone decomposition in aqueous solutions based on laboratory studies of suppressing the formation of “thermal” nitrogen oxides during the combustion of gaseous fuel using ozonated solutions and to create kinetic models of the investigated process based on the mechanisms of ozone destruction in aqueous solutions, proposed by S.D. Razumovsky, and the mechanism, proposed by H.S. Stolyarenko. For this purpose, the following tasks were set:

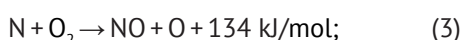
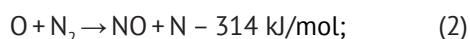
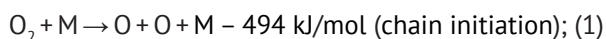
- to investigate the process of suppressing the formation of “thermal” nitrogen oxides during the combustion of gaseous fuel using ozonated solutions;
- to develop kinetic mathematical models based on the results of research into the process of ozone destruction in jet streams of aqueous solutions.

## MATERIALS AND METHODS

Two mechanisms have been singled out, for which kinetic mathematical models were compiled and solved: the mechanism proposed by S.D. Razumovsky (Mojiri *et al.*, 2019; Fan *et al.*, 2020) (hereinafter the first method) and the mechanism proposed by H.S. Stolyarenko (2021; 2023) (hereinafter the second method). The purpose of this mathematical model, based on literature data and the results of studies of the intensification of combustion processes, is to select from these two mechanisms the one that would correspond to real results of the studies. Research on the intensification of combustion process consists in the use of oxygen radicals to suppress the formation of “thermal” nitrogen oxides during the combustion of gaseous fuel. The results of these researches are compared with the

results of mathematical modelling and it is determined which of the two mechanisms best corresponds to the ongoing process.

The exit of radicals is determined by changing the concentration of "thermal" nitrogen(II) oxide in flue gases. By simulating the process of the formation of "thermal" nitrogen(II) oxide before and after the introduction of radicals into the combustion zone, it is possible to calculate theoretical values of the concentration of the radical in the combustion zone. By comparing the results of modelling by both mechanisms with the results of research, the mechanism of the process can be established. In laboratory studies, the degree of suppression of the formation of nitrogen(II) oxides is achieved by 80% (Stolyarenko, 2023). Ya.B. Zeldovich proposed a chain scheme of nitrogen(II) oxidation, in which free oxygen and nitrogen atoms play an active role according to reactions (1-2) (Cellek, 2022; Gao, 2022):



The concentration of oxygen in combustion products can be determined from the empirical equation (Cellek, 2022; Gao, 2022)

$$CO_2 = 0.21 \frac{\alpha L_o - L_o}{1 + \alpha L_o}, \quad (5)$$

where  $\alpha$  is the coefficient of excess air;  $L_o$  is theoretically necessary amount of air,  $m^3/m^3$ .

Initial concentration of atomic oxygen in the flame during the combustion with an excess of oxidiser according to the formula:

$$C_o^0 = [K] \sqrt{C_{O_2}}, \quad (6)$$

where  $[K]$  is the equilibrium constant (Cellek, 2022; Gao, 2022).

$$[K] = 1,3 \cdot 10^4 \exp\left(-\frac{61000}{RT}\right). \quad (7)$$

The reaction rate for each component taking into account the decomposition reaction of nitrogen oxide according to the reaction  $2NO \xrightarrow{k_5} N_2 + O_2$ :

$$\frac{dC_{O_2}}{d\tau} = 0; \quad (8)$$

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

$$\frac{dC_N}{d\tau} = k_2 C_O C_{N_2} - k_3 C_N C_{O_2}; \quad (10)$$

$$\frac{dC_O}{d\tau} = C_o^0 - k_2 C_{N_2} C_O + k_3 C_N C_{O_2} - k_4 (C_O)^2; \quad (11)$$

$$\frac{dC_{NO}}{d\tau} = k_2 C_O C_{N_2} + k_3 C_{O_2} C_N - k_5 (C_{NO})^2. \quad (12)$$

Reaction rate constants  $k_2, k_3, k_4, k_5$  according to equations (Surl *et al.*, 2021; Cellek, 2022; Gao, 2022):

$$k_2 = 5,01 \cdot 10^{13} \exp\left(-\frac{316500}{RT}\right); \quad (13)$$

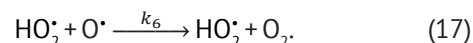
$$k_3 = 3,8 \cdot 10^{13} \exp\left(-\frac{33500}{RT}\right); \quad (14)$$

$$k_4 = 11039 \sqrt{T}; \quad (15)$$

$$k_5 = 3 \cdot 10^6 \exp\left(-\frac{385000}{RT}\right). \quad (16)$$

Solving the system of equations (8-12) by the Runge-Kutta method at  $T=1300\text{K}, \alpha=1.18, L_o=8.83\text{m}^3/\text{m}^3, CO_3=2.8\text{mg}/\text{dm}^3$  and  $pH=11$ , the dependence of the change in the concentration of nitrogen(II) oxide on time is obtained (Chauhan & Srivastava, 2019; Ince *et al.*, 2021). The formation time of the equilibrium concentration of nitrogen(II) oxide is taken to be 0.3 s.

The process of suppressing the formation of nitrogen(II) oxide during the combustion of gaseous fuel is based on the process of binding of atomic oxygen by  $HO_2^{\cdot}$  radical according to the reaction (Ragupathi *et al.*, 2023)



According to the chain scheme of nitrogen oxidation, proposed by Ya.B. Zeldovich, the formation of nitrogen(II) oxide decreases with a decrease in the concentration of atomic oxygen. Then the system of equations taking into account  $HO_2^{\cdot}$  radical will take the form (18-22):

$$\frac{dC_{O_2}}{d\tau} = 0; \quad (18)$$

$$\frac{dC_{N_2}}{d\tau} = -k_2 C_{N_2} C_O + k_5 (C_{NO})^2; \quad (19)$$

$$\frac{dC_N}{d\tau} = k_2 C_O C_{N_2} - k_3 C_N C_{O_2}; \quad (20)$$

$$\frac{dC_O}{d\tau} = C_o^0 - k_2 C_{N_2} C_O + k_3 C_N C_{O_2} - k_4 (C_O)^2 - k_6 C_O C_{HO_2^{\cdot}}; \quad (21)$$

$$\frac{dC_{NO}}{d\tau} = k_2 C_O C_{N_2} + k_3 C_{O_2} C_N - k_5 (C_{NO})^2. \quad (22)$$

Each mechanism of ozone decomposition in aqueous solutions is considered. The first mechanism of ozone decomposition process in aqueous solutions is presented in reactions (23-29). Reaction rate for  $O_3, OH^-, HO^{\cdot}, H^+, O_3^{\cdot}, HO_2^{\cdot}, HO_3^{\cdot}$  taking into account the reaction  $H_2O \xrightarrow{k_{13}} H^{\cdot} + HO^{\cdot}$  and assuming that  $CH_2O=1$ :

$$\frac{dC_{O_3}}{d\tau} = 0; \quad (23)$$

$$\frac{dC_{OH^-}}{d\tau} = -k_7 C_{O_3} C_{OH^-} - k_{11} C_{OH^-} C_{HO^{\cdot}} - k_{13}; \quad (24)$$

$$\frac{dC_{HO^{\cdot}}}{d\tau} = k_7 C_{O_3} C_{OH^-} - k_{10} C_{O_3} C_{OH^-} - k_{11} C_{OH^-} C_{HO^{\cdot}}; \quad (25)$$

$$\frac{dC_{H^+}}{d\tau} = -k_8 C_{O_3^-} C_{H^+} + k_{13}; \quad (26)$$

$$\frac{dC_{O_3^{\bullet-}}}{d\tau} = k_7 C_{O_3} C_{OH^-} - k_8 C_{O_3^-} C_{H^+}; \quad (27)$$

$$\frac{dC_{HO_2^{\bullet}}}{d\tau} = k_{10} C_{O_3} C_{HO^{\bullet}}; \quad (28)$$

$$\frac{dC_{HO_3^{\bullet}}}{d\tau} = k_2 C_{O_3^{\bullet-}} C_{H^+} - k_9 C_{HO_3^{\bullet}}; \quad (29)$$

Reaction rate constants:  $k_7 = 1.9 \cdot 10^5$ ,  $k_8 = 1.9 \cdot 10^5$ ,  $k_9 = 1 \cdot 10^7$ ,  $k_{10} = 2 \cdot 10^8$ ,  $k_{11} = 1.8 \cdot 10^5$ ,  $k_{12} = 3 \cdot 10^5$ ,  $k_{13} = 2.86 \cdot 10^{-4} s^{-1}$  (Feinberg, 2019; Tan *et al.*, 2019; Liu *et al.*, 2023). The concentration of ozone at the phase boundary is calculated according to the expression (Stolyarenko, 2023):

$$\frac{C_0 - C}{C_0 - C_p} = 11 - \frac{6}{\pi^2} \exp(-4\pi^2 F_0'), \quad (30)$$

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

## RESULTS AND DISCUSSION

The idea of using a kinetic mathematical model to confirm or disprove one or another mechanism of ozone decomposition in aqueous solutions belongs to the authors of this article. This article presents the results of these studies without comparison with the results of other researchers, which are presented in this form for the first time.

Reaction rate for  $O_3$ ,  $OH^-$ ,  $HO_2^{\bullet}$ ,  $O_2^{\bullet-}$ ,  $HO^{\bullet}$ ,  $O_3^-$ ,  $O^{\bullet}$  assuming that  $CH_2O = 1$ :

$$\frac{dC_{O_3}}{d\tau} = 0; \quad (31)$$

$$\frac{dC_{OH^-}}{d\tau} = -k_{14} \cdot C_{OH^-} + k_{15} \cdot C_{O_2^{\bullet-}} - k_{16} \cdot C_{O_3} \cdot C_{OH^-} + k_{21} \cdot C_{O_3^{\bullet-}}; \quad (32)$$

$$\frac{dC_{HO_2^{\bullet}}}{d\tau} = k_{14} \cdot C_{O_3} \cdot C_{OH^-} + k_{15} \cdot C_{O_2^{\bullet-}} - k_{17} \cdot C_{HO_2^{\bullet}} \cdot C_{O_3} - k_{19} \cdot C_{HO^{\bullet}} \cdot C_{HO_2^{\bullet}} + k_{20} \cdot C_{HO^{\bullet}} \cdot C_{O_3} + k_{22} \cdot C_{HO^{\bullet}} \cdot C_{O^{\bullet}}; \quad (33)$$

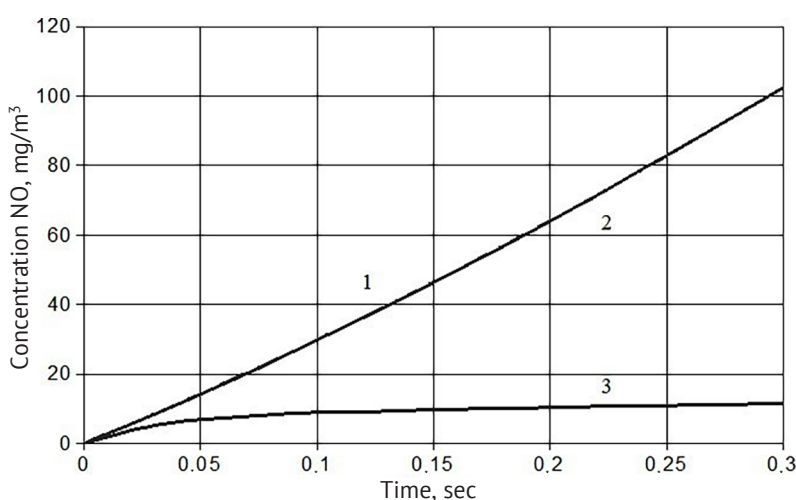
$$\frac{dC_{O_2^{\bullet-}}}{d\tau} = k_{14} \cdot C_{O_3} \cdot C_{OH^-} - k_{15} \cdot C_{O_2^{\bullet-}}; \quad (34)$$

$$\frac{dC_{OH^{\bullet}}}{d\tau} = k_{16} \cdot C_{O_3} \cdot C_{OH^-} + k_{17} \cdot C_{HO_2^{\bullet}} \cdot C_{O_3} - k_{18} \cdot C_{HO^{\bullet}}^2 - k_{19} \cdot C_{HO^{\bullet}} \cdot C_{HO_2^{\bullet}} - k_{22} \cdot C_{HO^{\bullet}} \cdot C_{O^{\bullet}}; \quad (35)$$

$$\frac{dC_{O_3^{\bullet-}}}{d\tau} = k_{16} \cdot C_{OH^-} \cdot C_{O_3} - k_{21} \cdot C_{O_3^{\bullet-}}; \quad (36)$$

$$\frac{dC_{O^{\bullet}}}{d\tau} = k_{18} \cdot C_{OH^{\bullet}} \cdot C_{HO^{\bullet}} - k_{22} \cdot C_{O^{\bullet}} \cdot C_{HO^{\bullet}}. \quad (37)$$

Reaction rate constants:  $k_{14} = 1.2 \cdot 10^4$ ,  $k_{15} = 1.2 \cdot 10^4$ ,  $k_{16} = 1.9 \cdot 10^5$ ,  $k_{17} = 8.4 \cdot 10^6$ ,  $k_{18} = 6.67 \cdot 10^{10}$ ,  $k_{19} = 7.5 \cdot 10^{12}$ ,  $k_{20} = 2 \cdot 10^8$ ,  $k_{21} = 9.05 \cdot 10^{11}$ ,  $k_{22} = 1.99 \cdot 10^{12} s^{-1}$  (Tan *et al.*, 2019; Murphy *et al.*, 2023). As a result of calculating the system of equations (23-29) and substituting the obtained concentration of  $HO_2^{\bullet}$  radical into the system (18-22), the dependence of the concentration of nitrogen(II) oxide on time in the process of suppressing the formation of nitrogen(II) oxide with the synthesis of  $HO_2^{\bullet}$  radical according to the first mechanism is established (Fig. 1). The results of solving the system of equations (31-37) are presented in Figure 1, the dependence of the concentration of nitrogen(II) oxide on time in the process of suppressing the formation of nitrogen oxide with the synthesis of  $HO_2^{\bullet}$  radical according to the second mechanism is also shown in Figure 1.



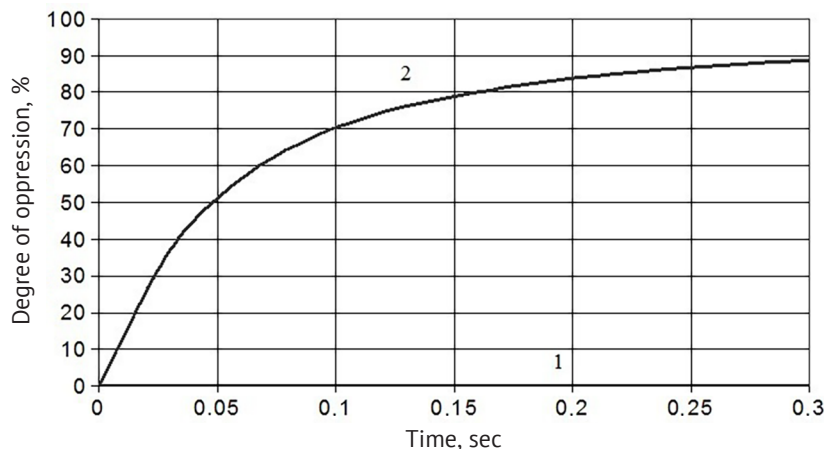
**Figure 1.** Dependence of the formation of nitrogen(II) oxide on time

**Notes:** 1 – before the introduction of radicals; 2 – according to the first mechanism; 3 – according to the second mechanism

**Source:** compiled by the authors based on compilation and solution of kinetic mathematical models of the ozone destruction process in aqueous solutions

Figure 2 shows the dependence of the degree of suppressing the formation of nitrogen(II) oxide on time by both mechanisms. The results of the calculation of

the system of equations (23-29) are presented in Figure 2. The second process mechanism is presented in reactions (1-5).



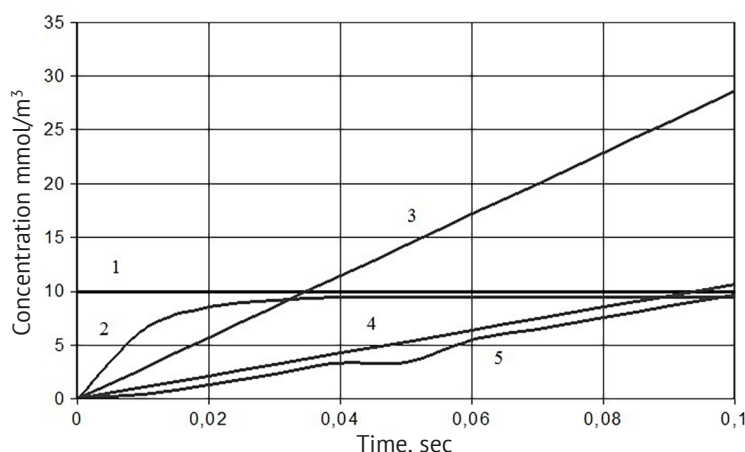
**Figure 2.** Dependence of the degree of suppressing the formation of nitrogen(II) oxide on time

**Notes:** 1 – according to the first mechanism; 2 – according to the second mechanism

**Source:** compiled by the authors based on compilation and solution of kinetic mathematical models of the ozone destruction process in aqueous solutions

As can be seen from Figure 2, suppression of the formation of nitrogen(II) oxide with the synthesis of  $HO_2^{\cdot}$  radical by the first mechanism almost does not occur, because the concentration of  $HO_2^{\cdot}$  radical is synthesised from  $HO^{\cdot}$  radical. On the other hand, the influence of  $HO^{\cdot}$  radical is impossible due to relatively low quenching rate of  $HO^{\cdot} + O^{\cdot}$ . In Figure 1, the curve of the change in the concentration of nitrogen(II) oxide over time when using suppression of the formation of nitrogen(II) oxide with the synthesis of  $HO_2^{\cdot}$  radical

according to the first mechanism coincides with the curve of the change in the concentration of nitrogen(II) oxide before the introduction of radicals, which also indicates a low degree suppression of nitrogen(II) oxide. Suppression of the formation of nitrogen(II) oxide with the synthesis of  $HO_2^{\cdot}$  radical by the second mechanism reaches almost 80% of the suppression of “thermal” oxides. Figure 3 shows the dependences obtained for the main compounds of the investigated process according to the first mechanism.



**Figure 3.** Dependence of changes in concentrations of substances over time according to the first mechanism

**Notes:** 1 – 100°C<sub>OH</sub>; 2 – 100°C<sub>HO</sub>; 3 – 10<sup>6</sup>°C<sub>H</sub>; 4 – 10 · C<sub>O<sub>3</sub></sub>; 5 – 1000 · C<sub>HO<sub>2</sub></sub>

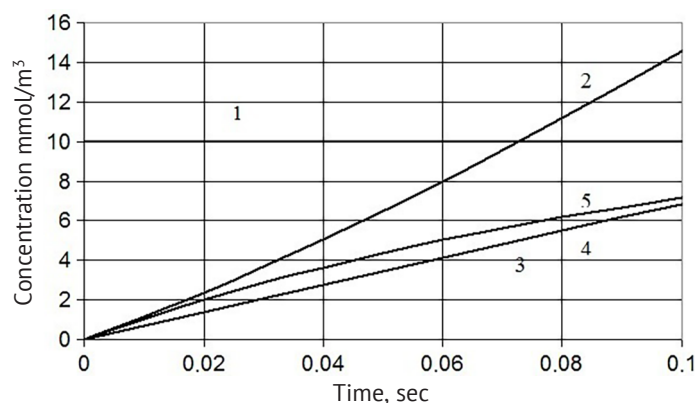
**Source:** compiled by the authors based on compilation and solution of kinetic mathematical models of the ozone destruction process in aqueous solutions

The exit of  $HO_2^{\cdot}$  radical according to the second mechanism is much higher than by the previous one (Fig. 4). Comparison of Figure 3 and Figure 4 shows that

the exit of  $HO_2^{\cdot}$  radical by the first mechanism is an order of magnitude lower than the formation by the second mechanism. At the same time, the formation of  $HO^{\cdot}$

radical according to the first mechanism is 20 times lower than according to the second mechanism, and several times more ozonide radical is formed than according

to the second mechanism. In the first mechanism, there is no superoxide radical, which plays an essential role in the formation of oxygen-containing radicals.



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

**Notes:** 1 –  $100^{\circ}\text{COH}^-$ ; 2 –  $10 \cdot \text{CHO}_2^-$ ; 3 –  $10^{6^{\circ}}\text{CO}_2^-$ ; 4 –  $100 \cdot \text{CHO}_2^-$  (coincides with  $\text{CO}_2^-$ ); 5 –  $10\text{CO}_3^-$

**Source:** compiled by the authors based on compilation and solution of kinetic mathematical models of the ozone destruction process in aqueous solutions

Due to the fact that only the concentration of “thermal” nitrogen(II) oxides decreases and the concentration of “fast” nitrogen(II) oxides remains constant, it is impossible to achieve 100% suppression. Thus, the results of the experiments on suppression of the formation of nitrogen(II) oxides, given in Table 1, and the

results of the simulation of the process of suppressing the formation of nitrogen(II) oxide are adequate. It can be concluded that the second mechanism of  $\text{HO}_2^-$  radical synthesis more realistically reflects the processes that take place during the decomposition of ozone with increasing pH of the solution.

**Table 1.** Ozone concentration after passing through alkaline solutions at a contact time,  $\tau=0.06$  s

OAM costs, $\text{dm}^3/\text{min}$	Ozone concentration, $\text{mg}/\text{dm}^3$			
	0.1 n	0.01 n	0.001 n	To the solution
0.5	2.5	2.55	2.61	2.8
1	1.6	2.3	2.35	2.4
2	1.7	1.9	1.95	2.1

**Source:** compiled by the authors based on G.S. Stolyarenko (2023)

Based on the data given in Tables 1-3, the dependence of the change in the concentration of  $\text{HO}_2^-$  and  $\text{HO}^{\cdot}$

radicals on time for a 0.1 n solution is calculated at different ozone-air mixture (OAM) rates.

**Table 2.** Ozone concentration after passing through alkaline solutions at a contact time,  $\tau=0.12$  s

OAM costs, $\text{dm}^3/\text{min}$	Ozone concentration, $\text{mg}/\text{dm}^3$			
	0.1 n	0.01 n	0.001 n	To the solution
0.5	2.5	2.6	2.8	2.8
1	2.0	2.05	2.1	2.4
2	1.65	1.85	2.0	2.1

**Source:** compiled by the authors based on G.S. Stolyarenko (2023)

**Table 3.** Ozone concentration after passing through alkaline solutions at a contact time,  $\tau=0.18$  s

OAM costs, $\text{dm}^3/\text{min}$	Ozone concentration, $\text{mg}/\text{dm}^3$			
	0.1 n	0.01 n	0.001 n	To the solution
0.5	2.3	2.6	2.7	2.8
1	1.6	2.25	2.28	2.4
2	1.55	1.8	1.9	2.1

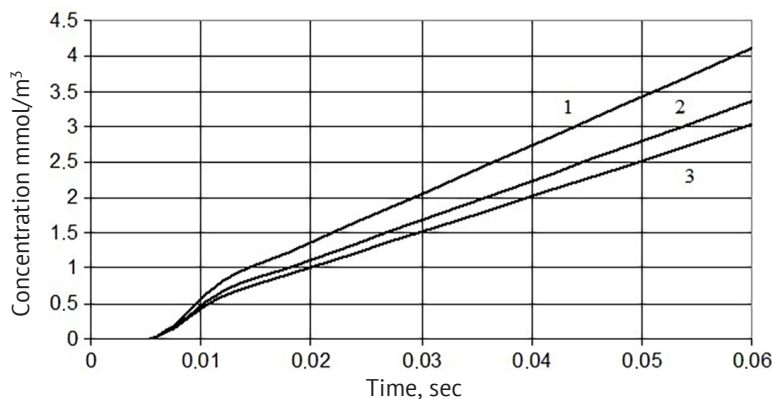
**Source:** compiled by the authors based on G.S. Stolyarenko (2023)



Figure 5 illustrates the formation of  $\text{HO}_2^\bullet$  radical at a specific time point, with the time parameter denoted as  $t=0.06$  s. This graph provides a snapshot of the concentration of  $\text{HO}_2^\bullet$  radical at this precise moment during the reaction or process under consideration.

The figure captures a moment in the kinetic process, allowing for a focused analysis of radical formation at the specified time of 0.06 s. The shape and trajectory

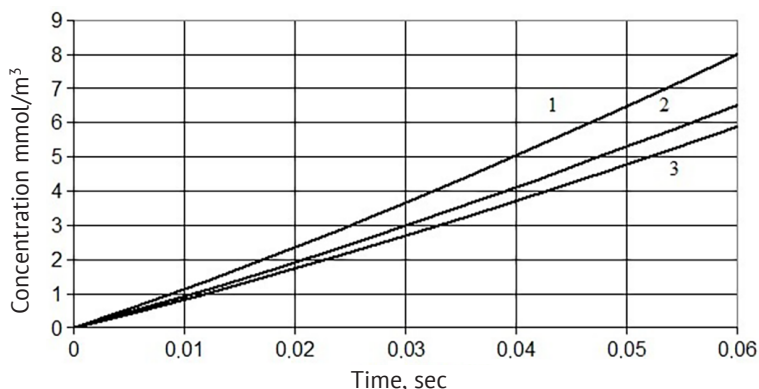
of the curves in Figure 5 convey information about the rate of radical formation or depletion at this particular time instance. Upon examining Figure 6, an analysis of the behaviour of  $\text{HO}_2^\bullet$  radical at the specific time instance is possible. The features observed, including the curve's shape, its slope, and any distinctive patterns present, provide valuable insights into the rate of radical formation or depletion during this particular period.



**Figure 5.** Formation of  $\text{HO}_2^\bullet$  radical,  $t=0.06$  s

**Notes:** 1 – OAM consumption is  $0.5 \text{ dm}^3/\text{min}$ ; 2 – OAM consumption is  $1 \text{ dm}^3/\text{min}$ ; 3 – OAM consumption is  $2 \text{ dm}^3/\text{min}$

**Source:** compiled by the authors based on compilation and solution of kinetic mathematical models of the ozone destruction process in aqueous solutions



**Figure 6.** Formation of  $\text{HO}_2^\bullet$  radical,  $\tau=0.12$  s

**Notes:** 1 – OAM consumption is  $0.5 \text{ dm}^3/\text{min}$ ; 2 – OAM consumption is  $1 \text{ dm}^3/\text{min}$ ; 3 – OAM consumption is  $2 \text{ dm}^3/\text{min}$

**Source:** compiled by the authors based on compilation and solution of kinetic mathematical models of the ozone destruction process in aqueous solutions

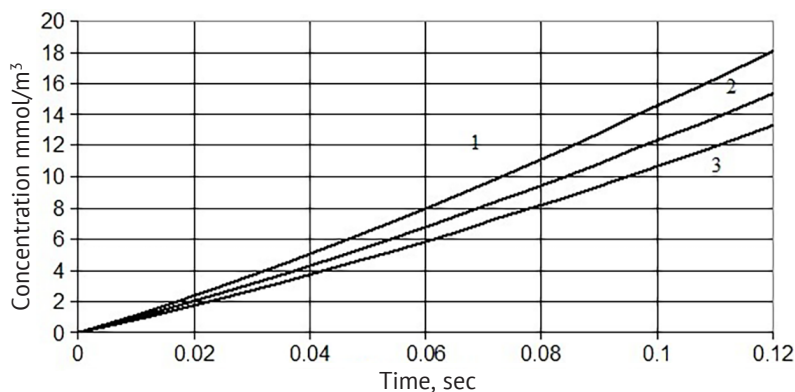
Figure 7 illustrates the formation of  $\text{HO}^\bullet$  radical at a specific time. The analysis of Figure 7 enables to examine the behaviour of  $\text{HO}^\bullet$  radical precisely at the time point  $\tau=0.12$  s. The features of the graph, including the curve's shape, its slope, and any distinctive patterns, provide valuable information regarding the rate of radical formation or depletion during this particular time segment.

In Figure 8, the graphs depict the relationships governing the formation of oxygen-containing radicals at different contact times, using kinetic mathematical models to describe the underlying processes. A similar trend is observed in Figure 9, where the concentration varies linearly with the contact time.

Figures 5-8 show the dependences of the formation of oxygen-containing radicals at different contact times according to kinetic mathematical models. As can be seen from Figures 5, 7, 8, the change in the concentration of  $\text{HO}_2^\bullet$  radical is linear and the time of the reaction almost does not affect the course of radical formation. The same is observed in Figures 7 and 9 for  $\text{HO}^\bullet$  radical. The concentration of  $\text{HO}^\bullet$  radical itself is an order of magnitude higher than the concentration of  $\text{HO}_2^\bullet$  radical. The issue of ozone decomposition in aqueous solutions has been discussed in the literature for a long time. Competitive kinetics and scavenging assay are commonly used for radical quantification.

However, the accuracy of the two methods has been challenged in electrochemical advanced oxidation processes since the strong reactivity of electrode

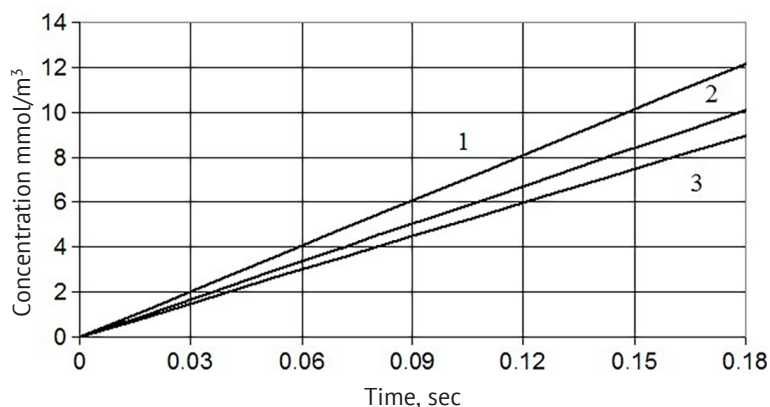
against organic indicators may disrupt the quantitative relationship between indicator consumption and radical concentration.



**Figure 7.** Formation of  $\text{HO}^\bullet$  radical,  $\tau = 0.12$  s

**Notes:** 1 – OAM consumption is  $0.5 \text{ dm}^3/\text{min}$ ; 2 – OAM consumption is  $1 \text{ dm}^3/\text{min}$ ; 3 – OAM consumption is  $2 \text{ dm}^3/\text{min}$

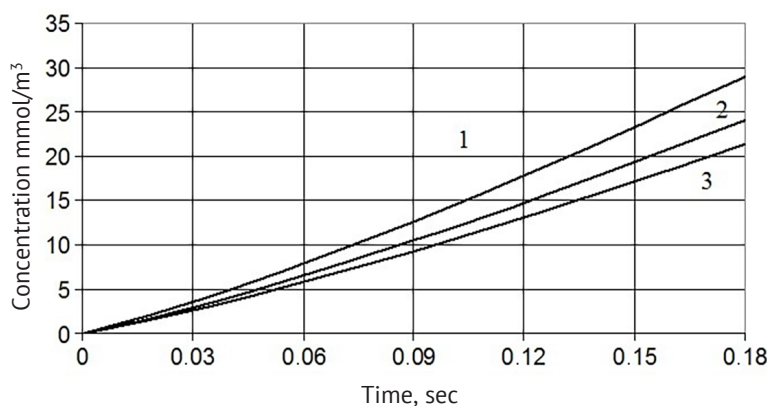
**Source:** compiled by the authors based on compilation and solution of kinetic mathematical models of the ozone destruction process in aqueous solutions



**Figure 8.** Formation of  $\text{HO}_2^\bullet$  radical,  $\tau = 0.18$  s

**Notes:** 1 – OAM consumption is  $0.5 \text{ dm}^3/\text{min}$ ; 2 – OAM consumption is  $1 \text{ dm}^3/\text{min}$ ; 3 – OAM consumption is  $2 \text{ dm}^3/\text{min}$

**Source:** compiled by the authors based on compilation and solution of kinetic mathematical models of the ozone destruction process in aqueous solutions



**Figure 9.** Formation of  $\text{HO}^\bullet$  radical at  $\tau = 0.18$  s

**Notes:** 1 – OAM consumption is  $0.5 \text{ dm}^3/\text{min}$ ; 2 – OAM consumption is  $1 \text{ dm}^3/\text{min}$ ; 3 – OAM consumption is  $2 \text{ dm}^3/\text{min}$

**Source:** compiled by the authors based on compilation and solution of kinetic mathematical models of the ozone destruction process in aqueous solutions



Authors S.Q. Yang *et al.* (2020) in the study focused on screening suitable indicators and developing suitable methods for determining steady-state concentrations of  $\text{SO}_4^{\cdot-}$  and  $\text{HO}^{\cdot}$  ( $\text{SO}_4^{\cdot-}$ ) and  $\text{HO}^{\cdot}$  in several EAOPs (Electrochemical Advanced Oxidation Processes) for water treatment based on competitive kinetics and scavenging assay. The applicability of modified methods and available indicators were investigated through experimental and kinetic analysis. Only in anodic process, the competitive kinetics was more appropriate than scavenging assay and benzoic acid met the basic requirement of being a competitor to determine the  $\text{HO}^{\cdot}$ . In the work of M. Nambari *et al.* (2021), a great role was given to the ozone decomposition process. But their attention was paid to catalytic decomposition. The catalytic decomposition approach showed higher efficiency and higher durability with no generation of considerable by-products, particularly manganese oxide ( $\text{MnOx}$ ) based catalysts, which can decompose ozone to oxygen at room temperature.

Researchers M. Whiteside and J.M. Herndon (2022) in their study paid attention to the catalytic effect of various compounds on the destruction of ozone. But in this work, iron is considered as a catalyst. Iron in primary and secondary aerosols plays a crucial role in the formation of ice crystals in cirrus clouds and in polar stratospheric clouds that are involved in the formation of ozone holes. Iron is associated with reactive oxygen species, like  $\text{HO}^{\cdot}$  hydroxyl radical that destroys ozone in the stratosphere. Iron is known to activate halogens including chlorine, bromine, and iodine.

Authors Y. Wang *et al.* (2021) attributed an important role to the formation of oxygen-containing radicals. But there, more attention was paid to the process of fluorescence assay by gas expansion of these radicals and no attention was paid to other compounds. E.R. Jans *et al.* (2022) also attributed a great role to the processes of the formation of  $\text{HO}_2^{\cdot}$  radical in diluted mixtures of  $\text{H}_2$  of  $\text{O}_2^-$  Ar single bond,  $\text{CH}_4$  of  $\text{O}_2^-$  Ar single bond, and  $\text{C}_2\text{H}_4$  of  $\text{O}_2^-$  Ar single bond excited by a repeated ns pulse discharge in a heated plasma flow reactor, measured by Cavity Ringdown Spectroscopy, a kinetic model was created. But there, more attention was paid to the process of the formation of  $\text{HO}_2^{\cdot}$  radical and how other compounds of ozone decomposition in the same solutions were not considered in the previous work. In the study of H. Zhang *et al.* (2021), the authors paid attention to the influence of external factors such as ultrasound on the destruction of ozone in the process of wastewater treatment, which also took into account the processes of ozone destruction, but with additional influence of ultrasound. This greatly accelerated the process of wastewater treatment.

However, all of them are based on the results of chemical and instrumental analysis of compounds involved in the process under investigation. As already mentioned, all these compounds exist for a very short time (hundredths and thousandths of a second), they

instantly change into one another, and even with modern methods it is impossible to claim with great confidence that one or another compound has been analysed and their concentrations are precisely determined. For this reason, it is proposed to use a fundamentally new approach to research the mechanism of ozone destruction in aqueous solutions, such as kinetic mathematical models, which allow to determine the concentrations and time of appearance of all necessary compounds using a mathematical apparatus and the results of laboratory studies of processes that are well studied and the main thing is that it is possible to accurately analyse the formation of compounds by chemical and instrumental methods.

## CONCLUSIONS

Oxygen-containing  $\text{HO}^{\cdot}$  and  $\text{HO}_2^{\cdot}$  radicals occur in various chemical processes. The ozonation of aqueous solutions is one of the common sources of oxygen-containing radicals. But until this moment there is no precisely formed mechanism of this process due to its very fast course and short existence time of most of compounds that take part in it. There are many mechanisms of decomposition of ozone in aqueous solutions. All of them contain  $\text{HO}^{\cdot}$  and  $\text{HO}_2^{\cdot}$  radicals, but each mechanism has a different role. The presence of other radicals has been proven in all mechanisms. Even in D. Weiss's mechanism, the presence of superoxide radical was proven using spectral analysis. In some mechanisms (for example, E. Abel's mechanism), the authors try to take into account complex compounds formed during the decomposition of ozone and determined spectrally. Among the more modern mechanisms of ozone destruction in aqueous solutions, there are mechanisms proposed by S.D. Razumovsky and H.S. Stolyarenko.

To establish the detailed mechanism of these reactions, kinetic mathematical models were compiled and solved. With the help of mathematical models, it is established that the formation of nitrogen(II) oxides when using the first mechanism almost coincides with the formation without the introduction of radicals into the fuel-air mixture. This indicates that this mechanism of ozone decomposition does not provide such an amount of oxygen-containing radicals, which is necessary for the degree of suppressing the formation of nitrogen(II) oxides. According to experimental data, the formation of nitrogen(II) oxides when using the second method is significantly less than without the introduction of radicals. The degree of suppressing the formation of nitrogen(II) oxides, obtained in the mathematical model and experimentally, is almost the same. It is established that the degree of suppressing the formation of nitrogen(II) oxides by both mechanisms is very different. According to the first mechanism, it is no more than 1%, which is very different from the experimental data, while according to the second mechanism, the degree of suppression almost coincides with the experimental data.

Based on all of the above, it can be stated that the second mechanism more realistically reflects the process of decomposition of ozone in aqueous solutions. Based on the results of mathematical modelling, time dependences of changes in the concentration of substances that participate in the decomposition of ozone in aqueous solutions have been established. The obtained results of research on the determination of the mechanism of ozone destruction in aqueous solutions will allow this process to be more widely used in chemical industry in the future as a source of environmentally friendly oxidants, which are oxygen-containing radicals. Using a kinetic model of the ozone destruction process in aqueous solutions, it is possible to determine more accurate concentrations of oxygen-containing radicals at any moment of the process, which in turn allows to design equipment (for example, injection systems) for the intensification of oxidation processes when obtaining various chemical compounds and purifying gaseous flows.

Perspective areas of research in the chosen topic are: the study of detailed reaction mechanisms and ways of decomposition of ozone in aqueous solutions; the study of the influence of environmental factors such as temperature, pH, and the presence of other chemicals on the kinetics of ozone decomposition. They also include the study of catalytic effect of certain ions or compounds in aqueous solutions on the ozone decomposition process; the use of quantum chemical calculations to complement experimental data, as well as the development of dynamic system models that consider the interaction between ozone decomposition, the formation of radicals, and other relevant chemical processes, etc.

#### ACKNOWLEDGEMENTS

None.

#### CONFLICT OF INTEREST

None.

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## Кінетичні моделі механізмів розкладу озону у водних розчинах як джерел кисневмісних радикалів $\text{HO}_2^\bullet$ і $\text{HO}^\bullet$

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**Анотація.** Оксигеновмісні радикали  $\text{HO}_2^\bullet$  і  $\text{HO}^\bullet$  є одними з найефективніших і екологічно чистих окисників, одним з джерел яких є озоновані водні розчини, механізм процесів, що відбуваються в них, дотепер точно не встановлений. Мета роботи – порівняти, підтвердити або спростувати механізми, запропоновані С. Д. Разумовським та Г. С. Столяренком як найбільш сучасні, що базуються на процесах пригнічення утворення «термічних» оксидів нітрогену(II) під час спалювання палива. Для цього за допомогою кінетичної математичної моделі досліджено зміну концентрації всіх сполук, що беруть участь у процесах озоноруйнування, у водних розчинах та вплив цих сполук на утворення «термічних» оксидів азоту. В ході дослідження отримано кінетичні математичні моделі процесу пригнічення утворення «термічних» оксидів нітрогену(II) при спалюванні палива з використанням процесу деструкції озону у водних розчинах за механізмами, запропонованими С. Д. Разумовським та Г. С. Столяренком. За результатами порівняння обох механізмів можна стверджувати, що механізм Г. С. Столяренка більш реалістично відображає процес розкладання озону у водних розчинах. Визначено залежності зміни концентрації речовин, які беруть участь у процесі розкладу озону у водних розчинах, від часу, а також кількості озону, що витрачається на цей процес. Встановлення механізму руйнування озону в цих же розчинах і отримані залежності дозволять більш вільно використовувати кисневмісні радикали  $\text{HO}_2^\bullet$  і  $\text{HO}^\bullet$ , які утворюються при руйнуванні озону в цих же розчинах, для процесів очищення газових потоків, особливо для їх денітрифікації, а також для інтенсифікації окислювальних процесів у хімічній промисловості, наприклад, у виробництві азотної кислоти

**Ключові слова:** гідроксильний радикал; пероксидний радикал; руйнування озону; нітроген(II) оксиди; окислювач