



Review Article

Development the Theory of Chain Reactions and Analysis of Relatively Recently Studied Chain Processes

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Abstract: The history of the formation and development of the theory of chain reactions is briefly presented. In specific examples the mechanisms of branched chain processes, conditions inhibiting and accelerating chain reactions, criteria characterizing the chain nature of chemical processes are described. The modern state in the development of the theory of chain reactions is analyzed. The mechanisms describing regularities of formation of molecular products of the chain processes occurring in different systems with the use of different initiators at different conditions are discussed. A summary of the radical-chain character of the radiation sewing of elastomers /non stitched rubbers/ at high pressures (2 GPa) and at temperatures above 300°K is provided and the ionic character of this process at low temperatures (77°K) has been studied. Mechanisms of photolytic and radiolytic processes transformations of any organic pollutants and natural toxins in oxygen-free and oxygen-containing aqueous solutions are proposed. Significant decomposition of natural toxins is observed under influence of ionizing radiation of ⁶⁰Co source. The short description of the revealed chain processes proceeding in gaseous, liquid, amorphous and solid phases is provided. These studies are an essential contribution to researches in the field of studying of chain chemical processes.

Keywords: Theory of Chain Reactions, Active Centers, Initiation of Chain Reactions, Photolytic and Radiolytic Conversion, Gas-Phase Mixtures, Water Solutions

1. Introduction

Experimental and theoretical prerequisites of creation of the theory of chain reactions were observation of unusual chemical processes in various gas mixes, a luminescence of vapors of phosphorus in oxygen-containing mixes with various pressure and repayment of this luminescence in the presence of sulfur particles, combustion of hydrogen with explosion, influence of foreign impurity (methane, nitrous oxide, hydrogen sulfide, ethylene, catalysts), temperatures, pressure, a form and material of vessels on the speed of reactions, the photochemical chain reaction of formation of hydrogen chloride in a gaseous phase [1].

Created during the periods empirical (since the end of the 17th century before the beginning of the 19th century), empirical-theoretical (since the beginning of the 19th century to the 70th years of the 19th century) and systematic studying of gas mixes (since the end of the 19th century before the

beginning of the 20th century) experimental and theoretical prerequisites have formed a basis for development of the theory of chain reactions [2].

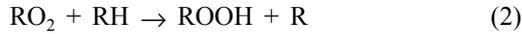
2. Formation and Development of the Fundamental Theory of Chain Reactions

In contrast to the theory of energy chains in 1918 for the first time described the radical-chain nature of the reaction of formation of hydrogen chloride in the gaseous phase, the active centers of which are chlorine and hydrogen atoms [3].

Influence of the size of a reactionary vessel and material of a wall, presence of foreign substances – inhibitors on the rate of chain reaction, neutralization of the active centers, break of a reactionary chain was studied in 1931-1933 and the theory of chain reactions with a degenerate branching of chains has been

put forward for an explanation of kinetic regularities of oxidation of hydrocarbons [4].

Hydroperoxides are formed approximately up to 200°C in the bimolecular reactions of chain continuation:



Along with hydroperoxide, aldehydes are formed by the monomolecular reaction at higher temperatures:



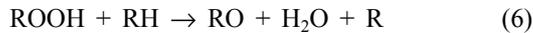
Aldehydes lead to branching of the chain at high temperatures:



During gas-phase oxidation with increasing temperature and a decrease in the concentration of the oxidizing substance, the rate of isomerization and monomolecular decomposition of hydroperoxides increases with the formation of radicals, leading to a degenerate branching of the chain [5]:



In addition to the monomolecular decomposition, the bimolecular interaction of the hydroperoxide with the oxidizing substance and the degenerate branching of the chain occurs in the liquid phase:



According to N. N. Semenov, this reaction of interaction between two saturated molecules is energetically more favorable than the monomolecular decomposition of hydroperoxide molecules on free radicals [5].

In L. Bateman and E. T. Denisov's works are shown that at sufficient formation in system the hydroperoxides, their decomposition takes place along bimolecular mechanism and this interaction is facilitated by the preliminary association of hydroperoxide molecules by the formation of a hydrogen bond between them. In the oxidation of olefins, hydroperoxides react

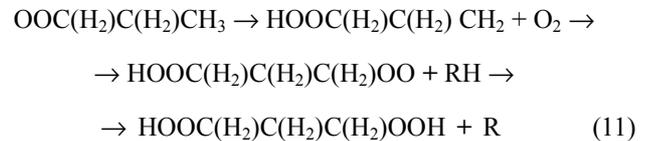
with a double bond and form RO' and olefin radicals [6]:



Formed in a stage of initiation radicals react with the molecules of initial substances and provide continuation of a chain. At oxidation of organic substances, the chain is continued by reactions:



These reactions proceed in a liquid phase very quickly and practically without energy of activation. The continuation of the chain at solid-state oxidation of polymers occurs by a relay mechanism [6]:



The reaction of connection of radicals with oxygen molecules in polymers are slowed down due to diffusive difficulties and continuation of a chain thus is carried out by reaction:



The appreciable amounts of low-molecular products of oxidation which are present in the polymeric matrix play an important role in the continuation of the chain. Break of chains happens at a mutual recombination of the active centers (atoms, radicals, ions), and also at interaction of the active centers with the wall or with inhibitors. Kinetic curves the dividing areas of catalytic oxidation of hydrogen and area of ignition of stoichiometric mix of hydrogen with oxygen (the branched-chain oxidation regime of hydrogen, studied by C. N. Hinshelwood and N. N. Semenov) are given in the Figure 1.

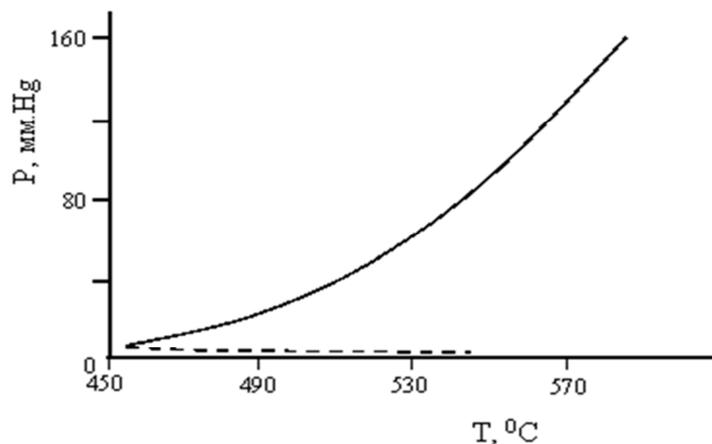


Figure 1. Area of ignition (branched-chain process of oxidation) of stoichiometric mixture of hydrogen and oxygen.

At temperatures above 460°C at very low pressures (several mmHg) and at pressures lying above the upper curve, and at temperatures below 450°C for any values of pressure of mixture a slow catalytic oxidation process is observed. The branched-chain oxidation process (ignition) observed only in the internal area of two crossed curves. The curves are characterized by the equality of the branching speed and speed

of break of a chain. The pressure values lying above the upper curve are exponentially dependent on E and T ($p = \text{const. } e^{-(E/RT)}$, p - the total pressure of the mixture on a limit of ignition, E = 18 kcal/mol, and T - absolute temperature). Similar curves for mixtures of hydrocarbons with oxygen are shown in Figure 2.

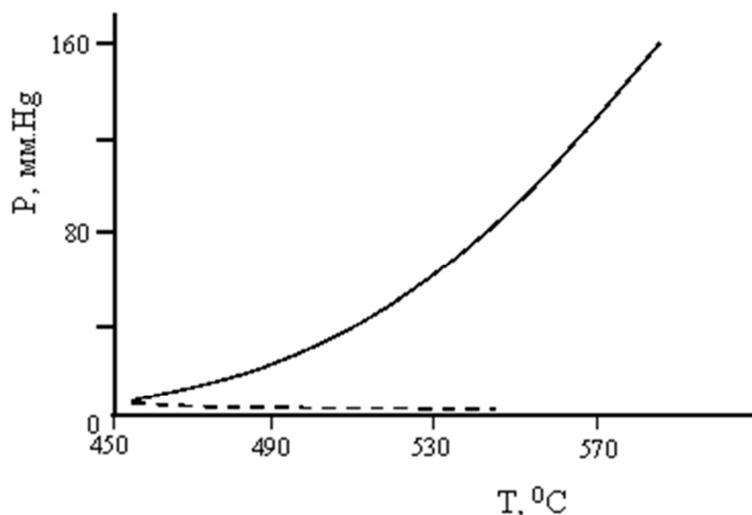
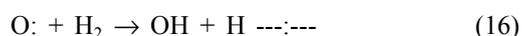
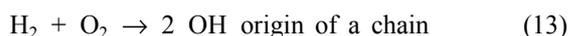


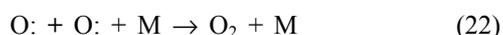
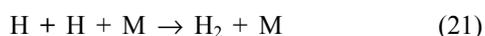
Figure 2. Areas of ignition of mixtures of hydrocarbons with oxygen.

Note: 1 - 15% of methane in air, a quartz vessel;
2 - 1,8% of heksan in air, a glass vessel;
3 - 1,8% of heksan in air, a steel vessel;
4 - 2,6% isobutane in air, a steel vessel.

The limits of ignition of gaseous hydrogen and carbon monoxide and the mechanism of the course of these processes have been studied [4], [6]:



In the further to the reaction scheme, for gas-phase chain processes have been included the reactions of atomic oxygen with a hydrocarbon and the tri-molecular chain termination reactions:



The conditions for transition from the stationary regime to

the ignition mode (see Figure 1) are determined by the equation:

$$2 k_2[\text{O}_2] - (k_4 + k_6[\text{O}_2][\text{M}]) = 0 \quad (23)$$

At temperatures significantly much higher than the temperature of the cape, the values of the first (P_1) and second (P_2) limiting pressures are determined by the equations:

$$P_1 = k_4/2k_2\gamma \quad (24)$$

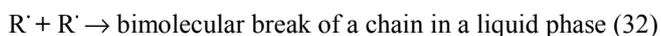
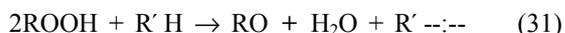
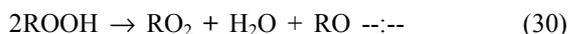
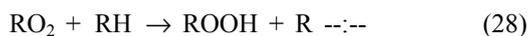
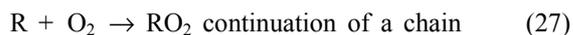
- where γ - molar fraction of oxygen,

$$P_2 = 2k_2/2k_6 \quad (25)$$

The following sequence of conversion of products during the oxidation of organic substances "hydrocarbon - hydroperoxide - alcohols or acids" are determined in the fifties of the twentieth century by N. M. Emanuel [4]. The formed hydroperoxides besides transformation into alcohols, directly or through a stage of formation of ketones are converted into organic acids.

Radical and ionic chain polymerization processes were studied and a principal scheme for the liquid-phase oxidation of organic substances was developed in the second half of the last century [6]:





The last reaction of this scheme is usually a bimolecular reaction of breaking the chain process in the liquid phase, since the value of the rate constant of this reaction is much larger (greater) than rate constant of reaction of hydroperoxide with the organic compound (RH). Intermediate molecular products are formed at oxidation of organic compounds. These products break up in further to free radicals, forming new chains and accelerating the general process. Therefore, process oxidation of organic substances is chemical process with a degenerate branching of a chain. The criteria for estimating chain and branched chain processes have been studied [1], [6].

For the solution of this question it is necessary in each case to consider all obtained experimental data. In most cases, the rate of chain reactions depends on the high and changeable concentrations of the reacting substances, have a varying order. However, non-chain complex reactions can have such characteristics.

Non-chain complex reactions, like chain reactions, can have a velocity dependence on the diameter and material of the reaction vessel and the presence of an inert gas in it. Sometimes, there are undeniable criteria that unequivocally prove the chain nature of the process, such as large quantum or radiation-chemical yields, respectively photochemical and radiation-chemical processes, as well as the presence of regions of chain or degenerate-chain processes [1], [6].

3. A New Stage in the Development of the Theory of Chain Reactions

Studies for the detection and creation of chemical lasers based on partial or complete inversion on the vibrational-rotational levels of molecules, as well as the studies for a laser effect in chain reactions actively conducted in the second half of the 20th century and was synthesized organic substances containing simultaneously two trivalent carbon atoms - organic biradicals, similar fatty series compounds of unsaturated ketones with metals, stable nitroxide radicals - organic paramagnetic substances [4], [7]. Often reacting these substances don't lose free valences and are used as spin traps of marked active components in the most various areas of physical and chemical researches (in chemical kinetics, studying of the mechanism of chain processes, for

researches by application of EPR, etc.) and also in medicine (development of diagnostics methods, antitumor drugs, etc.) [4], [7].

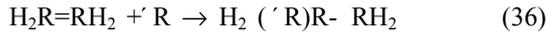
The processes of conversion of carbon monoxide to molecular hydrogen were developed in the second half of the 20th century. Conversion of carbon monoxide with water vapor ($CO + 3H_2 + H_2O \rightarrow CO_2 + 4H_2 + 41 \text{ kJ}$) at 370-440°C is carried out in the presence of an iron-chromium catalyst and at 230-260°C in the presence of a zinc-chromium-copper catalyst. A chain reaction of the conversion of carbon monoxide to molecular hydrogen by radiolysis of a mixture of CO-H₂O was also studied [8].

Classification of amorphous elastomers /non stitched rubbers/ (phase transition of the elastomer to a structurally solid state, i.e., freezing of an amorphous structure) or crystallization (a first-order jump-like phase transition accompanied by streamlining of macromolecules) depending on temperature occurs at high pressures with all-round compression. Radiation-chemical radical-chain processes of elastomer's sewing at high pressures were studied and developed at the branch of the Scientific Research Physical-Chemical institute named after L. Y. Karpov [9].

A stationary radiation research facility with an isotope ⁶⁰Co (absorbed dose rate equal to 0.3 Gy/s ($2 \cdot 10^{15} \text{ eV/g}\cdot\text{s}$) was used as the source of gamma radiation for our experiments. The radiation-chemical yield of sewing of hydrocarbon chains in elastomers was determined by the method of "ash-gel analysis" (extraction in the extractor with hot cyclic-hexane and determination of the vacuum-dried ash fraction) and calculated by the equation of Charlesby-Pinner. Studies of compounds containing electrons with unpaired spins were carried out using the electronic paramagnetic resonance P3-1301 spectrometer, the identification of organic compounds was carried out by IR-spectroscopy (Specord-IR, "Carl-Zeiss"). Radically-chain processes of radiation sewing of natural, synthetic methyl-butadiene, butadiene-nitrile and butadiene-styrene elastomers were studied using the above-described experimental base and known technique (irradiation of 0.2-1.0 cm³ volume of elastomers /in a thick-walled metal vessel with a double wall, inside which a high pressure is created by the hydraulic press/ by doses 10-100 kGy of ionizing radiation). The value of the radiation-chemical yield of sewing chains in these elastomers at normal conditions (1atm, 300°K) respectively was 3-20, at pressure 2 GPa and 300°K was 15-150, at 2 GPa and 450°K was 30-250 stitches/100 eV.

Irradiation of elastomers at high pressures ensured the almost complete sewing of all hydrocarbon chains in elastomers and the formation of a single mass (polymer) resistant to physical effects, friction and irradiation. Increase of above properties with increasing of temperature at high pressures was occurs. As can be seen, in the examples of studied elastomers, radical-chain sewing of hydrocarbon chains was observed, despite the reduction in the formation of radicals with increasing of pressure.





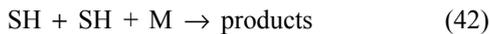
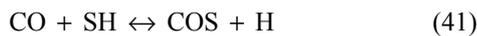
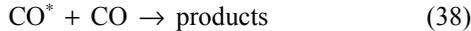
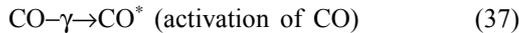
The chain sewing process acquires an ionic character in sewed elastomers at high pressures and low temperatures (77°K), in the EPR spectra of these irradiated and sewed polymers at low temperatures thin /hyperfine/ structures are observed.

4. Description of the Revealed New Chain Processes

The chain reaction of the conversion of molecular hydrogen to carbon monoxide was studied at the Institute of Radiation Problems of the National Academy of Sciences of Azerbaijan in 1984 [10].

Further, decomposition of carbonyl sulfide (COS), radiation-chemical and photochemical transformations in gas-phase systems CO - H₂S, H₂S - CH₄, H₂S - CO₂, H₂S - CH₄ - O₂ were studied at different temperatures. The mechanisms of the radiolytic and photolytic chain processes of transformations in gas-phase systems CO + H₂S → H₂ + COS (H₂ + CO + S + CO₂ + CS₂), H₂S + O₂ → H₂ + SO₂ (H₂ + S_n + H₂S₂ + H₂O + SO₃ + H₂SO₄) are compiled [11].

The following mechanism of course of process describing regularities of formation of molecular products is offered for CO - H₂S system:



The values for the rate constants of reactions (40) and (-41) are given in the literature ($k_{40} = 9 \times 10^9 \times e^{-850/T} \text{ M}^{-1}\text{s}^{-1}$, $k_{-41} = 5,5 \times 10^9 \times e^{-1925/T} \text{ M}^{-1}\text{s}^{-1}$) [12].

Using the thermodynamic data for the reaction components and the Vant Hoff equation ($\Delta G = -RT \ln K$) for the equilibrium between the forward and backward reactions ($k_{-40} = 5,5 \times 10^9 \times e^{-62500/RT} \text{ M}^{-1}\text{s}^{-1}$, $k_{41} = 2,5 \times 10^7 \times e^{-63800/RT} \text{ M}^{-1}\text{s}^{-1}$) we obtain for the corresponding backward reactions.

Using the variation's intervals of rate constants of the forward and backward reactions we obtain for the ratio of (5) and (-4) reaction rates:

$$W_{41}/W_{-40} = (0.4 \text{ -} \text{ } 2.2) \times 10^{-2} [\text{CO}]/[\text{H}_2] \quad (47).$$

Hence, it is easy to estimate stationary concentration of hydrogen, which does not exceed 2.2% of the initial amount of carbon monoxide in the mix CO-H₂S:

$$[\text{H}_2]_{\text{stationary}} = (0.4\text{-}2.2) \times 10^{-2} [\text{CO}] \quad (48).$$

The dependence of the temperature on the absorbed dose rate is obtained from the conditions for the equality of the rates of radiolytic generation and termination of active centers, as well as the equality of the speed of the chain's termination and continuation at equilibrium, i.e. when reaching the stationary concentrations of the initial and final components of reaction ($W_i = G_o \cdot J \cdot 10^{-2} = W_{\text{break}} = k_{\text{break}} \cdot [\text{SH}]^2 \cdot [\text{M}] = W_{\text{contin.chain}} = k_{41} \cdot [\text{SH}] \cdot [\text{CO}]$; $k_{41} = 2.5 \cdot 10^7 \cdot e^{-63800/RT} \cdot [\text{SH}] \cdot [\text{CO}]$):

$$T = (-Ea^{\text{cont.chain}}/R) / (\ln((k_{\text{break}} \cdot [\text{M}] \cdot G_o \cdot 10^{-2})^{1/2} / (k_o^{\text{cont.chain}} \cdot [\text{CO}])) + \ln J) \quad (49)$$

where: J – power of the absorbed dose in system, eV/sm³.s (1Gy/s = 7.8·10¹² eV/sm³.s);

$$G_o = 7; k_{\text{break}} = k_6 \quad (50)$$

$$k_o^{\text{cont.chain}} = k_{38}^o \quad (51)$$

The dependence of temperature on the absorbed dose rate is also obtained from the conditions for the equality of the rates of radiolytic and thermal generation of active centers ($W_{\text{generator}} = G_o \cdot J \cdot 10^{-2} = W_{\text{thermo.gener.}} = k_{40}^o \cdot e^{-Ea}/RT \cdot [\text{H}_2\text{S}] \cdot [\text{M}]$; $k_{40} = 2 \cdot 10^{11} \cdot e^{-37290/T} \text{ M}^{-1}\text{s}^{-1}$):

$$T = (-Ea/R) / (\ln(G_o \cdot 10^{-2} / (k_o \cdot [\text{H}_2\text{S}] \cdot [\text{M}])) + \ln J) \quad (52)$$

where: $k_o = k_{40}^o$.

The dependence of the absorbed dose rate (at which this chain process is realized) on the temperature at different concentration of initial components of CO-H₂S mixture, calculated on the condition that the rates of radiolytic generation and termination of active centers (lower curves) are equal and if the rates of radiolytic and thermal generation of active centers are equal (upper curves) are given on 3 and 4 figures.

The area below the lower curves characterize the zone of exclusively radiation initiation of reaction (CO + H₂S → COS + H₂) proceeding in not chain mode. The area inside the lower and upper curve characterize the zone of predominantly radiation initiation of the reaction, proceeding in chain mode, the area above the upper curve characterize the zone of predominantly thermal initiation of the reaction proceeding in chain mode.

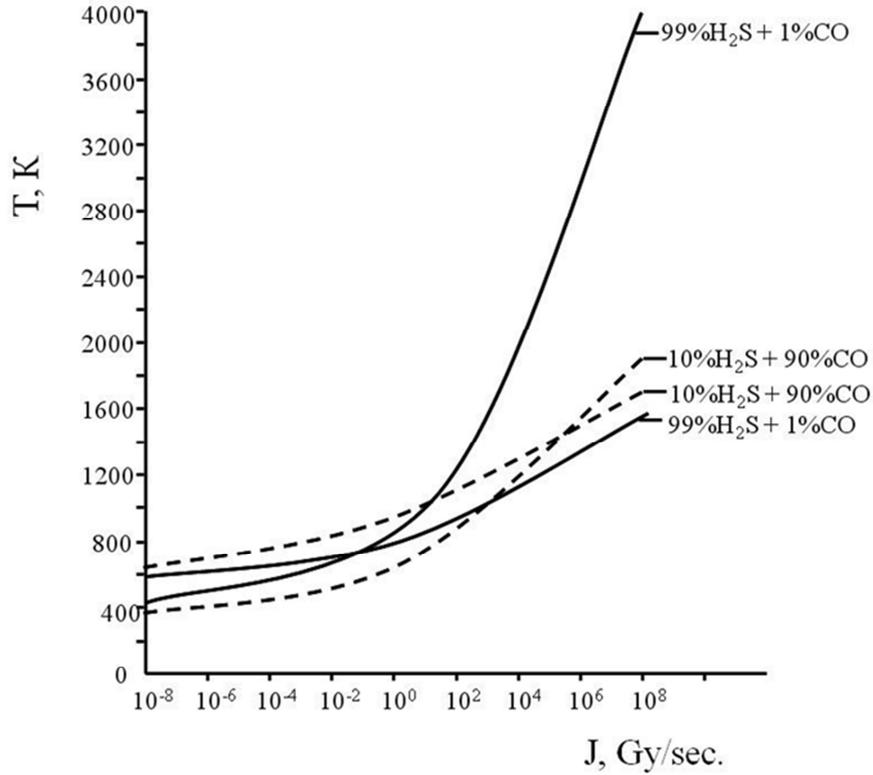


Figure 3. The curves of the dependence of the absorbed in the mixtures of CO (90%)-H₂S (10%) and CO (1%) - H₂S (99%) dose rate from the temperature.

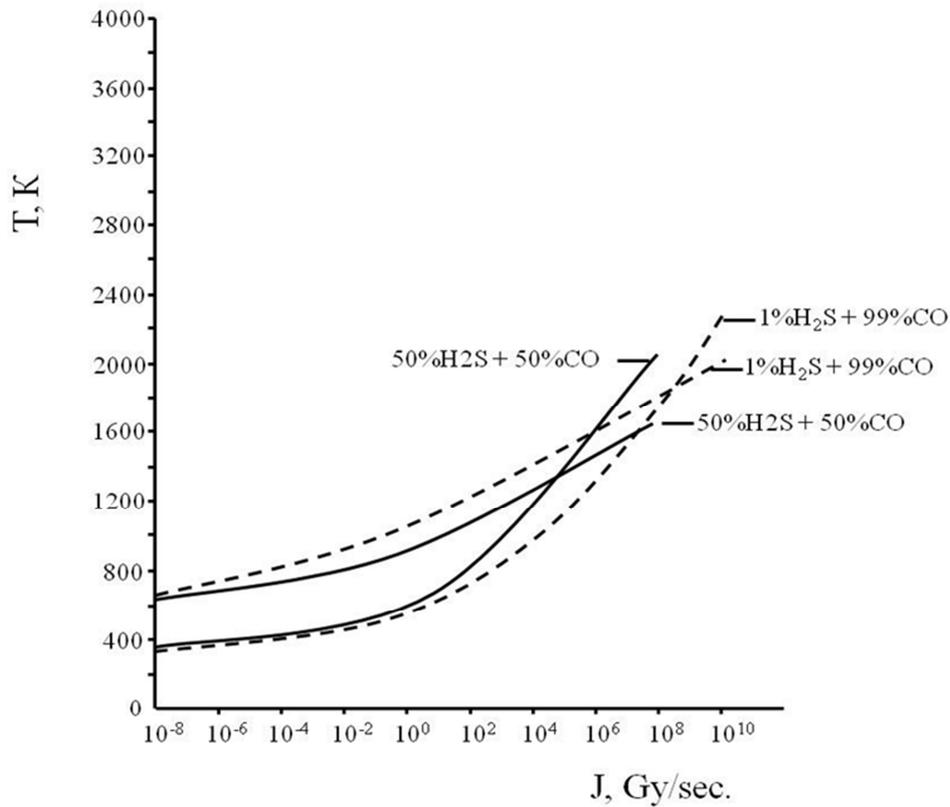


Figure 4. Curve dependence of the absorbed in the mixtures CO(99%)-H₂S(1%) and CO(50%)-H₂S(50%).

Note: - the radiation initiation of the not chain process (areas below the lower curves),
 - the predominantly the thermal initiation of the chain process (areas above the upper curves),
 - the predominantly radiation initiation of the chain process (area between the upper and lower curves).

The areas of predominantly radiation initiation of chain transformation processes with different ratios of the initial components allow us to choose the optimal conditions for carrying out these processes, depending on the existing type and form of the radiation-chemical installation, the dose rate of ionizing radiation emitted by a specific type of installation.

In the future, on the basis of the study of thermodynamic data of elementary reactions of photolytic and radiolytic processes taking place in oxygen-free and oxygen-containing aqueous solutions of phenol, the kinetic regularities of the formation of reaction products, detailed and satisfactorily describing the experimental results mechanisms of photolytic and radiolytic processes taking place in oxygen-free and oxygen-containing aqueous solutions of phenol are proposed. It has been established that photolytic and radiolytic processes acquire a chain character in oxygen-containing solutions of phenol. At photolytic processing treatment of oxygen-containing aqueous solutions, the final products of the photolytic chain process are phenol polymerization products and consequently the process of photolytic treatment of oxygen-containing water solutions of phenol is an efficient technological process. The main products of radiolytic processes are hydroxy-substituted phenols (hydroquinone, pyrocatechol, hydroxy-hydroquinone, resorcinol, floroglucin). Mechanisms of photolytic and radiolytic processes describing transformations in oxygen-free and oxygen-containing aqueous solutions of phenol are compiled [13].

We used the studied photolytic and radiolytic processes to develop highly efficient chain processes for the decomposition of natural toxins that contaminate plant products. The kinetics of destruction of natural toxins in cereals, dried fruits and granulated forages under the influence of UV-light and ionizing radiation of ^{60}Co has been studied [11], [14].

Consumer and organoleptic properties, microbiological, physical and chemical parameters of the irradiated vegetable products and goods didn't worsen after radiation by a dose 2.5 kJ/kg of UF-light.

However, at the same time completeness of a detoxification, i.e. suppression of toxic properties of toxins of microscopic fungi (mycotoxins), complete conversion of toxins into non-toxic compounds or reduction of their concentrations to values below of maximum allowable concentration - isn't reached. The effective quantum yields of conversion of mycotoxins in water solutions are on average 2 times higher than in dry plant products.

The effective quantum yields of transformation of mycotoxins in damp vegetable products have intermediate values between these two values. The effective quantum yields of conversion of mycotoxin increase on the average by 2-3 times at the air bubbling of water solutions of mycotoxins. The main channels for the photolytic conversion of mycotoxins are the formation of their hydroxyl-replaced derivatives, organic peroxides and dimerization by oxygen bridges.

The possibility of radiolytic decomposition of mycotoxins

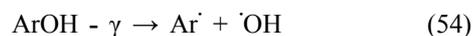
synthesized by microorganisms, i.e. the dependence decrease of mycotoxin quantity from the absorbed dose has been studied. Existing methods of decomposition (mechanical, chemical and thermal) are characterized by many deficiencies [15], [16], [17]. Significant decomposition of mycotoxins is observed under influence of ionizing radiation of ^{60}Co source and the possibility of radiolytic detoxification of cereals, dried fruits and granulated forages has been determined at the different values of absorbed dose of ionizing radiation.

The values of radiation-chemical yields of mycotoxin's decomposition vary in the range $10^{-3} - 10^{-5}/100\text{eV}$, depending on their concentration. But, the dose of ionizing radiation of ^{60}Co , equal to 10 kGy, absorbed in studied products leads to decrease in the detected quantities (4-400 $\mu\text{g}/\text{kg}$) of mycotoxins to values below their maximum allowable concentrations. Radiolytic decomposition of mycotoxins by absorbed doses equal to 10 kGy doesn't hold to any negative changes in organoleptic and chemical properties of studied plant products.

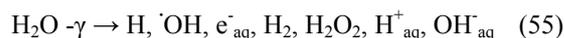
The share of elementary reactions of chain branching in the general process of transformation of mycotoxins is essential at γ -radiation of oxygen-containing water solutions of mycotoxins and the damp plant products polluted by mycotoxins.

The speed of radiolytic transformations of mycotoxins in damp plant products increases with increasing of humidity of plant product (amount of the dissolved oxygen in free water of plant product). The value of radiation-chemical yield of mycotoxin's decomposition in water solution is 1.3-3.1 times more than in damp plant product. This fact specified the formation of e_{aq}^- at the radiolyse of water solutions and participation of these hydrated electrons in the further decomposition of mycotoxin. All free-radical products of water solutions (e_{aq}^- , H, OH, O, H_{aq}^+ , OH_{aq}^-) can take part at the decomposition of mycotoxins.

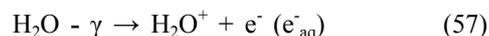
Radiolytic decomposition mycotoxins in water solution and in damp plant products are described by following mechanism (ArOH – mycotoxins, RH – macromolecules of plant products, J – absorbed dose rate in irradiated object – 0.33 Gy/s), [18], [19], [20], [21].

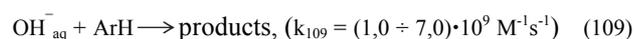
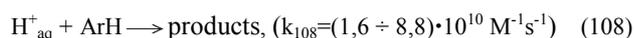
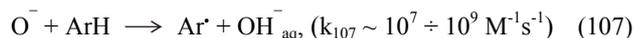
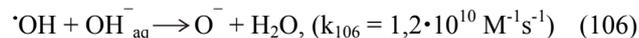
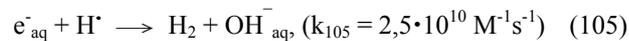
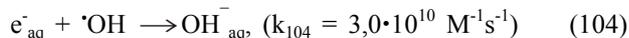
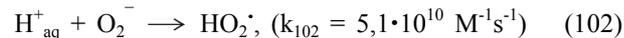
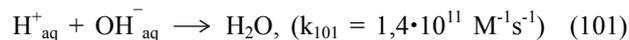
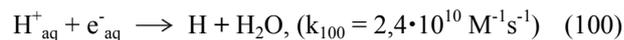
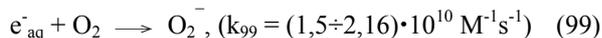
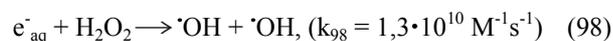
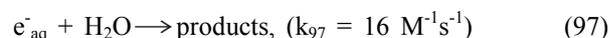
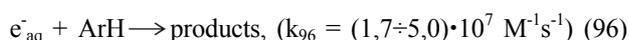
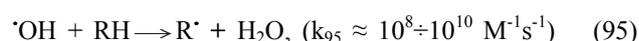
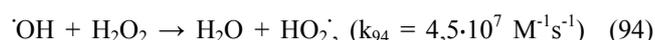
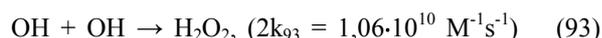
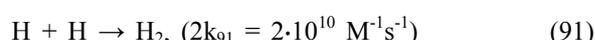
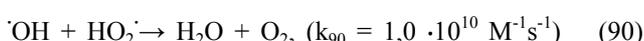
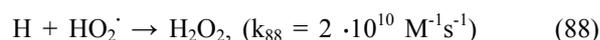
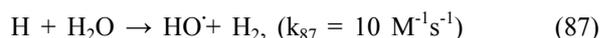
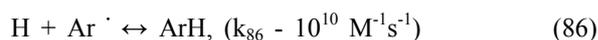
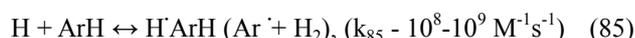
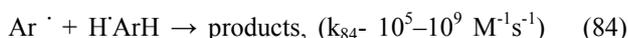
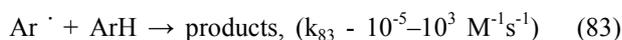
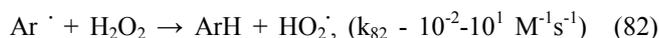
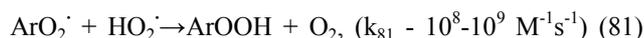
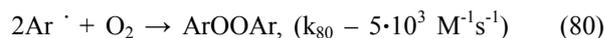
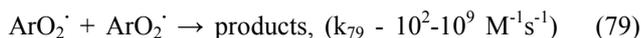
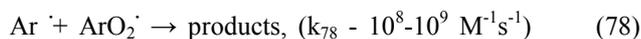
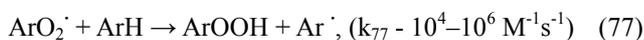
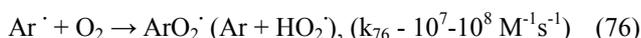
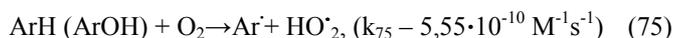
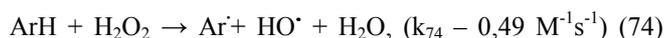
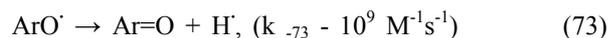
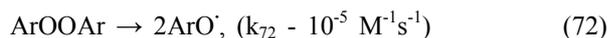
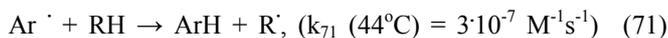
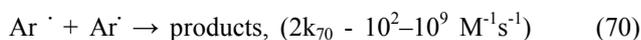
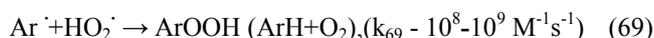
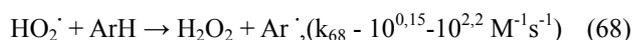
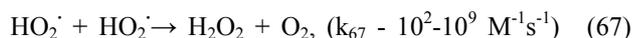
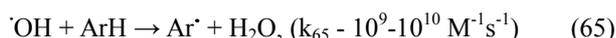
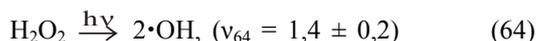
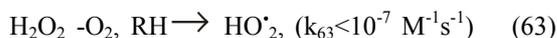
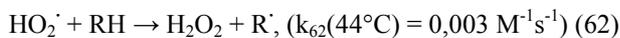
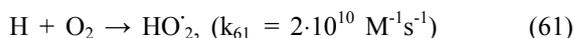
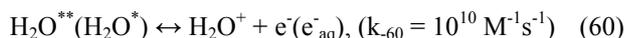
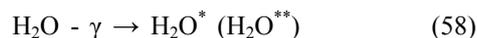


$$(J = 0,33 \text{ Gy/s}, G_{\text{Ar}^\cdot} = 0.2-5.7/100\text{eV})$$



$$\begin{aligned} (J = 0.33 \text{ Gy/s}; G_{e_{\text{aq}}^-} = 2.8 \div 2.9 \rightarrow 10^{-7} \text{ M/s}; \\ G_{\text{H}^\cdot} = 0.6 \rightarrow 2 \cdot 10^{-8} \text{ M/s}; G_{\cdot\text{OH}} = 2.8 \div 2.9 \rightarrow 10^{-7} \text{ M/s}; \\ G_{\text{H}_2} = 0.45 \rightarrow 1.5 \cdot 10^{-8} \text{ M/s}; G_{\text{H}_2\text{O}_2} = 0.75 \rightarrow 2.5 \cdot 10^{-8} \text{ M/s}; G_{\text{H}_{\text{aq}}^+} \\ = 3.3 \div 3.4 \rightarrow 1.1 \cdot 10^{-7} \text{ M/s}; G_{\text{OH}_{\text{aq}}^-} = 0.5 \div 0.6 \rightarrow 2 \cdot 10^{-8} \text{ M/s}; G_{-\text{H}_2\text{O}} \\ = 4.3-4.4 \text{ molecule}/100\text{eV} \rightarrow 2.5 \cdot 10^{-8} \text{ M/s}) \end{aligned}$$





The main products of the radiolytic transformation of mycotoxins in oxygenated aqueous solutions, as seen from the above mechanism, are the macromolecules formed by the recombination of mycotoxin radicals or macromolecules formed by the combination of these radicals through an oxygen bridge. In the case of irradiation of damp plant products the radicals of mycotoxin recombined with macroradicals of organic matrix of plant product. Products of radiolytic transformation of natural toxins and organic xenobiotics unlike initial molecules, don't show physical and chemical properties characteristic for natural toxins and organic xenobiotics.

All active centers of reactions of chain branching are directed, like all primary radicals, to the formation of mycotoxin macroradicals, products of its disproportionation, their peroxides and hydroxy-substituted derivatives, which are comparatively slow to combine through oxygen bridges with other macroradicals, as well as with macroradicals of the organic matrix of plant products. This important effect can also be considered at radiolytic water purification contaminated by organic xenobiotics.

5. Conclusion

Created during the periods empirical, empirical-theoretical and systematic studying of different systems experimental and theoretical prerequisites have formed a basis for development of the theory of chain reactions.

The modern state of the theory of chain processes is analyzed. The mechanisms of branched chain processes, conditions inhibiting and accelerating chain reactions, criteria characterizing the chain nature of chemical processes are described. The mechanisms describing regularities of formation of molecular products of the chain processes are discussed. The short description of the revealed chain processes proceeding in gaseous, liquid, amorphous and solid phases is provided.

These studies are an essential contribution to researches in the field of studying of chain chemical processes.

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