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Heterocyclic inhibitors of autoxidation of hydrocarbons and alcohols

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The antioxidant properties of heterocyclic metal complexes based on the derivatives of benzothiazole, isoxazole, and antipyrine were examined in the article. The ability to inhibit the oxidation of a heterocycle containing a fragment of thiobarbituric acid and a 4-nuclear metal chelate was studied. The results of the analysis of the particle sizes of the complexes using atomic force microscopy are given here. The inhibitory properties were studied by autoxidation of hydrocarbons (n-decane, n-dodecane) and benzyl alcohol. Among the metal complexes based on isoxazole derivatives, the metal chelate based on La, which almost completely inhibits the oxidation of benzyl alcohol, was the most effective. The copper complex based on benzothiazole was shown to reduce the oxidation rate of n-dodecane, while the Co metal complex accelerates its oxidation. Cu and Ni metal chelates based on antipyrine, a copper complex based on a benzothiazole and isoxazole derivative, and a sulfur-containing heterocycle with a thiocarbonyl fragment were found to be effective inhibitors of benzyl alcohol autoxidation. Increasing the number of metal atoms, which are prone to one-electron transformations in the central core of the complex to 4 (in our case, by introducing the Mn_2Ni_2 group) also contributes to antioxidant activity during the autoxidation of benzyl alcohol and n-decane.

Keywords: heterocycles, metal complexes, atomic force microscopy, nanoparticles, autoxidation, benzyl alcohol, n-decane, n-dodecane.

Гетероциклічні інгібітори автоокиснення вуглеводнів та спиртів. *О.В.Павлюк, М.М.Баран, Є.В.Шелудько, Ю.І.Богомолов*.

У статті досліджено антиоксидантні властивості гетероциклічних металокомплексів на основі похідних бензотіазолу, ізоксазолу, антипіріну. Вивчена здатність до інгібування окиснення гетероциклу, який містить фрагмент тіобарбітурової кислоти, та 4-х ядерного металохелату. Наведено результати аналізу розмірів частинок комплексів за допомогою атомної силової мікроскопії. Інгібіторні властивості вивчені шляхом автоокиснення вуглеводнів (н-декан, н-додекан) та бензилового спирту. Серед металокомплексів на основі похідних ізоксазолу найбільш ефективним виявився металохелат на основі La, який практично повністю інгібує окиснення бензилового спирту. Показано, що мідний комплекс на основі бензотіазолу зменшує швидкість окиснення н-додекану, тоді як металокомплекс Co пришвидшує його окиснення. Досліджено, що металохелати Cu та Ni на основі антипіріну, мідний комплекс на основі похідного бензотіазолу та ізоксазолу і сірковмістовний гетероцикл із тіокарбонільним фрагментом являються ефективними інгібіторами автоокиснення бензилового спирту. Збільшення кількості атомів металу, які схильні до одноелектронних перетворень, у центральному ядрі комплексу до 4-х (у нашому випадку введенням групи Mn_2Ni_2) також сприяє антиоксидантній активності при автоокисненні бензилового спирту та н-декану.

1. Introduction

Coordination chemistry studies a wide range of important scientific areas, starting from biological to current problems in the field of materials science. On its basis, significant advances have been made in the field of bio- and organometallic chemistry, catalysis, the creation of new modern materials: ferromagnetics, liquid crystalline and supramolecular structures, biomimetics, promising compounds with nonlinear optical properties for photonics, molecular electronics, etc. To study coordination compounds, not only theoretical (field theory of ligands, crystals), but also semi-empirical and quantum chemical approaches are used. Compounds that are capable of forming bi- and polynuclear homo- and heterometallic complexes include the Schiff bases that are the most common representatives of azomethine ligands. Biomimetic models of metalloproteins, catalysts, luminophores, liquid crystalline polymer and supramolecular structures have been developed on their base. The direction of constructing monomolecular structures (molecular design) forms the basis of modern research in the field of chemistry of metal complexes of azomethines and their analogues of cyclic structures [1-4]. Molecules containing azomethine groups in their structure have high complexing ability and can be used as thermal oxidation stabilizers [5]. The intensive development of applied aspects of the chemistry of metal complex inhibitors, along with the study of the patterns of oxidation of organic substrates, has stimulated interest in the study of the kinetics and mechanism of the inhibitory ability of metal complexes [6].

Among the many types of azomethine ligands and metal complexes, heteroligand, di- and polynuclear chelates, as well as heterocyclic metal complexes, the antioxidant properties of which have not been sufficiently studied, are of interest. The synthesis and structure of metal complexes of Zn, Cu, Co, Cd, Ni with ligands based on azomethine derivatives of mono- and bistiadiazoles has been described in [7-9].

Magnetic, thermal and electronic characteristics were studied. These compounds have not been studied as oxidation inhibitors. The macrocyclic Schiff bases were obtained, and di-, tri- and tetranuclear metal complexes were synthesized on their base [10, 11].

Binuclear copper complexes based on diacylhydrazones of formyl derivatives of pyrazole were synthesized and studied [12]. The hyperfine structure of EPR spectra and the nature of weak exchange interactions between paramagnetic centers have been studied. It should be noted that di- and polynuclear complexes have not been studied in terms of inhibition of oxidative processes. A similar situation is observed with metal complexes based on ligands of asymmetric structure. The introduction of additional neutral molecules or ligands of different structures into the coordination sphere of the central ion makes it possible to modify their solubility, luminescent properties, etc. Mixed-ligand metal complexes were obtained to study magnetic or catalytic properties. Metal complexes of macrocyclic Schiff bases with an asymmetric structure were obtained [13]. Mixed-ligand complexation affects the thermal and luminescent properties of the complexes in solutions [14]. The combination of such different ligands as [N – (salicylidene)sulfobenzamide] and 1,10 – phenanthroline in metal complexes leads to increased thermal stability and biological activity [15]. Azomethine metal complexes containing the fragments of sulfobenzamide, pyridine and pyrimidine were synthesized to study their antimicrobial activity. Similar metal complexes were synthesized using Schiff bases with fragments of sulfamerisine, sulfamethoxazole and sulfabenzamide derivatives of pyridine and pyrimidine [16-19]. Various complexes of Cu, Ni, Co, Zn, Sm, Mn, VO were obtained. They have been tested as antimicrobial and antibacterial agents. The properties of metal complexes based on Schiff bases with thiophene-hydrazide fragments have been studied in [20]. Spectral and magnetic characteristics, conductivity in dimethylsulfoxide, antibacterial and antifungistatic indicators are given here. When heated to a temperature of 600 °C, metal complexes turned out to form the corresponding oxides MnO, CoO, NiO, ZnO in the form of nanoparticles. Tridentate azomethine compounds obtained by condensation of 2-tosylaminobenzaldehydes with 2-butylamino-5-nitroaniline, served as the basis for the preparation of Zn and Pd metal complexes containing azomethine and benzimidazole ligands in one molecule. Differences in the coordination of azomethine and benzimidazole ligands in such a heterocyclic system were established. It was concluded that the complex is additionally stabilized both due to stacking interactions between the azomethine and benzimidazole ligands and between the benzimidazole fragments themselves [21]. The work [22] describes

metal complexes of Co, Cu, Ni based on azomethine derivatives of 5-nitrofuran-2-amidrazone, which are superior in biological activity to Furatsilin drug. The possibility of forming of metal complexes of transition metals with Schiff bases on the basis of heterocycles of iminoxyl radicals has been studied [23-24]. Strong complex formation of these ligands with various metals Fe, Co, Ni, Cu, etc. was discovered. The magnetic properties of such metal complexes were studied and complexes with paramagnetic and diamagnetic properties were discovered. Polymer Schiff bases and metal complexes based on them are of interest. Polyazomethines with fragments capable of photoisomerization, with electrically conducting thiophene inclusions, with benzoxazole derivatives as liquid crystal systems for nonlinear optics, as well as with inclusions of carbazole, furan, pyridine, and thiazole have been synthesized [25].

Recently, numerous studies have been carried out on magnetically active metal complexes with Schiff bases. New synthetic approaches to modeling azomethine ligands were applied and the magnetic characteristics of chelates were shown to depend on the electronic configuration and a variety of "metal-complexing agent" combinations [26]. New approaches to the development of ferromagnetics have been proposed, which consist in the synthesis of binuclear azomethine metal complexes by varying the fine structure of the ligand system [27]. This change in coordination sites leads to two types of magnetically anomalous structures: antiferro- and ferromagnetic coordination compounds.

The synthesis of Schiff bases based on thiadiazole derivatives and metal complexes of Cu, Co, and Zn is presented in [28]. It is noteworthy that these metal complexes are inhibitors of the formation of superoxide anion radical $O_2^{\cdot-}$, moreover, more effective than superoxide dismutase. At the end of the inhibition cycle, regeneration of the original valence form of the central atom occurs with simultaneous disproportionation of the radical anion with the formation of hydrogen peroxide. Thus, these complexes catalytically (many times) participate in the inhibition of the superoxide anion radical $O_2^{\cdot-}$.

The authors [29] studied the mechanism of inhibition of liquid-phase oxidation of hydrocarbons in the presence of sulfur-containing heterocyclic metal complexes of Ni, Co, Cu, Zn, Ag, for example, thiooxinates, derivatives of thiopicolinic acid, and have come to the conclusion that the transfer of an electron from the complex to the peroxide radical is decisive factor in the termination of oxidation chains and E_a decreases with increasing inhibitory activity. When studying the antioxidant properties of metal complexes with sulfur-containing ligands based on benzothiazole and pyridine, the concentration dependence of the direction of the reaction was established. At low concentrations, the complexes initiate oxidation, and at concentrations above critical they terminate the oxidation chains [30].The antioxidant activity of sulfolane-containing metal complexes, in particular, carboxylates, dithiocarbamates, and azomethines as high-temperature additives for oils, has been studied in detail [31]. Greater activity has been noted for additives containing fragments of N and S atoms in the coordination sphere. Complex compounds of Cu and tetrazole-containing Schiff bases were synthesized and studied [32]. These compounds are of interest because they contain several donor centers, which open up new opportunities for developing promising materials based on them. These metal complexes have not been studied as oxidation inhibitors.

The cited literature sources indicate that significant progress has been made in the synthesis of heterocyclic metal complexes. Basically, the structure, luminescent, magnetic, biological properties were studied; quantum chemical modeling of the structure, etc. was carried out. However, it should be noted that these bi- and polynuclear metal complexes as inhibitors of the oxidative processes of organic compounds has not been practically studied.

The purpose of the work is to synthesize heterocyclic compounds, metal complexes and study the possibility of their use in a new functional application, namely, as inhibitors of the autoxidation of hydrocarbons and alcohols.

2. Experimental

We have synthesized metal complexes of Cu, La, Co, Ni based on heterocyclic Schiff bases (derivatives of 6-methylbenzothiazole, isoxazole, antipyrine). In addition, the following were studied: a thiobarbiturate-based heterocycle and a 4-nuclear metal complex (to compare the inhibitory ability) in the autoxidation reaction of hydrocarbons (n-decane, n-dodecane) and benzyl alcohol.

The original Schiff bases were prepared by reacting salicylic aldehyde with the corresponding amines in boiling ethyl alcohol. Metal

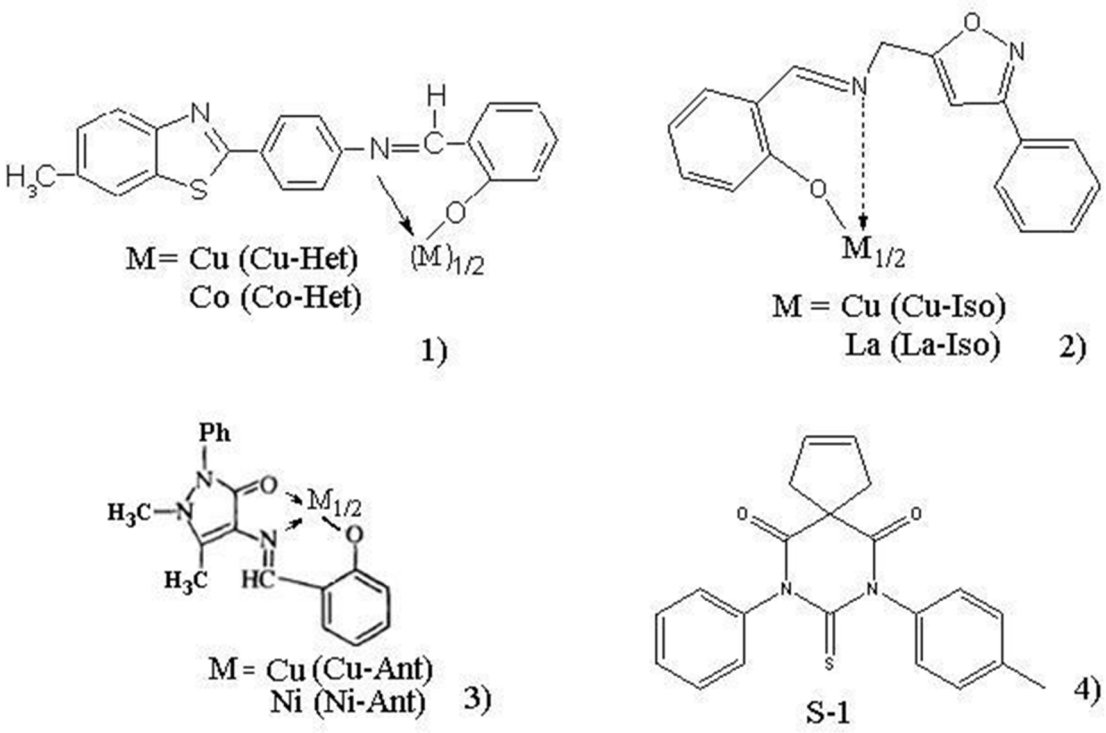

Fig.1 - Structural formulae of synthesized compounds (1-4)

complexes were synthesized in one step by the reaction of metal salts with Schiff bases [33]. The amine required for the synthesis of Schiff bases and metal complexes Cu-Iso and La-Iso was synthesized according to [34].

The reaction was carried out in ethyl alcohol in the presence of sodium hydroxide, or by direct interaction of Schiff bases with metal acetates. Molar ratio of the Schiff bases to metal salt is 2:1. The structural formulae of the synthesized compounds are below.

The following model compounds were used to study the inhibitory ability, namely benzyl alcohol, which is widely used as a solvent in perfumery, pharmaceuticals, cosmetics, as well as n-decane and n-dodecane, which are present in a mixture of hydrocarbons in diesel fuel. To study the surface topography and estimate particle sizes, a sample suspension (~4 mg) was prepared in 5 ml of ethyl alcohol. It was applied to quartz glass and then heated at 50°C to constant weight. The sample area was scanned with a CSC 37 probe of an NT-206 atomic force microscope (Microtestmachines, Gomel, Republic of Belarus). The rigidity of the console is 0.3-0.6 N/m, the scanning speed in the X-Y plane is up to 10 μm/s, scanning step is 0.3 nm.

The method of determining thermal-oxidative stability in a liquid substrate is to continuously introduce air into a certain volume of the substrate at a given temperature, with or without a catalyst. Selected model substances, both pure and with the addition of metal complexes, were placed in a flow-type metal reactor and continuously oxidized in an air flow at a speed of 10 l/h at a temperature of 150 °C (n-decane, n-dodecane) and 100 °C (benzyl alcohol). The addition of metal complexes in all cases was 0.1 wt. %. The sample volume is 25 cm^3. The total oxidation time is 3 hours. To determine the rate of autoxidation of the initial substrate over time, every 30 minutes, test samples were taken for gas chromatographic analysis. An Agilent Technologies 7890A chromatograph with a flame ionization detector using a quartz capillary column 25 m long and with an internal diameter of 0.320 mm, filled with stationary phase HP-5 (phenyl – 5 wt. %, methylpolysiloxane – 95 wt. %) was used in temperature programming mode from 40 to 250 °C at a speed of 5 °C/min.

3. Results and discussion

Figure 2 shows 2D images of surfaces formed by nanoparticles of Cu-Iso, Cu-Het and S-1 samples. After preparing the appropriate sections and analyzing the profiles, it was established that the surface relief shown in Fig. 1a is formed by particles of the Cu-Iso metal complex from 4.4 to 7.5 nm. Particles of Cu-Het

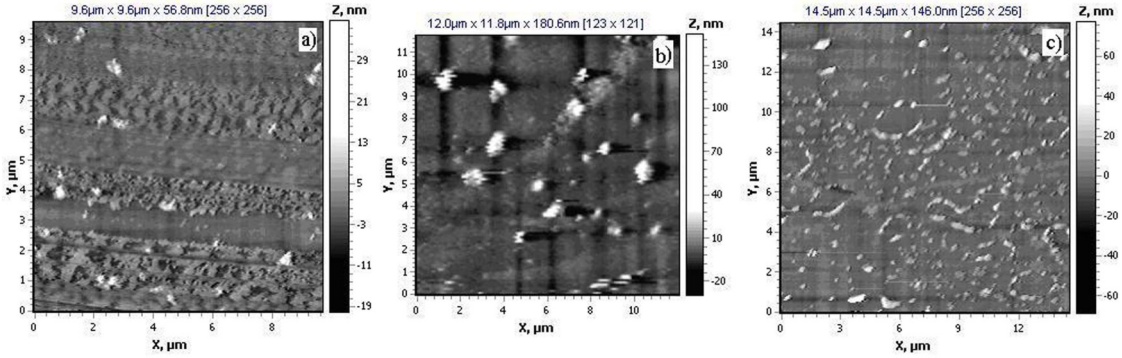

Fig.2 - 2D-images of surfaces formed by nanoparticles of metal complexes: Cu-Iso (a), Cu-Het (b), S-1 (c)

metal complex (Fig. 1b) and the sulfur-containing heterocycle S-1 (Fig. 1c) have slightly larger sizes: from 17.7 to 27.6 nm and from 15.3 to 24.2 nm, respectively. Particles of the S-1 heterocycle form even small chain aggregates in the form of a necklace.

It follows from these data that the particle sizes of the complexes are in the nanorange. According to [35], when the particle size decreases from 10^3 to 10 nm, the fraction of interfaces increases significantly from 0.3 to 30 wt. %. This indicates that in oxidation reactions the active surface of these nanoparticles will be significant, which contributes to effective inhibition.

According to the literature, the autoxidation reaction of organic compounds proceeds by a radical chain mechanism. Under the influence of elevated temperature, molecular oxygen interacts with the weakest bonds of the substrate with the formation of free radicals: alkyl $R^{\bullet}$, peroxyl $ROO^{\bullet}$ and unstable intermediate compounds – hydroperoxides [36]:

$$R^{\bullet} + O_2 \rightarrow R - O - O^{\bullet} \quad (1)$$

$$R - O - O^{\bullet} + R - H \rightarrow R - O - O - H + R^{\bullet} \quad (2)$$

Inhibitors break oxidation chains at the peroxyl or alkyl radical, and alkyl hydroperoxides with the ROOH structure are the main sources of the formation of oxygen-containing oxidation products of organic compounds – aldehydes, alcohols, ketones, acids etc. [36, 37]. The carriers of oxidation chains, when oxidizing n-dodecane, are the radicals $C_{12}H_{23}^{\bullet}$ and $C_{12}H_{23}–O–O^{\bullet}$.

The addition of the synthesized Me-complex Cu-Het to a non-polar medium - n-dodecane, chosen as a model of hydrocarbon fuel, inhibits its oxidation processes; this is confirmed by the results of gas chromatographic analysis (Fig. 3a).

Fig. 3a shows that at the first stage of autoxidation (first 30 min), due to the insufficient concentration of oxidation chain carriers, oxidation products accumulate slowly and do not depend on the presence of the Cu-Het metal complex additive in the substrate. With an increase in the concentration of $R^{\bullet}$ and $ROO^{\bullet}$ radicals with time, the content of autoxidation products increases; however, the addition of a metal complex inhibits this process by breaking the oxidation chains. The rate of n-dodecane oxidation in the presence of Cu-Het is almost half that of the original commercial n-dodecane.

Comparison of autoxidation of n-dodecane with the addition of 0.1 wt. % of the Co-Het complex (Fig. 3b) and the autoxidation of n-dodecane in the presence of Cu-Het indicates that the addition of the Cu-Het metal complex reduces the rate of oxidation of pure n-dodecane. The Co-Het metal complex, unlike Cu-Het, accelerates the oxidation of n-dodecane. After three hours of oxidation, the n-dodecane content decreased to 85.61 wt. %, whereas in the presence of Cu-Het, the n-dodecane content after oxidation was 91.86 wt. %.

The autoxidation reaction of alcohols, like hydrocarbons, proceeds by a radical chain mechanism. The most sensitive to oxidation in alcohols is the C-H bond of the carbon atom to which the hydroxyl group is attached. The carriers of benzyl alcohol oxidation chains are oxybenzyl and oxybenzylperoxyl radicals. The results of studying the influence of synthesized additives on the oxidation of benzyl alcohol, as a model of alcohol fuel, are shown in Fig. 3c, d. Gas chromatographic analysis of the autoxidation products of benzyl alcohol in an air flow established that the only autoxidation product of benzyl alcohol is benzaldehyde.

The data shown in Fig. 3c indicate that both metal complexes inhibit the oxidation of benzyl alcohol. In this case, the La-Iso complex is more effective and completely suppresses oxidation. During autoxidation from 0.16 to 0.17

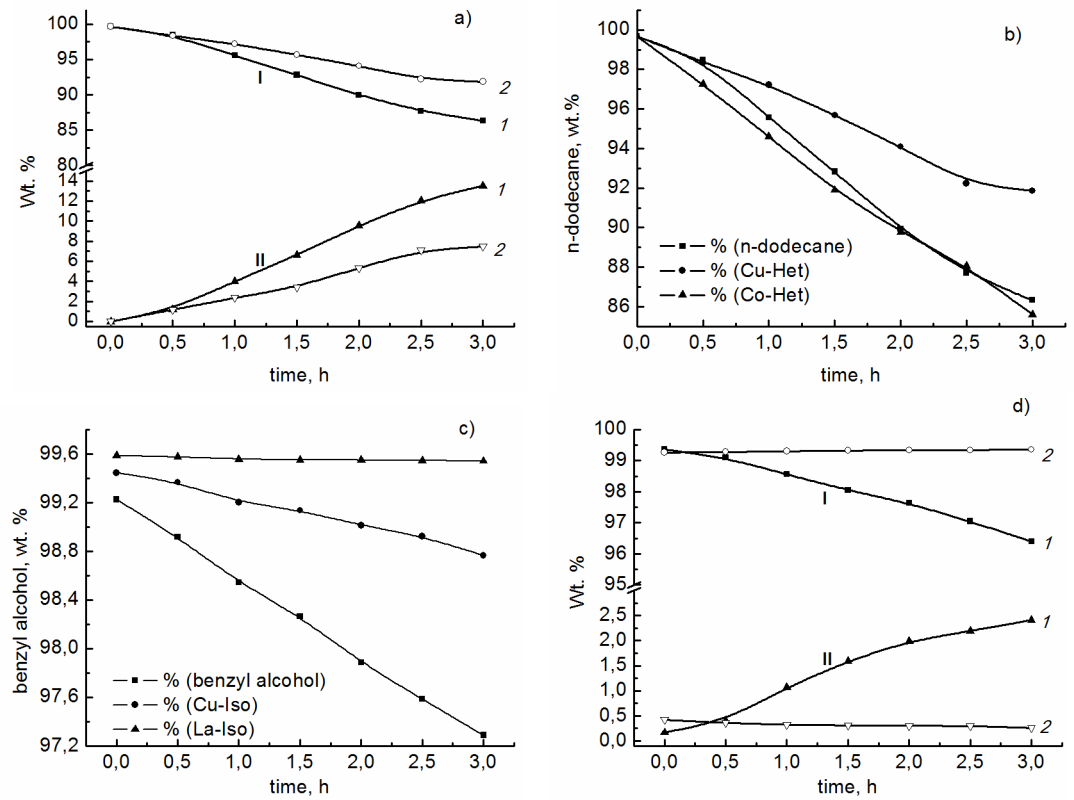

Fig. 3 - Concentration dependences of components on autoxidation time: **a** – change in the concentration of n-dodecane (I) and accumulation of the sum of its autoxidation products (II) with time: 1 – commercial n-dodecane; 2 – commercial n-dodecane with the addition of 0.1 wt.% Cu-Het metal complex; **b** – change in n-dodecane concentration with time without additives and with the addition of 0.1 wt. % metal complexes; **c** – change in the concentration of benzyl alcohol in the reaction mass depending on the time of autoxidation with the addition of 0.1 wt. % metal complexes; **d** – change in the concentration of benzyl alcohol (I) and benzaldehyde (II) in the reaction mass on the time of autoxidation: 1 – pure benzyl alcohol; 2-benzyl alcohol with the addition of 0.1 wt. % Cu-Het metal complex

wt. % in the presence of the Cu-Iso additive, the benzaldehyde content changes from 0.22 to 0.38 wt. %. Without additives, the benzaldehyde content increases by almost an order of magnitude (from 0.21 to 2.1 wt. %) under the same conditions of benzyl alcohol oxidizing.

The Cu-Het metal complex based on benzothiazole turned out to be similar in effectiveness, which also almost completely inhibits the autoxidation of benzyl alcohol (Fig. 3d).

As it can be seen from Fig. 3d, the concentration of the main component in the original benzyl alcohol drops sharply with oxidation time. At the same time, the amount of benzaldehyde increases. The addition of 0.1 wt. % Cu-Het metal complex to the initial alcohol does not simply reduce the rate of accumulation of oxidation products, as is the case with the nonpolar substrate – n-dodecane, but completely inhibits the process of alcohol oxidation under these experimental conditions. The difference in the inhibitory ability of the synthesized metal complex in nonpolar (n-dodecane) and polar (benzyl alcohol) media can be explained by the presence of the radical $C_6H_5CHOHOO^{\bullet}$ of a hydroxyl group in the α-position to the peroxyl group. This hydroxyl group stabilizes the carbocation formed during the interaction of the peroxyl radical with the chain-terminating oxidation metal complex [38, 39].

Fig. 4a,b shows the dependences of the content of benzyl alcohol and benzaldehyde in the reaction mixture on the time of autoxidation in the presence of metal complexes Cu-Ant, Ni-Ant and heterocycle S-1.

Under these conditions of benzyl alcohol autoxidation, the introduction of Cu-Ant and Ni-Ant metal complexes leads to almost complete inhibition of the oxidation process. In the presence of the Cu-Ant complex, the benzaldehyde content varies from 0.074 to 0.11 wt. %. The Ni-Ant complex is somewhat more efficient, in which the benzaldehyde content during oxidation varies from 0.067 to 0.075 wt. %.

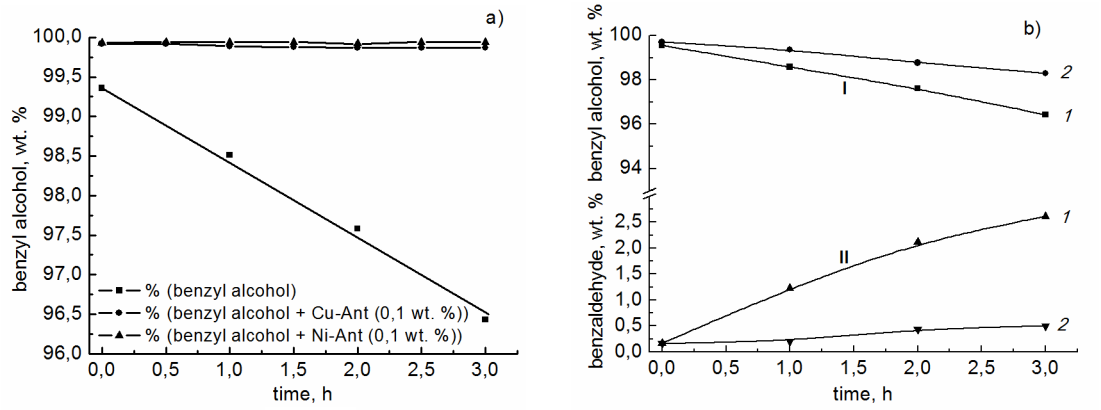

Fig. 4 – Concentration dependences of components in the reaction mixture on the time of autoxidation: **a** – change in the concentration of benzyl alcohol in the reaction mass depending on the time of autoxidation with the addition of Cu-Ant and Ni-Ant metal complexes; **b** – change in the concentration of benzyl alcohol (I) and benzaldehyde (II) in the reaction mass depending on the time of autoxidation with the addition of heterocycle S-1

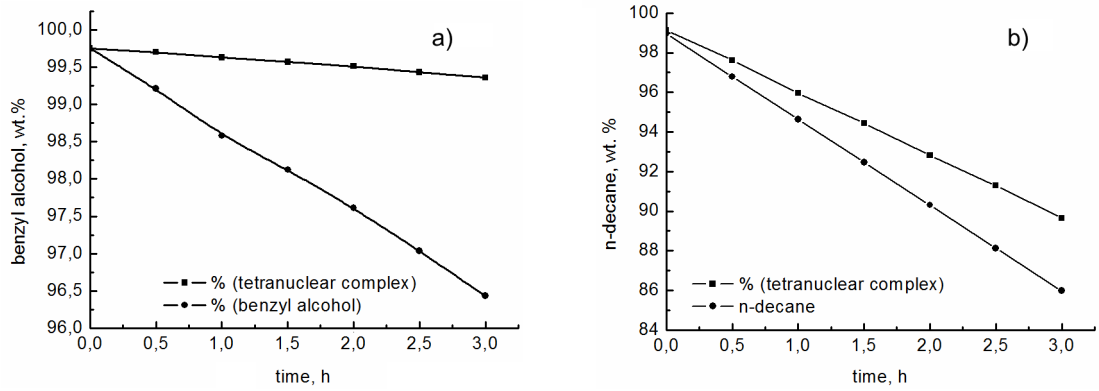

Fig. 5 – Content of benzyl alcohol (a) and n-decane (b) in the reaction mass without an additive and with the addition of 0.1 wt. % tetranuclear complex depending on the oxidation time

Among oxidation inhibitors, an important place is occupied by sulfur-containing compounds − mercapto derivatives, di- and polysulfides, sulfonic acids, which can decompose hydroperoxides without the formation of free radicals. Sulfur-containing heterocycles and their complexes with metals can be classified into a separate class, since they, along with antioxidant properties, exhibit anti-wear and anti-corrosion ones. It has been noted that condensed heterocyclic systems, for example, triazolothiazole, triazinotriazole, as well as thiazolidine and thiazolone derivatives, have high antioxidant properties [40]. It has been shown that sulfur-containing compounds catalytically (many times) participate in the decomposition of hydroperoxides [41]. Some of the sulfur-containing compounds described in the literature contain a thiocarbonyl group similar to that found in the structure of the S-1 compound [40]. In the S–1 heterocycle, sulfur is included in the structure of the thiobarbituric acid derivative. It was of interest to find out whether this compound would exhibit antioxidant activity under conditions of autoxidation of benzyl alcohol. Fig. 4b shows the dependence of the content of benzyl alcohol and benzaldehyde on the autoxidation time at 100 °C. The data presented indicate that the introduction of the S-1 additive into benzyl alcohol inhibits oxidative processes compared to pure benzyl alcohol. In this case, the benzaldehyde content in the reaction mass is 0.32 wt. % after 3 hours of oxidation, which is ~ 8 times less than during oxidation without the additive.

Fig. 5 shows the dependence of the content of benzyl alcohol and n-decane in the reaction mass on the autoxidation time without an additive and with the addition of 0.1 wt. % tetranuclear complex. The latter was synthesized by reacting a ligand based on 1-hydroxy-2-aminobutanol and salicylic aldehyde with nickel and manganese salts. Thus, there are two nickel atoms and two manganese atoms coordinated

with the ligand in this metal complex. Data of Fig. 5 indicate that the introduction of up to 4 (in our case) metal atoms capable of one-electron transformations into the central core of the complex effectively inhibits the autoxidation process in a medium of benzyl alcohol and n-decane.

Thus, the addition of the synthesized Cu-Het metal complex both to a non-polar medium – n-dodecane chosen as a model of hydrocarbon fuel, and to a polar medium – benzyl alcohol, which models alcohol fuel, inhibits oxidation processes. However, if in a hydrocarbon medium the addition of the Cu-Het metal complex can inhibit oxidation processes, then in a polar medium it completely eliminates them. The lanthanum metal complex La-Iso acts in a similar way: it effectively suppresses the oxidation of benzyl alcohol. The addition of Cu-Ant and Ni-Ant metal complexes also leads to complete inhibition of the autoxidation process of benzyl alcohol.

The data presented indicate the effectiveness of using the synthesized compounds in a new functional direction - as inhibitors of the autoxidation processes of aromatic alcohols and hydrocarbons.

4. Conclusion

1. Possible particle sizes of metal complexes are in the nanorange (from 4.4 to 24.2 nm), which was determined by atomic force microscopy.

2. The effect of adding synthesized heterocycles and metal complexes at a concentration of 0.1 wt % on the autoxidation of non-polar (n-decane, n-dodecane) and polar (benzyl alcohol) substrates simulating hydrocarbon and alcohol fuels was studied. Metal complexes Cu-Iso and La-Iso, as well as antipyrine-based Cu and Ni metal complexes, Cu-Het metal complex and S-1 heterocycle inhibit the oxidation of benzyl alcohol. However, La-Iso metal chelates and antipyrine-based Cu and Ni metal chelates are more effective and almost completely suppress oxidation.

3. It has been established that during the n-dodecane autoxidation, the introduction of the Cu-Het metal complex helps to slow down the process compared to the autoxidation of pure n-dodecane, reducing the oxidation rate. In contrast, the Co-Het metal complex accelerates the oxidation of n-dodecane.

4. The tetranuclear metal complex is more effective in the autoxidation of benzyl alcohol than in the oxidation of n-decane.

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