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Metal complex catalysis of initiated oxidation of hydrocarbons and alcohols: features of inhibition

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Kinetics of initiated oxidation of cumene and benzyl alcohol in the presence of Cu (II) *bis*-salicylaldiminate complexes containing trifluoromethyl or tetrafluoroethoxy substituents in ligand environments was investigated. The inhibitory properties of the complexes were studied by a gas-volumetric method at T = 343 K and P = 0.09-0.1 MPa. 2, 2^{I}–Azo–*bis*–isobutyronitrile (AIBN) was used as an initiator. During the oxidation of cumene, all studied Me-complexes exhibit catalytic properties at the concentrations of $1 \cdot 10^{-3}$ – 0.01 mol/lit, accelerating oxidation of cumene. An increase in the oxygen pressure also does not cause the change of the initial oxidation rate. During the oxidation of benzyl alcohol, all the complexes catalytically terminate the oxidation chains. It has been established that when storing the reaction solution without access to air, induction periods are observed on the kinetic curves, increasing with storage time. Theoretical and experimental induction periods and factors of inhibition were determined.

Keywords: metal complexes, catalysis, peroxyl radical, hydroperoxides, trifluoromethyl substituent, tetrafluoroethoxy group, induction period, factor inhibition.

Металокомплексний каталіз ініційованного окиснення вуглеводнів та спиртів: особливості інгібування. *Й.О.Опейда, О.О.Величко, Є.В.Шелудько, О.В.Павлюк, Р.Б.Шепарович, В.Є.Шелудько М.М.Баран*

У статті досліджено кінетику ініційованого окиснення кумолу та бензилового спирту у присутності *біс*-саліцилальдімінатних комплексів міді (II), які містять у лігандному оточенні відповідно трифторметильний або тетрафторетоксильний замісник. Інгібуючі властивості комплексів вивчали газоволюмометричним методом при T = 343 К та P = 0.09 – 0.1 МПа. Як ініціатор використовували $2{,}2^{I}$–азо–*біс*–ізобутиронітрил (АІБН). При окисненні кумолу досліджені металокомплекси проявляють каталітичні властивості при концентраціях $1 \cdot 10^{-3}$ – 0,01 моль/л, прискорюючи окиснення кумолу. Збільшення тиску кисню також не призводить до зміни початкової швидкості окиснення. При окисненні бензилового спирту комплекси каталітично обривають ланцюги окиснення. Встановлено, що при зберіганні реакційного розчину без доступу повітря на кінетичих кривих спостерігаються періоди індукції, які збільшуються із часом зберігання. Визначено теоретичні та експериментальні періоди індукції, а також фактори інгібування.

I. Introduction

Antioxidant stabilization of oil products and fuels contributing to the preservation of their functional properties has always been widely studied. Recently, interest in the search for new systems for the antioxidant stabilization of materials has grown in connection with the development and widespread introduction of alternative fuels (biodiesel, alcohol fuels) [1]. It should be noted that during the oxidation process, some inhibitors, for example, sterically hindered phenols, aromatic amines, phosphoprous-containing compounds, interact with peroxyl radicals – this is a low-temperature group (up to 150 °C). The high-temperature group (> 150 °C) is characterized by reactions with alkyl radicals (quinones, metal chelates, stable nitroxyl radicals). In addition, a number of inhibitors are capable of destroying hydroperoxides without the formation of free radicals (sulfides, phosphites, metal carbamates), and act as oxygen acceptors (especially at high temperatures) through nonchain inhibition. Some ashless heterocyclic compounds that have multifunctional (antioxidant, antiwear, anti-corrosion) characteristics are effective inhibitors. Among of antioxidant additives, metal complexes (Me-complexes) are becoming increasingly important. Studies have shown that Me-complex additives in many cases are characterized by higher antioxidant activity than known organic antioxidants. Me-complex catalysts for multiple oxidation chain termination [2] are particularly effective in this regard. Such compounds are capable of decomposing hydroperoxides with a low yield of free radicals and can enhance the antioxidant effectiveness of known organic antioxidants. As is known [3, 4], free radicals are formed at the initial stages of oxidation during the interaction of oxygen with C-H bonds. The continuation of oxidation chains is as follows:

$$R\bullet + O_2 \rightarrow ROO\bullet \qquad (1)$$

$$ROO\bullet + RH \rightarrow ROOH + R\bullet \qquad (2)$$

Hydroperoxides, which are formed by reaction (2), are branching agents and the main sources of free radicals. The reaction of hydroperoxide decomposition and chain branching in the presence of homogeneous catalysts is one of the main stages of the oxidation reaction. To produce effective oxidation inhibitors, it is necessary to synthesize such coordination compounds that would actively interact with hydroperoxides, but without the formation of free radicals.

The following mechanisms of decomposition of organic hydroperoxides are mainly discussed in the literature: radical, molecular and chain-induced. Attention is also drawn to the effect of solvents on the catalytic decomposition of hydroperoxides and their decomposition in the presence of compounds of transition metals. According to the proposed mechanism [4] of the catalytic action of transition Me compounds, hydroperoxide acts alternately as an oxidizer and then as a reducer in the reaction with the reduced or oxidized form of Me, respectively; this ensures a constant ratio of the valence forms of the catalyst and determines the effect of catalysis.

The molecular mechanism of hydroperoxide decomposition leads to the formation of non-radical products. Increasing the rate of hydroperoxide decomposition along the “molecular direction” reduces the rate of formation of free radicals in the system. If the rate of formation of radicals in the presence of a catalyst is lower than in the absence of a catalyst, then the introduction of Me-organic compounds leads to the appearance of induction periods.

The non-catalytic decomposition of hydroperoxides is characterized by chain decomposition induced by free radicals [5]. The chain decomposition of hydroperoxide depends on the nature of the catalyst. For example, in the presence of iron phthalocyanine, tret-butyl hydroperoxide decomposes in a chain direction, whereas in the presence of Co salts there is no chain direction. Such influence of the catalyst nature on the direction of decomposition of hydroperoxides may be a manifestation of the dual function of the catalyst [6]. This effect consists in the ability of the catalyst not only to generate the formation of free radicals, but also to take part in the chain termination reaction. In this case, metal compounds can interact with both peroxyl and alkoxyl radicals, which are formed during the decomposition of hydroperoxides.

A promising area of research is the use of metal complexes to catalyze the termination of chain reactions of the oxidation of organic compounds. This is due to the fact that Me-complexes can act not only as initiators, but also as inhibitors of radical chain oxidation processes. In [7], the first example of catalytic reaction of oxidation chain termination of cyclohexanol with copper metal complexes was shown, in which the braking time was 400 times longer than in the stoichiometric (single) reaction of oxidation chain termination. Using the example of a large number of amines, and then amino acids, alcohols, alkylsulfoxides, etc., metal complex catalysis of oxidation chain termination was proven. Based on the analysis of kinetic patterns, two mechanisms of Me-complex catalysis have been proposed: catalytic reactions localized at the central atom of the Me-complex and reactions localized at a coordinated ligand. The first catalytic cycle of oxidation chain termination is characteristic of transition metal complexes, the central atom of which is capable of one-electron transformations in radical reactions. These are metals Cu (I, II), Co (II, III), Mn (II, III), Ni, Fe, Ce with different ligands, for example, carboxylates, porphyrins, ß-diketonates, phenolates, Schiff bases, etc.

In reactions of the second type, the reaction centers are YH-groups (NH, NH_2, OH, NOH, SH) coordinated in the metal, etc. Peroxyl radicals interact with coordinated YH-groups to form Y-centered radicals, which are able to reduce by second radicals =C(OO•)X. In both the first and second cases, regeneration of the original Me-complexes occurs.

The effectiveness of inhibition is characterized by the value of the gross stoichiometric inhibition coefficient. For example, it has been established that substituted copper bis-salicylaldiminates catalyze multiple chain termination of cyclohexylamine oxidation. In this case, the values of the gross stoichiometric inhibition coefficients depend on the nature of the substituents in the imino-fragment of the Me-complex and are $8 \cdot 10^4$, $5 \cdot 10^3$, $9 \cdot 10^2$ for NO_2, H, OCH_3 respectively [8]. It should be noted that the gross rate constant for oxidation chain termination depends on both the nature of the central atom and the ligand environment. The introduction of electron-seeking radicals into the imino-component of copper salicylaldiminate increases the chain termination rate constant by ~2 orders of magnitude (oxidation of cyclohexylamine) or 5.4 times more in the oxidation of dimethyl sulfoxide.

Analysis of literature data shows that numerous antioxidant systems have been developed, and the kinetics of oxidation of various substrates - hydrocarbons, alcohols, amines, etc. has been studied. At the same time, an intensive search for new effective antioxidants continues. Among them, polyfunctional antioxidants whose molecules contain structural groups of inhibitors that catalyze through different mechanisms are important for practical applications. For example, shielded phenolic fragments or amines block radical chain oxidation by destroying hydroperoxide molecules (P, N, S) or structures – metal passivators (heterocycle derivatives) [9]. The ability to predict antioxidant activity is being widely studied. For example, it has been shown that the inhibition effectiveness of phenols and amines is achieved, if there is a certain balance between the energy of homolytic decomposition of ArO-H or ArN-H bonds and the ionization potential [9]. Quantum chemical calculations of the energies of molecular orbitals of antioxidants (HOMO and LUMO) [10], methods of molecular dynamics [11] and computer chemistry are promising and informative methods of forecasting. In the latter case, the structure-property relationship is analyzed using characteristic structural features and corresponding antioxidant activity, followed by the development of a mathematical model [12].

Analyzing the published data, it should be noted that the oxidation kinetics of hydrocarbons and alcohols in the presence of copper salicylaldiminates with fluorinated substituents in the ligand environment has been practically not studied.

The aim of this work is to study the kinetics of the initiated oxidation of cumene and benzyl alcohol in the presence of copper (II) metal complexes with different ligand environments, to establish the features of inhibition, and to determine the functional applications of the obtaining Me-complexes.

2. Experimental

To study the resistance of motor fuel to oxidation in the presence of Me-complex additives, the following compounds were selected: the aromatic hydrocarbon cumene as a model of hydrocarbon (diesel) fuel and benzyl alcohol as a model of alcohol fuels.

Copper salicylaldiminates Cu(II) with different ligand environments synthesized by the reaction of the corresponding Schiff bases with metal salts were studied as Me-complexes. The reaction was carried out in ethyl alcohol in the presence of sodium hydroxide at a molar ratio of Schiff base : metal salt = 2 : 1.

Inhibitory properties of the complexes were studied in model initiated oxidation reactions of organic substrates (cumene, benzyl alcohol) by molecular oxygen using the gas-volumetric method with constant stirring, T = 343 K, P =

0.09-0.1 MPa. The stirring speed was selected so that oxidation occurred in a kinetic mode (i.e. the rate of oxygen absorption did not depend on the frequency of shaking the reaction vessel). 2,2^{I}–azo-*bis*-isobutyronitrile (AIBN) was used as initiator.

0.0066 g of AIBN was weighted in the reactor and 2 ml of a solution of a copper complex in cumene or 1 ml of a solution of a copper complex in benzyl alcohol was added. Solutions with lower concentration of copper complexes in benzyl alcohol were prepared by serial dilution of the initial solutions. AIBN was cleaned by recrystallization with ethyl alcohol; cumene was used without additional cleaning (98%, Aldrich); benzyl alcohol was boiled with 40-% water solution of alkali during 2 hours, washed by water up to neutral reaction, dried by anhydrous potash and distilled under vacuum.

3. *Results and discussion*

It was noted above that the introduction of substituents of different electronic nature into the ligand component affects the reactivity of the inhibitor. In the Me-complexes we have synthesized, the ligand environment includes trifluoromethyl or tetrafluoroethoxy groups (Fig. 1).

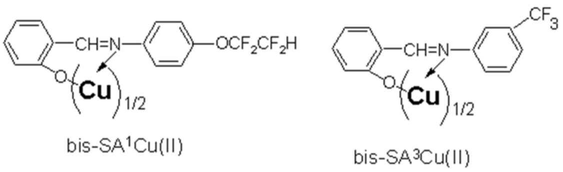

Fig.1. Structural formulas of substituted of *bis*-salicylaldiminat copper (II) complexes

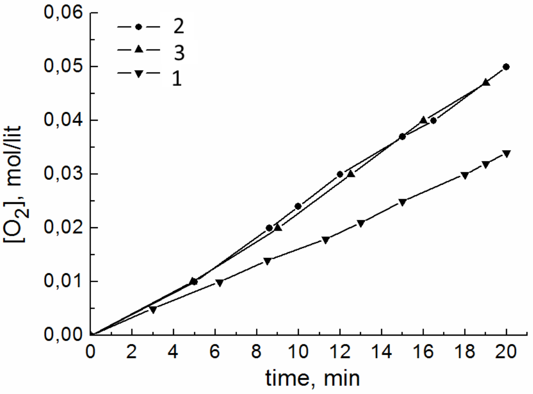

Fig. 2. Kinetic curves of oxygen absorption with initiated (W_i = 5.13·10^{-7}mol/lit·s) cumene oxidation (T = 343 K, P(O$_2$) = 0.08 MPa): 1 – [*bis*-SACu(II)] = 0 mol/lit, 2 – [*bis*-SA^{3}Cu(II)] = 1·10^{-3} mol/lit, 3 – [*bis*-SA^{1}Cu(II)] = 1·10^{-3} mol/lit

The trifluoromethyl group CF_3 is a strong acceptor with the Hammett inductive constant $\sigma_i = 0.43$. The tetrafluoroethoxy group is weaker in its influence – the σ_i value is 0.34 with a slight mesomeric effect.

To study inhibitory activity of *bis*-SACu(II) complexes we analyzed the process of cumene initiated oxidation in the presence of these complexes. Kinetic patterns of the relationships are presented in Fig. 2.

Analysis of kinetic curves (Fig. 2) allows us to conclude that in the “cumene – *bis*-SACu(II)” system the last component exhibits catalytic properties. Reactions of Me-complexes with hydroperoxides make the main contribution to the chain balance at the initiation stage. [4]. Hydroperoxide enters into one-electron redox reactions with the central atom of the complex:

$$Cu^{2+} + ROOH \rightarrow ROO^{\bullet} + H^{+} + Cu^{+} \quad (3)$$

$$Cu^{+} + ROOH \rightarrow RO^{\bullet} + {}^{-}OH + Cu^{2+} \quad (4)$$

It has been shown [4, 13] that the decomposition of hydroperoxide is preceded by the formation of a labile complex between the Me-complex and hydroperoxide as an intermediate compound. The coordination sphere of the central atom most often includes one hydroperoxide molecule [4]. Thereby, each molecule of the Me-complex takes a catalytic part in the decomposition of hydroperoxide[4, 8].

It should be noted that some copper complexes can manifest themselves in both antioxidant and prooxidant mechanisms of action [14].

When the concentration of the *bis*-SA^{1}Cu(II) complex increased by 10 times, no induction period was observed on the kinetic curve of cumene oxidation (Fig. 3a). The initial oxidation rate was not changed as well. Increasing oxygen pressure in the cumene - *bis*-SA^{1}Cu(II) system from 0.08 to 0.1 MPa doesn’t lead to a change in the initial oxidation rate (Fig. 3b). The obtained results allowed us to conclude that *bis*-SACu(II) complexes cannot inhibit aromatic hydrocarbon oxidation.

It was shown [15] that the chain-radical oxidation of alcohols at 80-110 °C is inhibited by copper complexes of the general composition CuL$_2$. Therefore, in the further study of the inhibitory properties of *bis*-SACu(II) complexes, we used benzyl alcohol as a substrate.

Oxidation properties of peroxyl radicals are presented by one-electron transformation [16]:

$$HOO^{\bullet} + M^{n} \rightarrow HOO^{-} + M^{n+1} \quad (5)$$

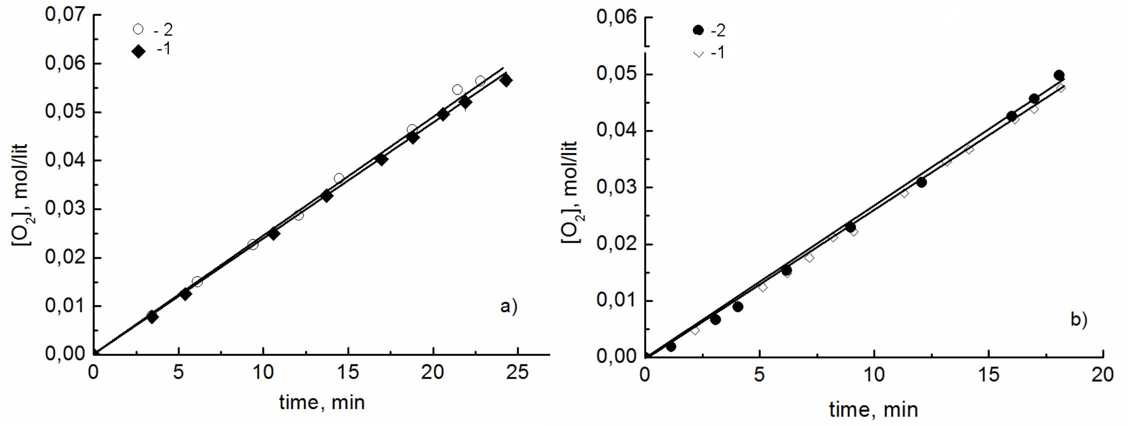

Fig. 3. Kinetic curves of oxygen absorption with initiated (W_i = 5.13·10^{-7}mol/lit·s) cumene oxidation in the presence of *bis*-SA^{1}Cu(II) = 1·10^{-3} mol/lit, T = 343 K: a) 1 – [*bis*-SA^{1}Cu(II)] = 1·10^{-3} mol/lit, 2 – [*bis*-SA^{1}Cu(II)] = 1·10^{-2} mol/lit; b) 1 – P(O_2) = 0.08 MPa, 2 – P(O_2) = 0.1 MPa.

$$>C(OO^{\bullet})X + M^n \rightarrow >C(OO^-)X + M^{n+1}, \quad (6)$$

where X: OH, NH_2, NHR, NR^1R^2, CH_3, C_6H_5, NHC(O)R, SR (R,R^1, R^2 – alkyl).

Reduction properties of $HOO^{\bullet}$ and >C(OO$^{\bullet}$)X radicals in solutions are determined by the reactions [16]:

$$HOO^{\bullet} + M^{n+1} \rightarrow H^+ + M^n + O_2 \quad (7)$$

$$>C(OO^{\bullet})X + M^{n+1} \rightarrow >C^+X + M^n + O_2 \quad (8)$$

The energy of stabilization of the carbonium center resulting from the interaction with *p*- or *π*-electrons of substituent X, promotes the occurrence of reaction (8).

When studying the mechanism of oxidation of benzyl alcohol [17, 18], it was shown that the transmitters of the oxidation chains of benzyl alcohol are both peroxyl radicals, which have not only oxidative but also reducing properties (due to the presence of a hydroxyl group in the α-position to the peroxyl group), and hydroperoxyl $HOO^{\bullet}$ radicals which are capable of participating in the chain termination reaction due to the exchange of a radical with a hydrogen atom:

$$HOO^{\bullet} + {}^{\bullet}OOR \rightarrow O_2 + HOOR \quad (9)$$

The presence of of hydroperoxyl radicals in the reaction explains inhibitory properties of hydrogen peroxide in the liquid-phase initiated radical-chain aerobic oxidation of cumene [19]. The reaction (9) along with the reactions (7) and (8) should be taken into account when explaining the action of copper complexes in the oxidation process of benzyl alcohol. The large role of $HOO^{\bullet}$ radicals may indicate that when considering the contributions of the reactions (7) and (8), preference should be given to the reaction (7).

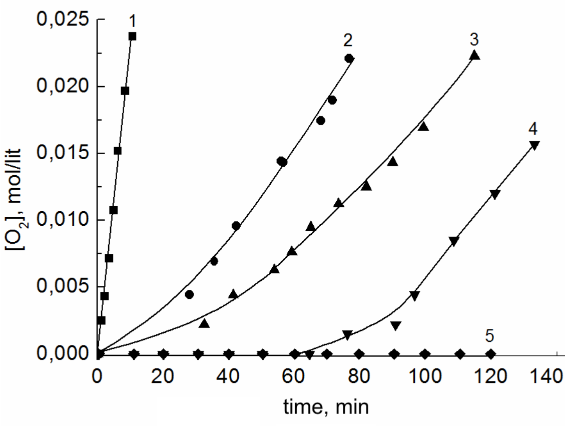

Fig. 4. Kinetic curves of oxygen absorption with initiated benzyl alcohol oxidation (W_i = 1·10^{-6}mol/lit·s) in the presence of *bis*-SA^{1}Cu(II), T = 343 K, *P*(O_2) = 0.09 MPa: 1 – [*bis*-SA^{1}Cu(II)] = 0 mol/lit; 2 – [*bis*-SA^{1}Cu(II)] = 1.3·10^{-4} mol/lit; 3 – [*bis*-SA^{1}Cu(II)] = 2,6·10^{-4} mol/lit; 4 – [*bis*-SA^{1}Cu(II)] = 2.6·10^{-4} mol/lit in 3 days; 5 – [*bis*-SA^{1}Cu(II)] = 2.6·10^{-4} mol/lit in 21 days

The kinetic curves obtained of the initiated oxidation of benzyl alcohol in the presence of the *bis*-SA^{1}Cu(II) complex show clearly defined induction periods (Fig. 4). The induction period shortens as the initial concentration of the *bis*-SA^{1}Cu(II) complex decreases. It was determined that the induction period is influenced by the time from the moment of dilution of copper complexes in benzyl alcohol to the start of measurements. So, with [*bis*-SA^{1}Cu(II)] = 2.6·10^{-4} mol/lit, the induction periods are 26 and 84 minutes, respectively, after 10 minutes and 3 days from the moment of preparation of the solution (Table 1). When the [*bis*-SA^{1}Cu(II)] = 2.6·10^{-4}

Table 1. Theoretical (τ_t) and experimental (τ_{ex}) periods of induction and inhibition factors (f_{obs}) observed for *bis*-SACu(II) complexes

[*bis*-SACu(II)], mol/lit	τ_t, min	τ_{ex}, min	f_{obs}	Time between preparation of solutions and start of measurements
bis-SA^{1}Cu(II)				
$1.3\cdot10^{-4}$	2	16	8	10 min
$2.6\cdot10^{-4}$	4	26	6.5	10 min
$2.6\cdot10^{-4}$	4	84	21	3 days
$2.6\cdot10^{-4}$	4	-	-	21 day
bis-SA^{3}Cu(II)				
$1.3\cdot10^{-4}$	2	27	13.5	10 min
$0.9\cdot10^{-4}$	1.5	25	17	2 days
$0.8\cdot10^{-5}$	0.13	8	62	3 days
$0.75\cdot10^{-6}$	0.0125	4	320	3 days

mol/l solution was stored without air access for 21 days, no initiated oxidation of benzyl alcohol was observed within 120 min (Fig. 4).

When studying the inhibitory activity of the *bis*-SA^{3}Cu(II) complex in a model reaction of benzyl alcohol initiation oxidation, it was found that the *bis*-SA^{3}Cu(II) complex inhibits stronger than *bis*-SA^{1}Cu(II) one (Table 1).

It was shown that the induction period of the *bis*-SA3Cu(II) complex depends on the initial concentration of the complex; and with [*bis*-SA3Cu(II)] = $0.8\cdot10^{-5}$ mol/l (after 3 days) a slight inhibitory effect is already observed (Fig. 5).

The theoretical and experimental induction periods and observed inhibition factors are presented in Table1. The experimental induction periods were obtained from kinetic curves as the points of intersection of tangents to curves with the abscissa axis. The theoretical induction periods for $f = 1$ and inhibition factors were calculated according to formulas (10, 11) for $W_i = 1\cdot10^{-6}$ mol/lit·s:

$$\tau = f \cdot [\mathrm{In}H]/W_i, \quad (10)$$

$$f_{obs} = \tau_{ex}/\tau_t, \quad (11)$$

where f_{obs} are the observed inhibition factors, τ_t is the theoretical induction periods, τ_{ex} is the experimental induction periods.

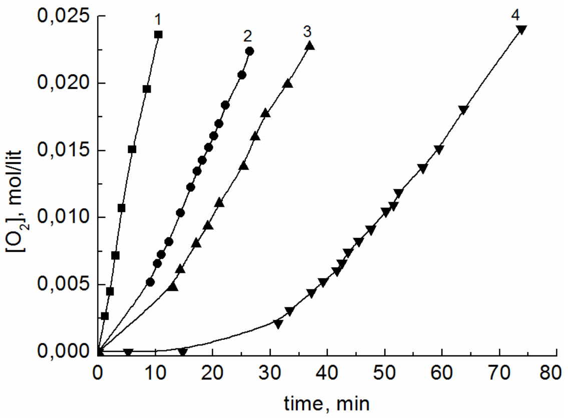

Fig. 5. Kinetic curves of oxygen absorption with initiated ($W_i = 1\cdot10^{-6}$mol/lit·s) benzyl alcohol oxidation, in presence of *bis*-SA^{3}Cu(II), T = 343 K, $P(O_2)$ = 0.09 MPa: 1 – [*bis*-SA^{3}Cu(II)] = 0 mol/lit; 2 – [*bis*-SA^{3}Cu(II)] = $0{,}75\cdot10^{-6}$ mol/lit in 3 days; 3 – [*bis*-SA^{3}Cu(II)] = $0{,}8\cdot10^{-5}$ mol/lit in 3 days; 4 –[*bis*-SA^{3}Cu(II)] = $0{,}9\cdot10^{-4}$ mol/lit in 2 days.

4. Conclusions

Analysis of the studies showed that in the examined cumene – *bis*-SACu(II) systems, the complexes exhibited catalytic properties even at a large concentration (0.01 mol/lit). Catalytic activity depends on the structure of *bis*-SACu(II).

In the benzyl alcohol – *bis*-SACu(II) systems, the complexes participate in catalytic termination of chains. The inhibiting activity is reduced in a row: *bis*-SA^{3}Cu(II) > *bis*-SA^{1}Cu(II) and depends on the initial concentration of the complexes (it is increased when their concentration is increased) as well as on the storage time of benzyl alcohol – *bis*-SACu(II) solutions (it is increased when the storage time is increased).

In practical applications, the studied compounds can be used as stimulants for the combustion of hydrocarbon fuels and effective inhibitors of alcohol oxidation.

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