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Kinetics and mechanism of the oxidation of dithiocarbamic acids in the presence of Co(II) phthalocyaninetetacarboxylic acid

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Abstract: The present work contains kinetic data of the oxidation of sodium diethyldithiocarbamate in the presence of phthalocyanine catalysts. It is shown that the nature of the peripheral substituent has a great influence on the self--association of phthalocyanines and on their catalytic activity. A mechanism of the oxidation of sodium diethyldithiocarbamate involving the formation of a triple complex of the substrate, the reduced form of the catalyst and oxygen is offered. It is also shown that the oxidation mechanism of dithiocarbamic acids is different from that for cysteine.

Keywords: Co(II)phthalocyanines; catalysts; oxidation; kinetics; mechanism.

INTRODUCTION

Phthalocyanine metal complexes are widely used as models of enzyme active sites responsible for aerobic catalytic oxidation, such as catalysts in the oxidation of various organic substrates, decomposition of hydrogen peroxide and other catalytic processes.[1–4]

Aliphatic and aromatic mercaptans (RSH) are important organic sulfur compounds contained in petroleum products. Mild oxidation of mercaptans allows disulfides, used in the vulcanization of rubbers and the manufacture of pharmaceuticals, of high purity to be obtained.[5–7]

Complexes of transition metals with substituted phthalocyanines are common catalysts in the selective homogeneous oxidation of mercaptans.[1] The Merox process[8–10] that is based on cobalt and iron complexes with phthalocyanine tetrasulfonic acid was established in 1964 and modifications of it are still used. The process proceeds according to Eq. (1):

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$$4RSH + O_2 \rightarrow 2RSSR + 2H_2O \quad (1)$$

Realization of liquid-phase Merox process with high efficiency is complicated by existence of associative processes of water-soluble phthalocyanine metal complexes.[10–13]

Increasing of catalysis efficiency in reaction (1) is complicated by a number of significant contradictions concerning the mechanisms of the process known from the literature.[14–21] Meanwhile, theoretical aspects of metallophthalocyanines functioning as catalysts, the mechanisms of catalysis, the influence of structure and associative state of the macrocycle in solution on the kinetic characteristics of reaction (1) are fundamentals for the chemistry of phthalocyanine catalysts. Wide opportunities exist for the modification of the phthalocyanine macrocycle by the introduction of peripherial substituents differing in structure and function, the nature of central metal and the existence of processes of additional axial coordinated ligands, thereby providing the possibility of controlling the rate and selectivity of processes catalyzed by phthalocyanines.

The mechanisms of homogeneous oxidation[14,17,21] of RSH compounds in the presence of phthalocyanine metal complexes have the main idea of coordinative interaction between the macrocycle, the oxidant and the substrate. Simultaneously, acknowledging the decreasing effect of association on the catalytic activity of metal phthalocyanines, not many authors[22–25] have studied the effect of association on the oxidation mechanism, which, in our opinion, is very important.

Some authors[14,15] proposed that the mechanism of RSH oxidation is radical–ionic, in which the oxidation degree of the central metal cation of the phthalocyanine molecule is reduced:

$$RS^- + Co^{III}Pc \underset{\longleftarrow}{\overset{\text{slow}}{\longrightarrow}} RS^\bullet + Co^{II}Pc$$

or (2)

$$RS^- + Co^{II}Pc \underset{\longleftarrow}{\overset{\text{slow}}{\longrightarrow}} RS^\bullet + Co^{I}Pc$$

$$2RS^\bullet \xrightarrow{\text{rapid}} RSSR \quad (3)$$

$$Co^{I}Pc \xrightarrow{O_2} Co^{II}Pc \xrightarrow{O_2} Co^{III}Pc \quad (4)$$

where CoPc is macrocycle, RS^- thiolate ion and RSSR disulfide.

In our opinion, the implementation of this mechanism is complicated. The mechanism described above suggests the possibility for the formation of disulfides in an inert atmosphere according to reaction (2), essentially independent of the state of the coordination unit of the metallophthalocyanine molecule. According to this mechanism, the change in the catalytic activity of different derivatives of cobalt phthalocyanine should be minor. However, the data obtained for sod-

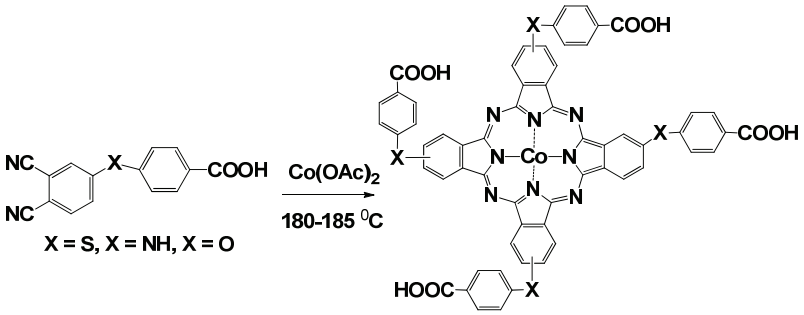
ium diethyldithiocarbamate (DTC) oxidation in the presence of phthalocyanine catalysts is in disagreement with this mechanism.

This scheme has significant limitation for catalysis caused by the state of mercaptan as ions. Dissociation of mercaptan according to Eq. (5) proceeds in aqueous-alkali solutions only when the pH is >8. This imposes an additional mechanistic step.

$$RSH \rightleftarrows H^+ + RS^- \quad (5)$$

The ascertainment of the relationship between the associative state of a macrocyclic structure in solution and catalytic activity would enhance the understanding of the mechanisms of catalysis and enable recommendations to be made to obtain new liquid-phase catalytic systems based on metallophthalocyanines.

An attempt to ascertain the relationship between the nature of peripheral substitution, aggregation and catalytic activity in reaction (1) for cobalt complexes with water-soluble phthalocyanines (Scheme 1) is described in the present work.



Scheme 1 Metallophthalocyanines.

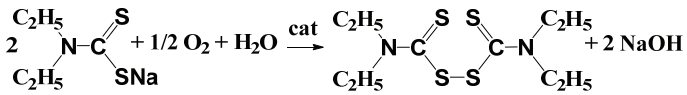
EXPERIMENTAL

Phthalocyanines synthesis

Three phthalocyanines were synthesized by the template synthesis method from the corresponding phthalodinitriles,[21] *i.e.*, cobalt tetrakis[(4-carboxyphenyl)amino]phthalocyanine (CoPc(NH)), cobalt tetrakis[(4-corboxyphenyl)sulfanyl]phthalocyanine (CoPc(S)) and cobalt tetrakis[(4′-carboxyphenyl)oxy]phthalocyanine (CoPc(O)) (Scheme 1). Characterization data for the synthesized phthalocyanines are given in the Supplementary material to this paper.

Kinetic studies

The oxidation reaction of sodium diethyldithiocarbamate was chosen as a model reaction of the process (1). It proceeds according to the general Scheme 2.



Scheme 2. Oxidation of DTC.

The advantages of this reaction are low toxicity of the initial materials, possibility to observe the concentration of the initial and desired materials and identification of reaction products using electron absorption (UV–Vis) and IR spectroscopic methods. The experiments to study the kinetics of sodium diethyldithiocarbamate (DTC) oxidation were realized in a thermostatic cell into which 650 mL of DTC was loaded.

The air required for oxidation was fed into the cell *via* a micro compressor at a constant rate of 2 L min^{-1}. Under these conditions, the reaction occurs in the kinetic region.[26] After reaching a constant temperature, the reaction mixture was mixed and sample of 2 mL was taken to determine initial concentration of DTC, then the compressor was turned on. This moment was taken as the beginning of the reaction. Samples of 2 mL were taken periodically during the experiment to determine current concentration of DTC. The concentration of DTC was monitored spectrophotometrically at a wavelength of 440 nm.

Under conditions of constant concentrations of oxygen and catalyst, and constant pH of the solution, the rate of DTC oxidation is described by the first order kinetic equation.

$$dc/dt = -k_{obs}c$$

where c is DTC concentration, t time and k_{obs} observed rate constant, s^{-1}.

The first order kinetics was confirmed by the straightness of graphics in coordinates $\ln c - t$ and the constancy of rate constants calculated according to the equation:

$$k_{obs} = (1/t)\cdot\ln(c_0/c_\tau)$$

where c_0 is the initial concentration of DTC, and c is the concentration of DTC at time t.

Degree of transformation was calculated according to the equation:

$$\chi_{RSSR} = (c_0 - c_\tau)/c_0$$

RESULTS AND DISCUSSION

The kinetic curves for DTC oxidation in presence of CoPc(NH), CoPc(S), CoPc(O) are presented in Fig. 1.

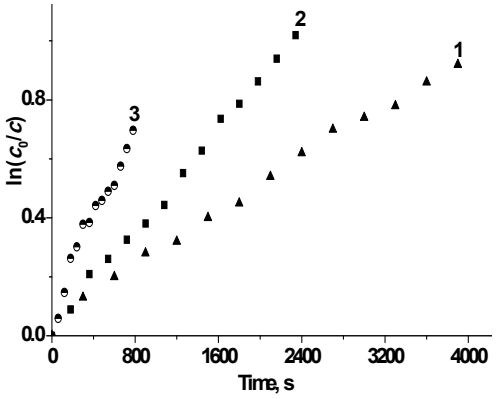


Fig. 1. Kinetic curves of DTC oxidation at 298.15 K, pH 8.2 in the presence of homogeneous phthalocyanine catalysts (c = = 8×10^{-5} M): 1) CoPc(O); 2) CoPc(NH) and 3) CoPc(S).

The structures of the investigated compounds are distinguished by the nature of the spacer atom linking the macrocycle with the functional group of the substituent. Data of Fig. 1 shows that the kinetic curves of DTC oxidation differ. Previously,[22] it was found that in the absence of catalyst, the reaction proceeds

slowly with k_{obs} of 1.7×10^{-5} s^{-1}. The totality of the data suggests the impossibility of DTC oxidation according the above mechanism (Eqs. (2–4)) because oxidation is slow even in excess of oxygen and there is no disulfide formation according to Eq. (2) in an inert medium. It is also matched with available literature data.[17–19]

Meanwhile, there is information in the literature[1,2] about the formation of a triple complex (Eqs. (6–9)), with further RS radical cleavage involved. This mechanism is indirectly confirmed by the data of Fig. 1:

$$RS^- + Co^{II}Pc \underset{}{\overset{K_1}{\rightleftharpoons}} RS^\bullet \cdot Co^{I}Pc \quad (6)$$

$$RS^\bullet \cdot Co^{I}Pc + O_2 \overset{K_2}{\rightleftharpoons} RS^\bullet \cdot Co^{II}Pc \cdot O_2^- \quad (7)$$

$$RS^\bullet \cdot Co^{II}Pc \cdot O_2^- + H_2O \xrightarrow{k_3,\ \text{slow}} RS^\bullet + H_2O \cdot Co^{III}Pc \cdot O_2^{2-} \quad (7a)$$

$$H_2O \cdot Co^{III}Pc \cdot O_2^{2-} \xrightarrow{2H^+,\ k_4} Co^{II}Pc + H_2O + 2OH^- \quad (8)$$

$$2RS^\bullet \xrightarrow{\text{Instantaneous}} RSSR \quad (9)$$

According to this mechanism, the effect of the nature of a peripheral substituent on the catalytic activity of the macrocycle will definitely depend on heteroatom effects, affecting the metal cation of the phthalocyanine molecule, which in turn determines the stability of the triple complex (Eqs. (7) and (7a)). The associative state and axial coordination processes of the ligands in solution were investigated to determine the laws of the peripheral substitution effect on the macrocycle.

It is known that carboxyl derivatives of metallophthalocyanines dimerize in aqueous solutions due to overlapping of the π-electron systems of two macrocycles forming a π–π dimer.[11,12] It is easy to observe the associative state of metallophthalocyanines using electronic absorption spectroscopy because of differences in the positions of absorption bands of monomeric and associated macrocycle forms.[26,27]

The electronic absorption spectra of aqueous alkali solutions of investigated macrocycles are shown in Fig. 2.

Matching of the absorption Q-band maximum and the width of the spectrum in Fig. 2 with literature data[11–13] indicates the dimerization of CoPc(O) and CoPc(S) macrocycles, whereas CoPc(NH) is almost monomeric. There are significant spectral changes on addition of pyridine, an axially coordinated ligand to solutions of CoPc(O) and CoPc(S) phthalocyanines. An example is presented in Fig. 3.

The significant bathochromic shift in the absorption of the Q-band (by 50 nm) and an increase in the absorption intensity indicate the dissociation of CoPc dimers and the formation of the monomeric form presented by the axial complex with pyridine. Similar values of the stability constants of the molecular com-

plexes of CoPc(S) and CoPc(NH) with pyridine indicate similar states of the coordination units of the macromolecules. This fact suggests a weak effect of the nature of peripheral substitution on the π-electronic structure of the monomeric macrocycle.

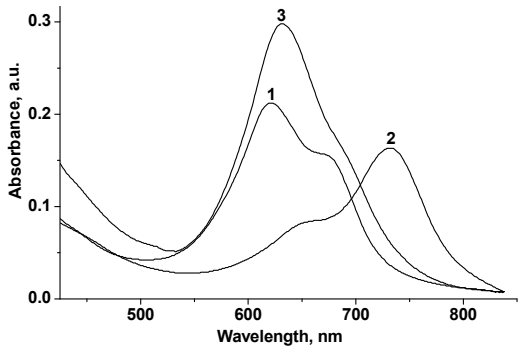


Fig. 2. UV–Vis spectra of aqueous-alkali solutions at 298.15 K, pH 9 (c = 5×10^{-5} M): 1) CoPc(O); 2) CoPc(NH); 3) CoPc(S).

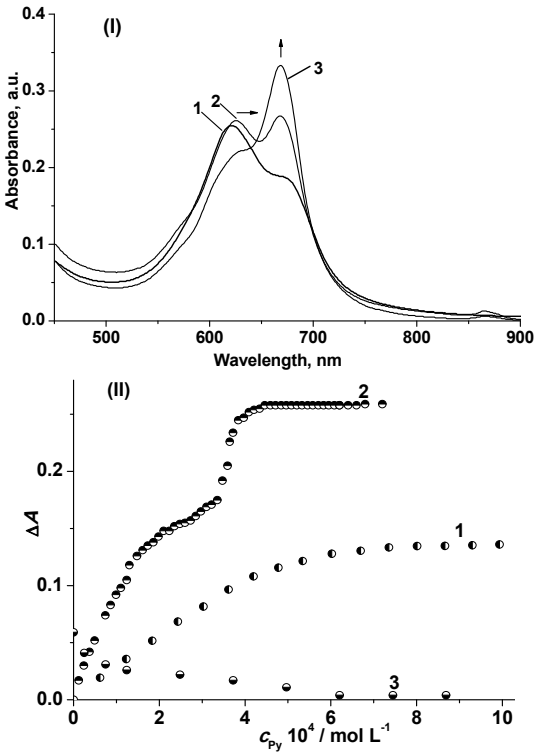


Fig. 3. I) UV–Vis spectra of CoPc(O) aqueous-alkali solution at 298.15 K, pH 9 (c = 6×10^{-5} M): 1) without pyridine, 2) c_{Py} = 1.9×10^{-4} M and 3) c_{Py} = 6.3×10^{-4} M; II) titration curves of phthalocyanine solutions (Q-band; c = 5×10^{-5} M) with pyridine 1) CoPc(O) (λ = 663 nm), 2) CoPc(S) (λ = 675 nm) and 3) CoPc(NH) (λ = 730 nm).

The reason for the difference in the catalytic activities becomes obvious when matching the obtained data of coordination interactions of studied macrocycles with the mechanism of the reactions (6)–(9). Redistribution of the electron

density within the macrocycle is due to the influence of the electronic effect of the substituent. A nitrogen atom in peripheral substituents promotes a shift of the electronic density to the macrocycle. This impedes coordination of pyridine (or substrate) and decreases the catalytic activity of the macrocycle. On the contrary, a sulfur atom promotes a shift of the electronic density from the macrocycle that increases the probability of pyridine–phthalocyanine coordination interactions and partially compensates for the deficit of electronic density caused by the association of metallophthalocyanines. The lower value of the stability constant of the CoPc(O) complex with pyridine (Table I) is caused by the impossibility of compensation of the lack of electronic density on the central metal cation. This is explained by the lower electron-donating ability of the oxygen atom compared to the sulfur atom.

TABLE I. Stability of molecular complexes with pyridine and catalytic activity in the oxidation of DTC for CoPc (c = 5×10^{-5} M) at 298.15 K, pH 9; K is the thermodynamic stability constant of Py-complex, k_{obs} is the observed constant of the DTC oxidation rate (determination of the constant is described in experimental part) and χ_{RSSR} is the degree of the DTC transformation to the disulfide

Macrocycle	K / L mol^{-1}	k_{obs}×10^5 / s^{-1}	χ_{RSSR} / %
CoPc(O)	1900±200	17±4	84.32
CoPc(S)	3200±300	85±3	92.15
CoPc(NH)	3200±300	38±6	83.61

It should be noted that UV–Vis spectra of investigated macrocycle solutions do not have bands characteristic of Co^{III}Pc.[17,28] This confirms the stability of initial state of Co^{2+} and hence the highest probability of the processes (Eqs. (6)–(9)).

The parameters k_{obs} and χ_{RSSR} for DTC oxidation under standard conditions are given in Table I. Kinetic research of DTC oxidation in dependence on the pH of solution shows a lack of linear correlation between pH and effective rate constant of DTC oxidation, Fig. 4.

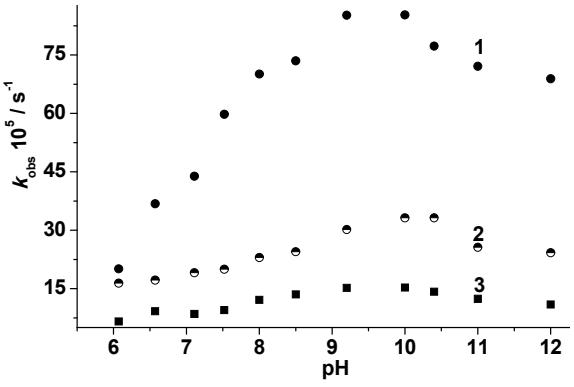


Fig. 4. Dependence of DTC oxidation rate on pH of medium in presence of phthalocyanine catalysts (c = 4.5×10^{-5} M): 1) CoPc(S), 2) CoPc(NH) and 3) CoPc(O).

The maximal activity of the catalysts was reached when pH values were in the range 9 to 10. This could be caused by a shift in the balance of Eq. (2) toward the thiolate ion. Increasing of solution basicity did not lead to an increase in the activity, on the contrary, it decreased the effective rate constant of oxidation. This is the result of competition between RS^- and OH^- for the central metal cation of the phthalocyanine molecule. Based on spectral data described above and the stability of the cobalt cation ($Co^{II}Pc$) contained in macrocycle, it could be concluded that the stage denoted by Eq. (2) could not be observed. In case of its processing, there is joint coordination of the two ligands (RS^- and OH^-) on one side of macrocycle accompanied by the formation of a stable axial complex due to compensation for the deficiency of electronic density on the central metal cation of the phthalocyanine molecule, which is known from the literature.[29] Similar changes for the sulfonic acids of cobalt phthalocyanines were previously observed.[30,31] In addition, it was shown[32,33] on the example of the tetrasulfonic acid of cobalt phthalocyanine and various substrates (2-mercaptoethanol and cysteine) that the increase in the reaction rate is caused by auto-oxidation processes of the substrate in alkali solutions. The highest activity of these catalysts was found in the pH range of 12–13, caused by the higher acidity of the sulfonic group compared to the carboxyl group.

Obviously, the maximum of reaction rate will be observed in pH range wherein the concentration of labile oxygen adducts is maximal and the balance (5) is shifted toward the formation of free thiocarbamic acid. In this case, all the catalyst is converted to an intermediate that is presented by oxidized thiocarbamic acid located in the outer coordination sphere and forms hydrogen bonds with coordinated oxygen molecules. There is a further transfer of the charge from the metal to oxygen. Increasing the pH leads to rivalry between DTC coordination and dimerization processes due to intensification of the latter one. It complicates the transfer of electrons. The process of electrons transfer to cobalt sulfophthalocyanines in aqueous alkali solutions was previously studied in detail.[34] There are transitions $CoPc^{II} \rightarrow CoPc^{I}$ and transfer of electrons from hydroxyl ion to monomeric CoPc in deaerated solutions when a detergent at concentrations in the range 10^{-2}–10^{-3} M is introduced into the system:

$$Co^{II}Pc + OH^- \rightleftarrows Co^{II}P_c \cdots OH^- \quad (10)$$

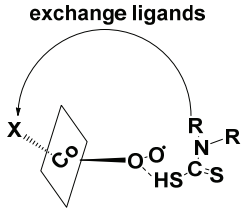
$$Co^{II}Pc \cdots OH^- + M \rightleftarrows Co^{I}P_c + \text{product} \quad (11)$$

where M is an acceptor of OH radical. There is no such process for associated phthalocyanine structures, *i.e.*, when no detergent is present.

Furthermore, it was found that the phthalocyanine may be an acceptor of OH radicals.[34] For this reason, it was assumed that electron transfer might be implemented in the reaction of complex $CoPc^{II}\cdots OH^-$ with other hydroxyl ions:

$$(CoPc^{II}\cdots OH^-)_2 + OH^- \rightarrow CoPc^{I}\cdots CoPc^{II}\cdots OH^- + O^- + H_2O$$
$$CoPc^{I} + O_2 \rightarrow CoPc^{II} + O_2^-,\ CoPc^{II} + O_2 \rightarrow CoPc^{III} + O_2^-$$

With an excess of oxygen, there is permanent formation of O_2^- and oxidized forms of $CoPc^{III}$ that impedes triple complex formation under conditions of increased content of hydroxyl ions in solution and decreases the catalytic activity of phthalocyanine. It is also characteristic of the systems studied herein. Obviously, there is an exchange between DTC and ligand coordinated by phthalocyanine (Scheme 3), which can be presented by solvent or molecular oxygen.[35] The exchange depends essentially on the electron-donor power of the second ligand, *i.e.*, for ions, on their basicity.



Scheme 3. Exchange of ligands in the triple complex; X: solvent.

The kinetic model may be analyzed by adopting in Eqs. (6–9), A for RS^-, M for $Co^{II}Pc$, X_1 for $RS^{\bullet}\cdot Co^{I}Pc$, B for O_2, X_2 for $RS^{\bullet}\cdot Co^{II}Pc\cdot O_2^-$, X_3 for $Co^{III}Pc\cdot O_2^{2-}$, D for $RS^{\bullet}$ and their concentrations for c with the corresponding index.

The sum of concentrations of all complexes (c_M^o / mol L^{-1}) containing catalysts is calculated according to:

$$c_M^o = c_M + c_{X_1} + c_{X_2} \quad (12),$$

where c_M is the concentration of proper catalyst (mol L^{-1}), c_{X_1} the concentration (mol L^{-1}) of $RS^{\bullet}\cdot Co^{I}Pc$ and c_{X_2} the concentration (mol L^{-1}) of $RS^{\bullet}\cdot Co^{II}Pc\cdot O_2^-$.

Hence, the function of catalyst complexation takes the form:

$$f(M) = c_M/c_M^o \quad (13)$$

$c_{X_1} = K_1 c_M c_A$, $c_{X_2} = K_2 c_{X_1} c_B^o$, under condition of $c_B^o >> c_A^o$ and assuming that steps (6) and (7) are in quasi-equilibrium before the slow step (7a), one obtains:

$$c_{X_2} = K_1 K_2 c_M c_A c_B^o \quad (14),$$

where c_A is the concentration (mol L^{-1}) of RS^- and c_B^o is the initial concentration of oxygen (mol L^{-1}).

The rate (r / mol L^{-1} s^{-1}) of the limiting stage (Eq. (7a)) is calculated by the following:

$$r = k_3 c_{X_2} \quad (15)$$

Taking into account Eq. (14) it follows:

$$r = k_3 K_1 K_2 c_M c_A c_B^o \quad (16)$$

The concentration of catalyst, c_M, is substituted by c_M^o and the final equation for calculation of the rate of DTC oxidation is given by:

$$r = c_A \frac{k_3 K_1 K_2 c_M^o c_B^o}{1 + K_1 c_A + K_1 K_2 c_B^o c_A} \quad (17)$$

The function $f(M)$ is linear with increasing concentration c_A. Possible deviation from the linearity is caused by a decreasing of concentration c_B^o. Equation (17) is linear in Lineweaver–Burk coordinates:[36]

$$\frac{1}{r} = \frac{1}{c_A k_3 K_1 K_2 c_M^o c_B^o} + \frac{1}{k_3 K_2 c_B^o c_M^o} + \frac{1}{k_3 c_M^o} \quad (18)$$

Under the condition of $K_1 K_2 c_A c_B^o << (1 + K_1 c_A)$, one has:

$$r = c_A \frac{k_3 K_1 K_2 c_M^o c_B^o}{1 + K_1 c_A} \quad (19)$$

The dependence $c_A = f(\tau)$ in this case takes the form:

$$\frac{K_1}{c_M^o c_B^o K_1 K_2} \ln \frac{c_A^o}{c_A} + \frac{1}{c_M^o c_B^o K_1 K_2} = \tau \quad (20)$$

The function ln c_A–τ has linear character. It is matched with experimental data of aerobic DTC oxidation kinetics. Thus, the most plausible mechanism of DTC oxidation is the set of sequential reactions (6)–(9). It should be noted that application of the Michaelis–Menten kinetics and its Lineweaver–Burke linearization to this system was realized[33] in the context of cysteine oxidation. However, the previous model ignored the formation of a triple complex. In this case, varied interpretation of mercaptans, thiocarbamic acids and cysteine oxidation mechanisms appears. This may be explained by the lack of coordination activity of DTC because of its low basicity compared to mercaptan. Nonlinearity of the dependence of the DTC oxidation rate on temperature observed in the temperature range of 273.15–313.15 K is most likely caused by a change of the limiting stage at system saturation. These experimental data are consistent with known results.[37]

CONCLUSION

New derivatives of cobalt phthalocyanine are synthesized. Their catalytic activity in aerobic oxidation of sodium diethyldithiocarbamate is studied. The influence of nature of peripheral substituent on catalytic activity of catalyst is established. The catalytic activity of phthalocyanines increases depending on the nature of the spacer bridge. The activity increases according to the following:

CoPc(S) > CoPc(NH) > CoPc(O). The mechanism of sodium diethyldithiocarbamate oxidation limited by the stage of $RS^{\bullet}$ formation is proposed. This mechanism is in good agreement with the experiment. The data obtained are fundamental for understanding the mechanism of metallophthalocyanines catalytic action in oxidation of mercaptans and further development of efficient catalysts.

SUPPLEMENTARY MATERIAL

Characterization data for the synthesized phthalocyanines are available electronically at the pages of journal website: http://www.shd.org.rs/JSCS/, or from the corresponding author on request.

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ИЗВОД

КИНЕТИКА И МЕХАНИЗАМ ОКСИДАЦИЈЕ ДИТИОКАРБАМИНСКИХ КИСЕЛИНА У ПРИСУСТВУ Co(II) ФТАЛОЦИЈАНИНТЕТРАКАРБОКСИЛНЕ КИСЕЛИНЕ

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Предмет овог рада је одређивање кинетичких параметара оксидације натријум-диетилдитиокарбамата у присуству фталоцијанинских катализатора. Показано је да природа периферних супституената има велики утицај на самоуређење фталоцијанина и њихову каталитичку ативност. Предложен је механизам оксидације натријум-диетилдитиокарбамата који укључује формирање троструког комплекса супстрата, редуковане форме катализатора и кисеоника. Такође је показано да се механизам оксидације дитиокарбаминских киселина разликује од механизма оксидације цистеина.

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