

CATALYSIS

Synthesis and Catalytic Properties of Copper(II) 1-Aryl-5-Benzothiazolylformazanates

Yu. A. Gorbatenko, I. G. Pervova, G. N. Lipunova, T. I. Maslakova,
I. N. Lipunov, and G. I. Sigeikin

Ural State Forestry Engineering University, Yekaterinburg, Russia

Ural State Technical University, Yekaterinburg, Russia

Interdepartmental Center for Analytical Investigations in Physics, Chemistry, and Biology,
Presidium of the Russian Academy of Sciences, Moscow, Russia

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Abstract—New copper(II) benzothiazolylformazane complexes were synthesized and immobilized on AN-18 anion exchanger. The influence of the composition of the coordination core of copper(II) benzthiazolylformazanates and temperature on their catalytic properties in decomposition of H_2O_2 and oxidation of Na_2S in aqueous solution was studied.

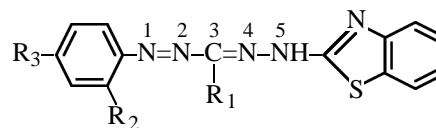
Development of heterogenized catalysts with a high concentration of active centers of known composition is an efficient way to obtain stable catalysts with a good reproducibility and high activity. The composition of active centers of such catalysts is similar to that of active centers of homogeneous catalysts; however, the active centers themselves are chemically bound with one or more ligands fixed on an insoluble support. Such complex catalysts combine properties of both homogeneous complexes (possibility of varying the type of the central atom and its ligand environment) and heterogeneous systems (formation of coordination-saturated structures on the support surface [1]). Ion exchangers of various types are widely used as solid supports. Their modification with functional complexing groups allows synthesis of new catalysts [2].

Anion exchangers with hetarylformazane groups have been prepared previously [3, 4], and it was shown that the formazan structure and the synthesis procedure substantially affect the catalytic activity of metal-formazan complexes in decomposition of H_2O_2 in aqueous solutions and liquid-phase oxidation of Na_2S .

In this study, we prepared certain copper(II) benzothiazolylformazanates and examined their composition and catalytic properties at various temperatures in the same reactions.

EXPERIMENTAL

To synthesize copper(II) complexes to be immobilized on the polymeric support, we used 1-aryl-3-alkyl-5-benzothiazolylformazans **I–III**:



where R_1 , R_2 , R_3 are CH_3 , H, 4- SO_3H (**I**); CH_2Br , H, H (**II**); and CH_2Br , OH, 4- NO_2 (**III**), respectively.

It is known [5] that hetarylformazans are rather labile polydentate ligands and can form metal complexes of various compositions and structures depending on the substituent in 1-, 3-, and 5-positions.

First, the complexation of compounds **I–III** with copper(II) acetate in solution was studied by spectrophotometric titration. This method allows direct monitoring of the complexation process and calculation of the stoichiometry of the complexes formed [6, 7].

The clearest spectral pattern is observed with formazan **I**. In the course of titration of the ethanolic solution of this compound ($c_I = 3 \times 10^{-5}$ M) with a copper(II) acetate aqueous solution ($c_{CuAc_2} = 10^{-3}$ M), the intensity of the absorption band of the initial formazan ($\lambda_{max} = 430$ nm) gradually decreases, and

that of the band at $\lambda_{\max} = 640$ nm grows (Fig. 1). The spectral curves intersect at two isobestic points of titration, which indicates formation of two complexes. The complex with L : M = 2 : 1, showing a broadened band at 470–500 nm, and 1 : 1 complex with $\lambda_{\max} = 640$ nm are formed when the copper(II) salt is in deficiency and excess, respectively.

Titration of formazan **II** with copper(II) acetate solution is also accompanied by a decrease in the intensity of the band of the initial compound ($\lambda_{\max} = 370$ nm) and by appearance of a weak band at 610 nm. Only one isobestic point is observed in the titration curves, which corresponds to formation of the CuL complex. In the case of formazan **III**, the spectral pattern for titration with the copper(II) salt is more complex and cannot be interpreted unambiguously.

Based on the spectrophotometric titration data, we synthesized crystalline complexes of copper(II) with formazan **I** at L : M ratio of 1 : 1 and 2 : 1 complexes **IV** and **V**, with formazan **II**, at L : M = 1 : 1 complex **VI**, and with formazan **III**, at L : M = 1 : 1 and 2 : 1 complexes **VII** and **VIII** (Table 1).

Copper(II) formazanates **IV–VIII** were prepared by the following general procedure. To a solution of 0.15 mmol (or 0.30 mmol) of formazan in a minimal amount of ethanol (or aqueous ethanol for formazane **I**), a solution of 0.15 mmol of copper(II) sulfate in the minimal amount of water was added at 40°C with stirring, and the mixture was left for 1 h. The precipitate thus formed was filtered off, washed with water, and dried.

It follows from the elemental analysis that complexes **IV**, **VI**, and **VII** have the composition CuL, and **V** and **VIII**, CuL₂ (Table 1). All the compounds are crystal solvates with ethanol. The electronic absorption spectra of complexes **IV–VIII** in ethanol are

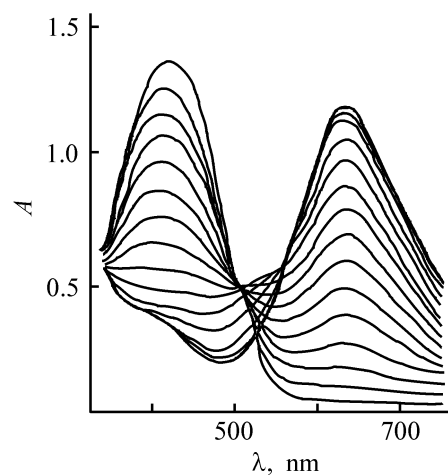


Fig. 1. Electronic absorption spectra of formazan **I** in ethanol in titration with aqueous solution of copper(II) acetate. $c_{\mathbf{I}} = 3 \times 10^{-5}$ M, $c_{\text{CuAc}_2} = 10^{-3}$ M, (λ) Wave-length; (A) transmittance.

similar to the spectra of Cu(II) formazanates obtained in titration of formazans **I–III**.

The ESR spectra of copper(II) formazanates in toluene [8] suggest formation of a Cu|4N| distorted tetrahedron for **V**, Cu|4N| square-planar structure for **VIII**, and mixed nitrogen–oxygen Cu|3N,O| structure for **VII**.

Our and published (for similar ligands [5]) data suggest structure **A** for copper(II) formazanates **V** and **VIII**:

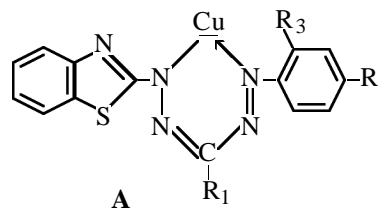


Table 1. Characteristics of copper(II) formazanates **IV–VIII**

Compound	Ligand	L : Cu	mp, °C	λ_{\max} , nm	Found, %				Empirical formula	Calculated, %			
					C	H	N (S)	Cu		C	H	N (S)	Cu
IV	I	1 : 1	>250	640	40.0	4.0	13.8	11.5	C ₁₅ H ₁₂ N ₅ S ₂ O ₃ Cu · 2C ₂ H ₅ OH	40.0	4.5	13.2	12.0
V	I	2 : 1	235	640	44.8	3.8	15.9	7.6	C ₃₀ H ₂₄ N ₁₀ S ₄ O ₆ Cu · 2C ₂ H ₅ OH	45.2	4.0	15.6	7.0
VI	II	1 : 1	>250	610	41.3	2.9	(6.9)	13.8	C ₁₅ H ₁₁ N ₅ SBrCu	41.2	2.5	(7.3)	14.6
VII	III	1 : 1	>250	470	37.3	3.1	15.3	11.7	C ₁₅ H ₉ N ₆ SBrO ₃ Cu · C ₂ H ₅ OH	37.6	2.8	15.5	11.7
VIII	III	2 : 1	240	470	40.0	3.0	16.0	5.4	C ₃₀ H ₂₀ N ₁₂ S ₂ Br ₂ O ₆ Cu · 3C ₂ H ₅ OH	40.4	3.5	15.7	5.9
				640			(5.9)					(6.0)	

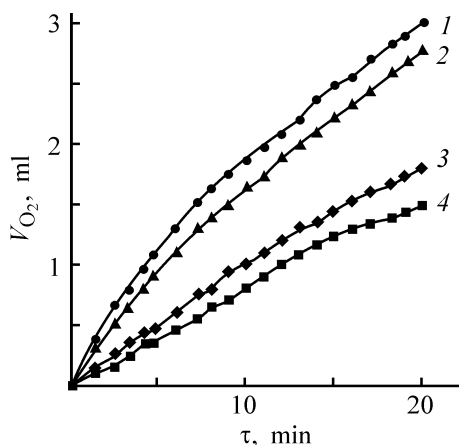


Fig. 2. Kinetic curves of decomposition of 1% H_2O_2 aqueous solution in the presence of copper(II) formazanates. $T = 20^\circ\text{C}$, $V_\Sigma = 27$ ml, and $c_{\text{Cu}} = 0.01$ M. (V_{O_2}) oxygen volume and (τ) reaction time. Compound: (1) **VIII**, (2) **VII**, (3) **VIIIp**, and (4) **VIIp**; the same for Fig. 3.

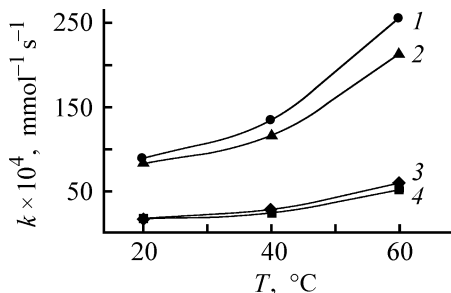
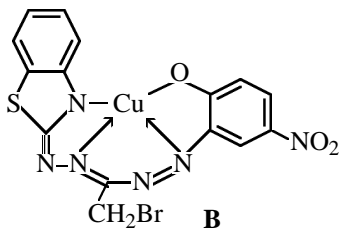


Fig. 3. Temperature (T) dependence of the rate constant of H_2O_2 decomposition (1% aqueous solution) in the presence of copper(II) formazanates.

The structure of complexes **IV** and **VI**, corresponding to the composition $L : M = 1 : 1$, is probably formed by additional coordination of CuSO_4 to nitrogen atoms of the benzothiazole fragment.

For complex **VII**, the structure **B** is the most probable:



To obtain metal complexes suitable for heterogeneous catalysis, we immobilized formazanates **IV–VIII** on AN-18 styrene-divinylbenzene anion exchanger. The presence in its structure of primary and secondary amino groups allowed immobilization of formazanates **IV** and **V** containing sulfonate group in the

ligand by ion exchange and of complexes **VI–VIII** containing labile bromine by covalent bonding.

Immobilization of Cu(II) formazanates was performed as follows. To a solution of **IV** in ethanol, a sample of AN-18 anion exchanger was added so that the copper ion concentration in the polymer was 0.01 mmol g^{-1} , and the mixture was stirred to complete decolorization of the solution. The modified anion exchanger was filtered off, washed with ethanol, and dried in air. In such a way, formazanate **IVp** was prepared. Similarly, formazanates **V–VIII** were immobilized to obtain catalysts **Vp–VIIIp**, which exhibit a high activity and can be easily separated from the reaction products.

The ESR data show the square-planar structure of the coordination core $\text{Cu} | 4\text{N} |$ for formazanate **VIIIp** and $\text{Cu} | 3\text{N}, \text{O} |$ for **VIIp**, similarly to the initial complexes **VIII** and **VII** [8, 9]. Presumably, immobilization of formazanates **IV–VI** on the polymeric support does not change the structure of the coordination core.

The catalytic properties of copper(II) formazanates **IV–VIII** and **IVp–VIIIp** were studied in the model reaction of H_2O_2 decomposition (1% aqueous solution). It is known [4] that complexes containing no more than 0.01 mmol of Cu(II) per gram of the polymeric matrix have the highest catalytic activity. Therefore, we studied the catalytic activity of **IV–VIII** and **IVp–VIIIp** under the similar conditions as follows. A sample of copper(II) formazanate [(0.1 g for **IVp–VIIIp** and $0.0028\text{--}0.0061$ g for **IV–VIII**)] was added to 27 ml of 1% H_2O_2 aqueous solution. The reaction course was monitored by the volume of liberated oxygen at 20, 40, and 60°C .

The kinetic curves of H_2O_2 decomposition at 20°C for **VII**, **VIIp**, **VIII**, and **VIIIp** are shown in Fig. 2. Formazanates **VII** and **VIII** exhibit a high catalytic activity in H_2O_2 decomposition, which is probably caused by the square-planar structure of the metal chelate core. Copper(II) formazanates immobilized on the anion exchanger (**VIIp** and **VIIIp**) behave similarly. It should be noted that the related metal complex systems studied in [3, 4] show lower rate constants of H_2O_2 decomposition under the same conditions ($0.12\text{--}11.78 \times 10^{-4} \text{ mmol}^{-1} \text{ s}^{-1}$).

Proceeding with the previous studies [3, 4], we examined the H_2O_2 decomposition in the presence of copper(II) formazanates at 40 and 60°C . The kinetic data obtained were used to calculate the rate constants of H_2O_2 decomposition [10] (Table 2).

The temperature dependences of the rate constants of H_2O_2 decomposition for complexes **VII**, **VIIp**, **VIII**, and **VIIIp**, as examples, are shown in Fig. 3.

Table 2. Catalytic activity of copper(II) formazanates in decomposition of 1% H₂O₂ aqueous solution and liquid-phase oxidation of 0.03% Na₂S solution at various temperatures

Com- pound no.	$k \times 10^4, \text{ mmol}^{-1} \text{ s}^{-1}$			Degree of conversion S ²⁻ , %		
	at indicated temperature, °C					
	20	40	60	20	40	60
IV	46.8	89.9	203.6	–	–	–
IVp	0.7	2.6	11.2	31.2	64.0	71.3
V	57.5	95.1	219.0	–	–	–
Vp	1.2	5.6	17.3	34.1	64.9	74.1
VI	42.4	71.3	162.4	–	–	–
VIp	2.9	8.3	20.4	59.9	62.8	67.1
VII	82.3	114.8	212.0	–	–	–
VIIp	16.1	23.7	51.3	32.7	54.3	74.7
VIII	86.5	133.6	254.6	–	–	–
VIIIp	17.8	27.1	58.5	38.3	58.3	73.5

As can be seen from Fig. 3 and Table 2, the decomposition rate increases with temperature. For copper(II) formazanates **IVp–VIIIp**, the rate constants are lower than those for **IV–VIII**. Probably, this is caused by partial solubility of the “free” complexes, which increases with the temperature of the reaction mixture, thereby making the reaction conditions similar those in homogeneous catalysis.

In spite of the relatively low catalytic activity of **IVp–VIIIp** as compared to their crystalline analogues **IV–VIII**, they can be successfully used in heterogeneous catalysis, since their composition and the structure of the coordination core, and hence the catalytic properties, do not change in repeated use [11].

The liquid-phase Na₂S oxidation with molecular oxygen and calculation of the degree of catalytic conversion S²⁻ → SO₄²⁻ were performed by the method described in [11]. The use of **IV–VIII** as oxidation catalysts was unsuccessful because of their solubility in the reaction mixture. The catalytic activity of formazanates **IVp–VIIIp** in liquid-phase Na₂S oxidation is virtually independent of the composition and structure of the complexes (this is characteristic of the previously studied benzothiazolylformazanates [3, 4]) and slightly changes with the reaction temperature (Table 2).

CONCLUSIONS

(1) Complexation of 1-aryl-5-benzothiazolylformazans with copper(II) was studied by spectrophotom-

etric titration, and the stoichiometry of complexes formed was calculated.

(2) It was found that the coordination core has the Cu|4N| or Cu|3N,O| structure. The crystalline copper(II) complexes synthesized were immobilized on a AN-18 solid support.

(3) The catalytic activity of immobilized copper(II) formazanates was studied in comparison with the initial analogues. The complexes with the square-planar copper environment show the highest activity.

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