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The Evolution of Reactive Ligands in the Catalysis of Radical Processes by Copper Complexes

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THE EVOLUTION OF REACTIVE LIGANDS IN THE CATALYSIS OF RADICAL PROCESSES BY COPPER COMPLEXES

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GRAPHICAL ABSTRACT



Abstract Two radical reactions (addition of CCl₄ to the double bond of oct-1-ene and oxidation of dodecane-1-thiol with air oxygen) catalyzed by copper complexes have been investigated. Various nitrogen-containing compounds (aliphatic and aromatic amines, aminoalcohols, aminoacids) were used as the ligands. In both cases, products of ligand transformation have been observed, products of the transformations have been identified by GLC-MS. In case of the CCl₄ addition, the reaction can be initiated by the either copper complex or the ligand. In case of the thiol coupling, the reaction proceeds as a conjugated oxidation of both the thiol and the ligand. A correlation between the donor ability of the ligand and its reactivity has been found.

Keywords Carbon tetrachloride; addition; oxidation; thiols; copper complexes; reaction mechanism

INTRODUCTION

Transition metal complexes are active initiators of various radical processes. These processes include redox steps with participation of metal ions. So the reactions should be sensitive to the nature of the ligand. However, the role of ligands in radical reactions has

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EVOLUTION OF REACTIVE LIGANDS IN THE CATALYSIS

not been adequately studied as yet. This work aims at determining the role and evolution pathways of the ligands in the catalysis of radical reactions by copper complexes and at estimating the relationship between the catalytic activity of copper complexes and the reactivity of the ligands. Two reactions [Equations (1) and (2)] were chosen as model processes: the addition of carbon tetrachloride to the double bond of oct-1-ene:

$$C_6H_{13} - CH = CH_2 + CCl_4 \rightarrow C_6H_{13} - CHCl - CH_2 - CCl_3$$
 (1)

and the oxidative coupling of thiols (the model thiols are dodecane-1-thiol (DT) and pentane-1-thiol)

$$2 \text{ RSH} + \frac{1}{2} \text{ O2} \rightarrow \text{RSSR} + \text{H}_2\text{O}$$
(2)

The chosen reactions are typical examples of radical-chain [Equation (1)] and radical [Equation (2)] processes. Both reactions are catalyzed by metal complexes and include a redox stage giving rise to reactive intermediates of radical nature. It is known that radical processes with participation of CCl_4 include intermediate formation of trichloromethyl radicals.¹ The generally accepted mechanism of reaction (2) implies consecutive steps of reduction of divalent copper with thiol and oxidation of Cu(I) with oxygen into the divalent state.²

In the present work, the evolution of ligands was studied by the example of copper(II) complexes of various composition containing ligands of three types: amino alcohols 3-(*N*-methylamino)-1-phenylpropan-1-ol (PMP) and 2-(*N*-methylamino)-1-phenylethanol [(PME)], benzylamine (BA), and dimethylsulfoxide (DMSO). These ligands possess different redox properties and are capable of initiating radical processes.³ It was stated earlier that the mentioned amino alcohols can initiate reaction (1). For thiol oxidation, ligands of two types were chosen. DMSO was chosen as the oxidizing ligand, as its ability to oxidize thiols is well known.⁴ As the reducing ligand, we chose BA, which has a structure similar to PMP and PME.

RESULTS AND DISCUSSION

Reactions with CCl₄

Complexes with PMP and PME show high activity in reaction (1) at temperatures as low as 80 °C. 1,1,1,3-Tetrachlorononane is the major product. In addition to the major product, allylic substitution products (mainly, 3-chlorooct-1-ene) were found, their total yield being less than 3%. The amount of telomerization products was less than 1%. Data on the activity of the complexes under investigation in comparison with the activity of the previously studied analogous complexes with amino alcohols and amino acids, which were active only at higher temperature, are given in Table 1. As can be seen from Table 1, the activity of complexes with aromatic amino alcohols exceeds several fold the activity of other complexes.

It is known that trichloromethyl radicals are formed as intermediates in the reactions of CCl₄ with alkenes.¹ The ability of copper complexes with PMP to initiate the formation of the above-mentioned species was proved by spin-trapping technique with the use of MNP. In a solution of the copper complex with PMP (0.1 M) in CCl₄ at room temperature, trichloromethyl radical spin adducts with 2-methyl-2-nitrosopropane (MNP) were detected;

TOF (80 $^{\circ}$ C), mol/mol·h	TOF (130 °C), mol/mol·h	
0	8.4	
0	7.2	
0	4.8	
0	5.9	
0.28	29.9	
0.34	32.1	
	TOF (80 °C), mol/mol·h 0 0 0 0 0 0.28 0.34	

Table 1 The activity of catalysts in the CCl₄ addition to oct-1-ene (turnover frequency, TOF $[C_8H_{16}] = 0.64$ M, $[CCl_4] = 9.6$ M, $[Cu^{2+}] = 0.015$ M)

they appeared as a triplet of multiplets in the ESR spectrum (Figure 1) with the following HFS constants $a_N = 11.9$ G (triplet) and a = 2.3 G (multiplet).

However, the concentration of spin adducts was very low as compared with the concentration of the complex, namely, 7×10^{-7} M. Such a content of free radicals in the system can be accounted for by two independent reasons. The first reason is low reactivity of the copper complex at room temperature. The second one is the fact that trichloromethyl radicals form and react in the coordination sphere of the metal ion. To check which of the reasons is valid, the products of Cu-PMP and Cu-PME complexes interaction with CCl₄ were analyzed by GC-MS. Also, solutions of the complexes in benzene as well as solutions of the amino alcohols in CCl₄ were kept under similar conditions. The products that form in all the systems are summarized in Table 2. As can be seen from the table, the products of reactions of free ligands and the copper complexes differ. In all cases where CCl₄ was used as the solvent, amino alcohols were oxidized to benzaldehyde even at room temperature. Furthermore, there are polymeric nitrogen-containing products. Probably, they were formed as a result of condensation of the amino alcohol with the formed aldehyde. No low-molecular-weight chloro-containing compounds were found among the reaction products of copper complexes with CCl₄.

In contrast to copper-containing systems, the systems with amino alcohols contain products of recombination and subsequent transformations of trichloromethyl radicals such



Figure 1 The ESR spectrum of the system, containing PMP, CCl₄, and MNP. The concentrations were as follows $[PMP] = 0.1 \text{ M}, [MNP] = 0.1 \text{ M}, [CCl_4] = 9.6 \text{ M}, 25 \text{ }^{\circ}\text{C} (dark).$

Reagent	Solvent	Temperature 100 °C
Cu-PMP	CCl ₄	PhCHO
Cu-PMP	C ₆ H ₆	PhCHO
PMP	CCl ₄	$CHCl_3, CHCl=CCl_2,$
		$CCl_2 = CCl_2, PhCOCH_3,$
		PhCOCl, PhCOCH= CH_2 ,
		N O CH ₃ O OH
Cu-PME	CCl ₄	PhCHO
Cu-PME	C ₆ H ₆	PhCHO
PME	CCl ₄	C_2Cl_6 , $CCl_2=CCl-CCl=CCl_2$ PhCHO,

Table 2 The major products of transformations of aromatic amino alcohols and copper complexes (0.015 M solution of the initiator in CCl₄ or benzene, the reaction time was 1 h at 100 °C or 24 h at room temperature)

Products

=CCl₂ CHCl=CCl₂, and CHCl₃. The reactions of aromatic amino alcohols with haloalkanes were studied in detail previously.³ The fact that no products of CCl₄ transformations are produced in the presence of copper complexes proves that trichloromethyl radicals remain in the copper coordination sphere and cannot react with one another. At the same time, the ability of copper complexes to interact with CCl₄ and to form the trichloromethyl radicals even at room temperature is responsible for the high activity of these compounds in the radical chain addition of CCl_4 to the double bond.

Oxidation of Thiols

Copper complexes were also tested in the DT oxidation in isooctane solution.

$$4 C_{12}H_{25}SH + O_2 = 2 C_{12}H_{25}SSC_{12}H_{25} + 2 H_2O$$

It was found that complexes with the aromatic amino alcohols PMP and PME were inactive in the process. This is apparently caused by the fact that Cu(II) in these complexes cannot be reduced by DT. Indeed, the characteristic *d*-*d* transition band at 720 nm does not disappear and the whole UV spectrum stays invariable upon the addition of DT to the complexes.

However, the copper complex with the aromatic amine (BA) is active in thiol oxidation [Equation (2)]. Air oxygen selectively oxidizes the thiol to the corresponding disulfide at room temperature in the presence of this complex. In accordance with iodometric titration data, H_2O_2 is the primary product of the oxygen reduction. The amount of H_2O_2 that forms in the beginning of the reaction is comparable with the amount of the oxidized thiol. In a standard solution of DT (5 \times 10⁻² M) in isooctane containing the copper complex with BA $(2 \times 10^{-3} \text{ M})$ and a 10-fold excess of the ligand, the thiol consumption was 1.5×10^{-2}

Room temperature

 $C_2Cl_6, CCl_2 = CCl_2,$ CHCl=CCl₂, PhCHO

 $C_2Cl_6, CCl_2 = CCl_2,$ CHCl=CCl2, PhCHO

PhCHO

PhCHO



Figure 2 Kinetics of decrease in BA concentration (•) and pentane-1-thiol concentration (\blacksquare) in the presence of copper complex with BA (T = 25 °C, initial concentrations [thiol] = 5.3 M, [Cu] = 2×10^{-3} M, [PhCH₂NH₂] = 1.9 M).

M and the concentration of the formed hydrogen peroxide was 10^{-2} M. The activity of the catalyst calculated on the basis of these data was 8.3 moles of thiol/(mole of copper hour). However, the maximum conversion of DT was not very high, namely, 23 moles of thiol per mole of copper. When the new portions of the ligand and the substrate were repeatedly added to the reaction mixture, the conversion of thiol over 72 h increased to about 800 moles of thiol per mole of copper. The effect of the additional amounts of ligand is attributable to the fact that the catalytic thiol oxidation is accompanied by a process involving the ligand. Since in the absence of thiol no consumption of amine was observed, we can state that conjugated processes of both thiol and amine oxidation take place. Moreover, as can be seen from Figure 2, an average of 1.3 moles of the thiol is consumed per mole of the amine.

The GC-MS data showed that the major product of BA transformations was benzaldehyde (90%), the minor product was benzonitrile (5%), and also heavy products of polymerization were found (5%). These products probably result from consecutive oxidation of amine according to the following route (Scheme 1, water is formed as a result of thiol or amine oxidation.).

$$PhCH_{2}NH_{2} \xrightarrow{[O], -H_{2}O} PhCH = NH \xrightarrow{[O], -H_{2}O} PhC \equiv N$$
$$\downarrow +H_{2}O, -NH_{3}$$
$$Ph-COH$$

Scheme 1



Figure 3 The ESR spectrum of the system, containing copper chloride, amine (BA or cyclohexylamine), dodecanethiol, and MNP. (1—di*tert*butylnitroxide, 2—spin-adduct of MNP with hydrogen atom).

It is well known that amines can be oxidized via radical mechanism in the presence of copper compounds but the process occurs only at high temperature.⁶ The oxidation of amine becomes possible at room temperature only owing to the presence of thiol. Radical intermediates of the conjugated oxidation of thiol and amine were studied by ESR spectroscopy using the spin trapping technique by the example of the system DT–copper complex with BA–excess of BA–isooctane–oxygen. As can be seen from Figure 3, in the presence of the MNP trap, the spectrum exhibits two signals. The first one refers to di-*tert*butylnitroxide. The second one appears as a triplet of doublets. The triplet splitting constant on the nitrogen atom $a_N = 14.3$ G, the doublet constant $a_H = 11.3$ G. This spectral pattern and HFC values correspond to the spin adduct with hydrogen.

These adducts are described in the literature. They were observed in systems, containing alkanethiol (propanethiol, octanethiol, or cysteine), hydrogenperoxide, and MNP.⁷ Taking into account both the ESR data and the data on the structures of products of amine oxidation, one can assume that the oxidation of amine involves consecutive steps giving to radical species as intermediates (Scheme 2).

$$Ph - CH_{2} - NH_{2} \xrightarrow{Ox} Ph - CH_{2} - \overset{\leftrightarrow}{N}H_{2} (1)$$

$$Ph - CH_{2} - \overset{\leftrightarrow}{N}H_{2} \xrightarrow{-H^{+}} Ph - CH_{2} - \overset{\bullet}{N}H (2)$$

$$Ph - CH_{2} - \overset{\bullet}{N}H \Leftrightarrow Ph - \overset{\bullet}{C}H - NH_{2} (R \cdot) (3)$$

Scheme 2

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Thus, in this process, as in reaction (1) involving CCl_4 considered above, the ligands act as electron or hydrogen donors, participating in the activation of the oxidizing agent, namely, CCl_4 in reaction (1) and O_2 in reaction (2). Reaction (2) was also used as an example to study the ability of copper complexes with DMSO to activate thiols. It is well known⁴ that in the absence of a metal ion, DMSO oxidizes thiols at temperatures above 120 °C to give the corresponding disulfides:

$CH_3S(O)CH_3 + 2RSH \rightarrow RSSR + (CH_3)_2S + H_2O$

The complex $CuCl_2(DMSO)_2$, like the complex with BA, catalyzes the oxidation of DT even at room temperature. This is accompanied by consumption of both DT and DMSO. An example of kinetic curves of the consumption of thiol and DMSO in the system $CuCl_2$ –DMSO–pentanethiol is presented in Figure 4. The catalytic activity estimated from these data was 10 moles of thiol per mole of copper per hour. The maximum conversion of the substrate was comparable with that of the copper complex with BA and still it was not very high, 26 moles of thiol per mole of copper.

As can be seen from the figure, the rate of substrate consumption exceeds the rate of DMSO consumption. Taking into account the stoichiometry of the reaction, we can suppose that in the presence of copper ions, thiol is oxidized by air oxygen together with DMSO (molar ratio 2:1). To check this statement, the products that form in the system $CuCl_2$ -DMSO-pentane-1-thiol in the absence of oxygen were studied. It was found that in an isooctane solution (5 ml) of the DMSO copper complex (0.005 g), pentane-1-thiol (0.2 wt% of the thiol sulfur) is oxidized at room temperature in the absence of oxygen (see Table 3).

The consumption of thiol is equal to 2.5 ± 0.5 moles per mole of the copper complex. The oxidation of thiol is accompanied by the formation of dimethyl sulfide (DMS).



Figure 4 Kinetics of pentane-1-thiol (\blacksquare) and DMSO (\circ) consumption. [Cu(DMSO)₂Cl₂] = 0.087 M, [C₅H₁₁SH] = 5.2 M, [DMSO] = 2.3 M, room temperature.

Table 3 Change of the amount of pentane-1-thiol (moles) in isooctane solution under various conditions. The Cu^{2+} amount is 10^{-5} moles in all samples

System components and reaction conditions	0 h	1 h	2 h	
CuCl ₂				
$C_5H_{11}SH$ under vacuum	1.5×10^{-4}	1.3×10^{-4}	1.3×10^{-4}	
CuCl ₂ (DMSO) ₂				
$C_5H_{11}SH$ under vacuum	1.5×10^{-4}	1.05×10^{-4}	1.05×10^{-4}	
CuCl ₂ (DMSO) ₂				
$C_5H_{11}SH$ in air	$1.5 imes 10^{-4}$	$0.3 imes 10^{-4}$	0	

According to published data,⁸ DMS was also found in the systems prepared by mixing cuprous chloride with DMSO under vacuum. In the absence of copper ions under similar conditions, the reaction does not proceed. If DT was mixed with CuCl₂ in isooctane, the thiol consumption was equal to the amount of copper, copper being reduced to the univalent state. The obtained data can be summarized in the following scheme (Scheme 3).

Scheme 3

This scheme describes satisfactorily the stoichometry of the consumption of DMSO while the reaction of thiol and the copper complex with DMSO proceeds (2 moles of copper per mole of thiol). On the basis of the published data,⁸ we can assume that DMS formed during the process is oxidized to DMSO by oxygen in the presence of Cu(II) ions (Scheme 4).

$$\begin{split} \mathsf{Me}_{2}\mathsf{S} + \mathsf{Cu}^{2+} &\to \left[\mathsf{Me}_{2}\mathsf{S} \cdots \mathsf{Cu}^{2+}\right] \to \left[\mathsf{Me}_{2}\overset{\leftrightarrow}{\mathsf{S}} \cdots \mathsf{Cu}^{+}\right] \\ \left[\mathsf{Me}_{2}\overset{\leftrightarrow}{\mathsf{S}} \cdots \mathsf{Cu}^{+}\right] + \mathsf{O}_{2} \to \left[\mathsf{Me}_{2}\overset{2+}{\mathsf{S}} - \mathsf{OO}^{-} \cdots \mathsf{Cu}^{+}\right] \overset{\mathsf{+Me}_{2}\mathsf{S}}{\longrightarrow} 2\mathsf{Me}_{2}\mathsf{SO} + \mathsf{Cu}^{2+} \end{split}$$

Scheme 4

The given equations reflect the general pattern of the mechanism of thiol oxidation with air oxygen in the presence of copper complex with DMSO. This mechanism assumes consecutive reduction of copper ions with thiol followed by reoxidation of Cu(I) to the divalent state with DMSO, DMS being formed during this process. Partial reoxidation of DMS to DMSO with air oxygen in the presence of copper ions accounts for the catalytic properties of the complex. The mentioned processes form catalytic cycle, which breaks only because of low efficiency of DMS oxidation to DMSO. Consequently, DMSO copper complexes show low durability of operation (TON ≤ 23).

Unlike BA, the addition of excess DMSO did not increase the efficiency of the catalytic action of the system. As can be seen from Figure 5, the catalytic activity (or the rate or durability or both) decreases after the addition of DMSO. This fact can be attributed to low solubility of DMSO in isooctane and heterogenization of the system. The excess of DMSO forms a separate phase, which contains the greater part of the metal complex. The



Figure 5 Catalytic activity of the DMSO copper complex versus the volume of added DMSO. Initial concentration of complex 2×10^{-3} M, thiol concentration 5×10^{-2} M, $25 \,^{\circ}$ C.

green-blue coloring of the copper-containing layer proves this assumption. At the same time, the thiol most likely occurs in the isooctane layer. As a result of separation of the catalyst and the reactant, the reaction rate appreciably decreases.

CONCLUSIONS

Thus, in the studied radical processes catalyzed by copper complexes, the ligands undergo a number of transformations, which influence greatly the rate and the mechanism of the process. As opposed to the generally accepted views, these transformations are not always auxiliary and lead to the destruction of the catalyst. The considered examples show that in some cases, these transformations are inherent components of the catalytic cycle. In the reactions with participation of CCl₄, copper complexes with strongly reducing ligands are the most active catalysts. Ligands such as aromatic amino alcohols participate in the radical chain initiation. An additional low-temperature pathway of generation of trichloromethyl radicals appears (Scheme 5).

In the oxidation of thiols, two pathways are also possible. The reaction can follow the classical mechanism, which assumes participation of the ligand only in the formation of metal complex. This mechanism does not imply direct interaction between the ligand and the substrate. On the contrary, active ligands act simultaneously as complexing agents and reagents that react with either the oxidizing substrate, oxygen (in the case of BA), or the reducing substrate, the thiol (in the case of DMSO) (see Scheme 6).

The joint action of the metal ion and the ligand increases the efficiency of the catalysis.



Scheme 5



Scheme 6

EXPERIMENTAL PART

Catalyst Synthesis

Copper(II) complexes were synthesized as described in ref. 9. The composition was determined by complexometric titration of copper with a solution of EDTA and elemental analysis.

The IR spectra were recorded on a Fourier Transform spectrometer in the 3500– 650 cm⁻¹ range. Pellets (100 μ m thick) were prepared with a hand press after grinding of the studied substance and KBr in a 1:20 ratio in a jasper mortar.

The electronic spectra were measured at λ 200–800 nm on a Shimadzu UV-320 spectrometer in quartz cells (1 cm length) in a chlorobenzene solution.

The ESR spectra were recorded at 77 K on an X-range radiospectrometer (high-frequency modulation 100 kHz) in a thin-walled ampoule of 4 mm diameter. The *g*-factor was determined by simultaneous recording of the studied sample with hyperfine structure components of Mn^{2+} resonance in MgO.

Copper(II) complex with BA was obtained by the reaction of an ethanolic solution (25 mL) of copper(II) chloride dihydrate (0.5 g, 0.0037 mol) with BA (0.8 mL, 0.0074 mol). The precipitate was filtered off and dried in air.

The composition of the complex represented by elemental analysis (Cu, 13.4%; Cl, 14.0%; C, 55.2%; N, 9.5%; H, 6%) corresponds to the formula $CuCl_2(NH_2CH_2Ph)_3$. The shape and the position of the N–H stretching band in the IR spectrum of the complex changed with respect to that in the spectrum of pure BA. The symmetric vibration band shifted from 3315 to 3293 cm⁻¹ and the asymmetric band shifted from 3390 to 3320 cm⁻¹; this is in good agreement with the literature data for analogous complexes (3328 and 3320 cm⁻¹, respectively).¹⁰



Figure 6 The structure of DMSO copper complex.

Copper(II) complex with DMSO was obtained in ethanol at 40 °C. Copper(II) chloride (0.5 g, 0.0037 mol) was dissolved in ethanol (3.5 mL). DMSO (0.7 mL, 0.009 mol) was added with stirring and heating. The precipitate was filtered off and dried in air.

The characteristics of the obtained copper complex with DMSO are in good agreement with the literature data.¹¹ Elemental analysis showed that the content of copper in the substance is 22.0 wt%. This corresponds to $CuCl_2(DMSO)_2$. The electronic spectrum of the compound contains a Cu(II) *d*-*d* transition band at 730 nm. However, only 2% of the total amount of copper ions is manifested in the ESR spectrum. This indicates that the complex has a polynuclear structure.

The S=O and C–S stretching bands of DMSO molecules bound to the copper ion are located at 980 and 726 cm⁻¹, respectively, in the IR spectrum (in ref. 11, the same bands were recorded at 987 and 727 cm⁻¹). Thus, it can be stated that the ligand and the metal ion are bound via oxygen and that the complex has the following structure Figure 6.

Copper(II) complexes with amino alcohols are soluble in ethanol; therefore, they were obtained from CuCl in acetonitrile solution as described in ref. 12. To an acetonitrile solution (25 mL) of CuCl (0.11 g, 0.001 mol), an equimolar amount of PMP (0.038 g) or PME (0.035 g) was added. The formed copper(II) complexes were filtered off and dried in air.

The results of complexometric titration and elemental analysis (24.0% Cu; 13.4% Cl; 5.3% N; 6.1% O; 45.5% C; 5.7% H for PMP and 25.5% Cu; 14.2% Cl; 5.6% N; 6.3% O; 42.8% C; 5.6% H for PME) prove that the composition of complexes is CuLCl (L is PMP or PME). Published data on the geometry of copper complexes with ephedrine¹³ (a structural analogue of the amino alcohols used) suggest the following structure for the obtained complexes (Figure 7).

Reaction Studies

The reaction of oct-1-ene with CCl₄ [Equation (1)] was carried out in the temperature range of 80 °C–130 °C in sealed glass ampoules as described in ref. 13. The reaction mixtures were prepared in a vacuum setup, CCl₄ was used as the solvent ([CCl₄] = 9.6 M), the concentration of complexes was 0.015 M, [C₈H₁₆] = 0.63 M.



Figure 7 The structure of aromatic aminoalcohols complexes of copper.

The oxidation of thiols [Equation (2)] was carried out at room temperature and normal pressure in a flat-bottom flask with intense stirring such that the reaction rate was independent of the intensity of stirring. A standard solution of DT in isooctane was prepared beforehand and placed into the flask together with the catalyst. The volume of the solution was 25 mL. The initial content of thiol sulfur was 0.2 wt% (300 μ L of dodecanethiol, 5×10^{-2} M), the concentration of copper complexes was 2×10^{-3} M (the sample weight was 0.016 g in the case of BA and 0.011 g in the case of DMSO). To study the influence of excess DMSO on the catalytic activity, different portions (10–100 μ L) of DMSO were added to the system. When the experiments were performed in the absence of oxygen, the samples were prepared in a vacuum setup (air residual pressure $\leq 10^{-2}$ atm).

The content of thiols in the reaction mixture was characterized by the weight percent of thiol sulfur. The amount of thiol sulfur was determined by potentiometric titration with a solution of diamminesilver nitrate using an EA-2 silver sulfide electrode. A silver chloride electrode was used as the reference electrode.¹⁴

The organic products formed upon BA and DMSO transformations were analyzed by GLC-FID and GLC-MS (a Varian 3400 chromatograph with a HP-101 capillary column (25 m long, inner diameter 0.2 mm, thickness of liquid phase layer 0.2 μ m), a Finnigan MAT ITD-700 ion trap as the mass-spectrometric detector).

Based on the data on the compositions of reaction mixtures versus process duration, the catalytic activities were found as the ratios of the number of product moles formed during 1 h to the number of copper moles (TOF).

MNP was used as the spin trap. The ESR spectra of spin adducts with MNP were recorded in the dark. Typical samples for the investigation of reaction (1) contained CCl₄ (0.05 mL), MNP (0.0015 g, 0.1 M), and the copper complex with PMP (0.0043 g, 0.1 M). The reaction was performed under vacuum. Reaction (2) was held at the atmospheric pressure, typical sample had a following composition: copper(II) chloride (0.0006 g, 3.7×10^{-3} M), BA (10 μ L, 0.38 M), penatne-1-thiol (20 μ L, 0.38 M), MNP (0.017 g, 0.38 M), isooctane was used as a solvent (isooctane was added up to a volume of 0.5 mL).

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