ISSN 0023-1584, Kinetics and Catalysis, 2011, Vol. 52, No. 1, pp. 82–88. © Pleiades Publishing, Ltd., 2011.
Original Russian Text © I.G. Tarkhanova, M.G. Gantman, 2011, published in Kinetika i Kataliz, 2011, Vol. 52, No. 1, pp. 83–89.

Reactive Ligands in Radical Processes Catalyzed by Copper Complexes

I. G. Tarkhanova and M. G. Gantman

Faculty of Chemistry, Moscow State University, Moscow, 119992 Russia

e-mail: mikhail.gantman@gmail.com

Received January 26, 2010

Abstract—The effect of the reactivity of donor ligands on the catalytic properties of copper complexes in the oxidative dimerization of mercaptans is considered. Catalytic compositions containing metal complexes in an excess of organic reagent ligands, which can show pronounced reductive properties (aromatic amines) or, on the contrary, oxidative properties (dimethyl sulfoxide) toward substrates, exhibit the greatest activity. In the course of the oxidation of mercaptans catalyzed by copper complexes, redox reactions accompanied by not only a change in the oxidation state of the metal but also the direct interaction of a substrate with an organic donor occur. In the presence of aromatic amines, the coupled oxidation of thiols and amines occurs, whereas dimethyl sulfoxide participates in the reaction as an oxidizing agent.

DOI: 10.1134/S0023158411010198

INTRODUCTION

In the studies of radical reactions initiated by transition metal complexes, attention has been focused on redox steps with the participation of metals, whereas the transformations of ligands have almost not been considered. We found that organic donors from among aromatic aminoalcohols (ephedrine analogs, which are readily oxidized by polyhalogenated alkanes under mild conditions) increase the catalytic activity of copper complexes in the reactions of CCl_4 and CBr_4 addition at a double bond; moreover, they can independently participate in various steps of these radical reactions, in particular, in the steps of chain initiation and chain propagation [1, 2]. It was of interest to ascertain whether the found regularities hold true for other radical processes, for example, those in which oxygen is an oxidizing agent. In particular, the oxidative dimerization of mercaptans belongs to these processes. This reaction has common features with the addition reactions of polyhaloalkanes: it occurs by a radical mechanism, it is catalyzed by transition metal (in particular, copper) complexes, and it involves a redox step. Substrates act as clearly pronounced oxidizing (oxygen) and reducing (thiol) agents. Thus, we can hypothesize that, in the given reaction, both ligands possessing oxidative properties and oxidant ligands are active in this reaction. Reducing ligands were structurally different amines (benzylamine, *N*-methylphenethylamine $PhCH_2NHMe$, triethylamine, and cyclohexylamine), and dimethyl sulfoxide (DMSO) was used as a model ligand possessing oxidative properties.

EXPERIMENTAL

The following chemicals were used without additional purification: 2,2,4-trimethylpentane (isooctane), isopropanol, toluene, ethanol, silver nitrate, ammonia solution (25%), 2-methyl-2-nitrosopropane (MNP), copper(II) chloride dehydrate, dodecylmercaptan, and amylmercaptan from Sigma-Aldrich and DMSO, *N*-methylphenethylamine $PhCH_2NHMe$, triethylamine, cyclohexylamine, and benzylamine from Fluka. The purity of all of the organic compounds was checked by gas–liquid chromatography (GLC) on a Kristall-Lyuks 4000 instrument with a flame-ionization detector.

The synthesis of complexes with amines was performed in accordance with a standard procedure: a twofold molar amount of an amine (0.45–0.50 ml of benzylamine, triethylamine, *N*-methylphenethylamine, or cyclohexylamine) was added to a solution of copper chloride (0.2 g, 1.2 mmol) in ethanol (25 ml). The resulting precipitate was filtered off and dried in air. The copper complex with DMSO was prepared in ethanol at 40°C. For this purpose, 0.5 g of copper chloride (3.0×10^{-3} mol) was dissolved in 3.5 ml of the alcohol, and 0.7 ml (9×10^{-3} mol) of DMSO was added to the resulting solution with stirring on heating. The resulting precipitate was filtered off and dried in air. The composition of complexes was determined by chelatometric titration with a solution of EDTA and by elemental analysis.

EPR spectra were measured at 77 K on a Varian E-3 X-band radiospectrometer (100-kHz high-frequency modulation) in thin-walled quartz ampoules 4 mm in diameter. The *g*-factor values were determined by measuring the hyperfine structure components of

Table 1. Concentrations of elements (wt %) in copper complexes with amines*

Ligand	Cu	C	N or S	H	Cl	O
	experimental/calculated					
Et_3N	19.1/19.0	43.3/42.7	8.4/8.3	7.8/9.0	21.4/21.0	–/–
$PhCH_2NH_2$	13.4/14.0	54.2/55.3	8.9/9.2	6.0/5.9	17.5/15.6	–/–
cyclo-$C_6H_{11}NH_2$	11.9/12.1	57.1/54.2	8.5/10.5	10.1/9.8	12.4/13.4	–/–
$MeNHCH_2CH_2Ph$	9.5/9.5	64.2/64.0	7.8/8.3	8.4/7.7	10.1/10.5	–/–
DMSO	22.0/22.0	16.4/16.5	21.9/22.0	4.3/4.1	24.4/24.4	11.0/11.0

* Calculated values belong to the empirical formulas discussed in the text.

Mn^{2+} ions in MgO simultaneously with the EPR spectra of the test substances.

The IR spectra were recorded on an Infralum FT-801 Fourier transform spectrometer over a range of 3500–650 cm^{-1}. The samples for analysis were prepared by grinding powdered test material and KBr in a ratio of 1 : 20 in an agate mortar followed by pressing the mixture as pellets 100 μm in thickness.

The electronic spectra were measured on a Shimadzu UV 320 instrument over a wavelength range from 200 to 800 nm in quartz cells 1 cm in thickness in chlorobenzene.

The EPR spectra of spin adducts with MNP were recorded in the dark. A typical sample consisted of the trap, a thiol, copper chloride, and an amine (cyclohexylamine or benzylamine). The concentrations of reagents dissolved in isooctane were the following: 3.7×10^{-3} mol/l for copper(II) chloride, 0.58 mol/l for the amine, 0.38 mol/l for pentanethiol, and 0.37 mol/l for MNP.

The oxidation of mercaptans was performed at room temperature under conditions that the rate of reaction became independent of the intensity of stirring. A previously prepared standard solution of dodecylmercaptan in isooctane and a weighed portion of a catalyst were placed in a flask. The standard loading included 25 ml of a solvent (2,2,4-trimethylpentane), 0.2 wt % mercaptide sulfur (5×10^{-2} mol/l dodecylmercaptan), and 2×10^{-3} mol/l copper complexes. In the experiments of studying the effect of an excess of a ligand on the catalytic activity, from 10 to 100 μl of DMSO or an amine was added to the system.

The concentration of mercaptans in the reaction mixture was estimated from the weight fraction of mercaptide sulfur, which was determined by potentiometric titration with diaminosilver nitrate using an EA-2 silver–silver sulfide electrode. A silver–silver chloride electrode was used as a reference electrode [3].

The organic products of amine and DMSO conversion were analyzed by GLC (a Kristall-Lyuks 4000 chromatograph with a flame-ionization detector) and gas chromatography–mass spectrometry (GC–MS) (a Varian 3400 chromatograph with an HP-101 column 25 m in length and 0.2 mm in i.d. with a film thickness of 0.2 μm; mass-spectrometric detector, Finnigan MAT ITD-700 ion trap). The concentrations of reagents and products (pentanethiol, benzylamine, DMSO, and diamyl disulfide) were quantitatively determined using an external standard technique. Ethanol or *n*-butanol was used as a standard substance in the case of benzylamine or DMSO, respectively.

RESULTS AND DISCUSSION

Table 1 summarizes the weight fractions of the elements in the prepared complexes. These compositions correspond to complexes with triethylamine, benzylamine, cyclohexylamine, and *N*-methylphenethylamine having the empirical formulas $CuCl_2(Et_3N)_2$, $Cu(PhCH_2NH_2)_3Cl_2$, $Cu(cyclo\text{-}C_6H_{11}NH_2)_4Cl_2$, and $Cu(MeNHCH_2CH_2Ph)_4Cl_2$, respectively. The electronic spectra of all of the above complexes contain a broad band due to *d–d* transition in the range of 700–800 nm, which suggests the bivalent state of copper. The EPR spectra of amine complexes exhibit a broad asymmetric singlet; the number of paramagnetic centers in the test samples is no higher than 15%. The experimental results suggest the occurrence of spin-exchange interactions between closely spaced copper ions; consequently, the above compounds have polynuclear structures, which are characteristic of chlorine-containing complexes [4].

The complex of copper with DMSO has the composition $Cu(DMSO)_2Cl_2$. In the EPR spectrum, only 2% of total copper was detected, whereas a band due to the *d–d* transition at 730 nm was present in the

Table 2. Absorption bands due to stretching vibrations (cm^{-1}) in the spectra of individual DMSO and DMSO as a constituent of copper complexes

Vibrations	DMSO	$Cu(DMSO)_2Cl_2$ ([5])	$CuCl_2 \cdot 2DMSO$ (this work)
S=O	1050	987	980
C–S	672	727	726

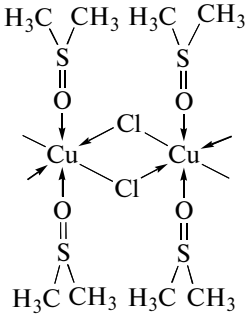
Table 3. Activity of copper complex–ligand and copper mercaptide–ligand catalytic compositions in the reaction of dodecylmercaptan oxidation in isooctane

Ligand (L)	Turnover number, mol (mol Cu)$^{-1}$ h^{-1}	
	in the presence of copper mercaptide and excess amine	in the presence of a copper amine complex
Benzylamine	0.85	7.3
Cyclohexylamine	0.35	1.2
Triethylamine	0.14	0.84
N-Methylphenethylamine	0	0.17

Note: Concentrations in the presence of a composition with a mercaptide, mol/l: [Cu] = 3×10^{-4}, [L] = 7×10^{-3}, and [RSH] = 5×10^{-2}. Concentrations in the presence of a composition with a copper complex, mol/l: [Cu] = 2×10^{-3}, [L] = 3×10^{-2}, and [RSH] = 5×10^{-2}. Reaction temperatures: 293 K.

spectrum of the complex in acetonitrile; this suggests that the metal occurred in the state Cu(II). Table 2 summarizes bands due to the stretching vibrations of the individual sulfoxide and the sulfoxide bound in complexes.

From an analysis of the IR spectrum, it follows that the positions and shapes of bands underwent considerable changes upon complexation, as compared with the spectrum of individual DMSO. A shift of the absorption band due to SO vibrations to a low-frequency region suggests that the metal ion is coordinated to the ligand through an oxygen atom [6]. Based on an analysis of the experimental data, we can propose the following structure:



The results of chromatographic analysis suggest that, in the presence of all of the test amine complexes of copper, the oxidation of dodecyl- and pentanethiols in an isooctane solution occurs selectively with the formation of corresponding disulfides:

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

According to published data [7, 8], the reaction occurs in accordance with the following scheme:

$$Cu^{2+} + RSH = Cu^{+} + 0.5RSSR + H^{+};$$

$$Cu^{+} + RSH = CuSR + H^{+};$$

$$CuSR + 0.5O_2 + 2H^{+} = Cu^{2+} + 0.5RSSR + H_2O.$$

It was hypothesized that the thiolate of univalent copper is an intermediate. However, we found previously [9, 10] that copper(I) dodecylmercaptide exhibited extremely low activity. The activity increased only upon the addition of donor organic additives, in particular, amines (in an excess with respect to thiolate), to the reaction solution. Thus, upon the addition of benzylamine in an amount of 3×10^{-2} mol/l to the system containing copper dodecylthiolate and dodecanethiol in isooctane in concentrations of 2×10^{-2} and 5×10^{-2} mol/l, respectively, its activity increased from 0.11 to 0.85 (mol RSH) (mol Cu)$^{-1}$ h^{-1}. Individual copper complexes with amines exhibited higher activity, as compared with thiolate (Table 3).

It is of interest that the amine complexes of copper in the presence of an excess of an amine were found much more active and stable than analogous systems containing only a complex or a thiolate. The maximum consumption of a substrate even in the presence of the most active individual complex with benzylamine for 3 h was no higher than 8 mol of a thiol per mole of copper, and it then remained unchanged (for comparison, the maximum conversion of dodecylmercaptan in the presence of individual $CuCl_2$ was as high as 2.5–3 mol per mole of Cu). However, the activity of the copper complex with benzylamine in the reaction of dodecylmercaptan oxidation was 2.7 mol (mol Cu)$^{-1}$ h^{-1}, whereas it was as high as 7.3 mol (mol Cu)$^{-1}$ h^{-1} in the presence of an excess of the ligand (15 : 1). Moreover, the complex with *N*-methylphenethylamine, which is inactive in an individual state, exerted a catalytic effect in an excess of a donor (Table 3).

As can be seen in Table 3, among the tested systems, catalytic compositions containing benzylamine exhibited the greatest activity. Moreover, the repeated addition of an amine and a substrate (but not copper) to the reaction solution makes it possible to almost infinitely increase the productivity of the catalytic system: for example, the amount of oxidized mercaptan was as high as ~800 mol per mole of copper after 72 h. This change in the reaction turnover number (TON) was due to the fact that a reaction with the participation of an amine occurred along with mercaptan oxidation. Taking into account the fact that the consumption of an amine was not observed in the absence of a mercaptan, we can consider coupled reactions of amine and mercaptan oxidation. The results of chromatographic studies supported this assumption: in the system containing a thiol, a copper complex with benzylamine, and an excess of the amine, the concentrations of both the amine and the thiol decreased simultaneously (Fig. 1). In this case, on average, 1.3 ± 0.2 mol of the thiol was consumed per mole of the amine. Analogous experiments performed with a less active system containing cyclohexylamine showed that the coupled reactions of amine and mercaptan oxidation also occurred in this case; however, the consumption of the amine was lower: 1 mol of the amine per

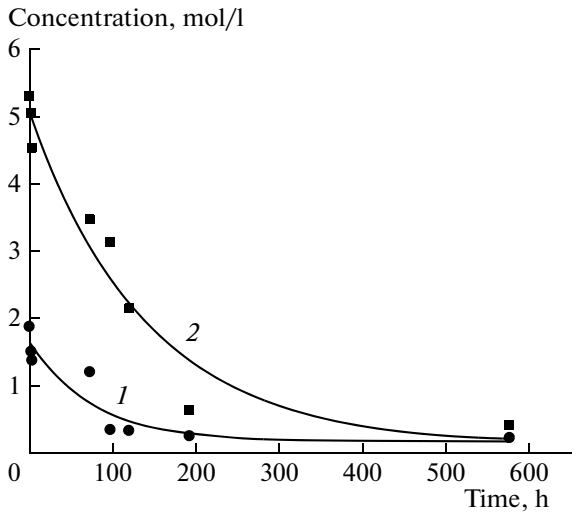
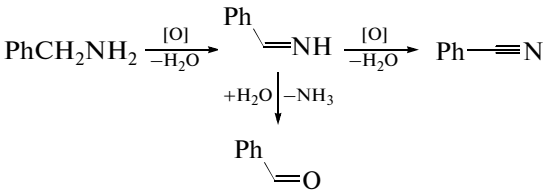


Fig. 1. Changes in the concentrations of (*1*) benzylamine and (*2*) pentanethiol with time in the presence of a copper complex with benzylamine. Initial concentrations, mol/l: [thiol] = 5.3, [Cu] = 2×10^{-3}, and $[PhCH_2NH_2] = 1.9$. The concentrations were measured using an external standard technique.

3 mol of the thiol. Thus, the activity of the complex–amine catalytic composition correlates with the rate of amine oxidation.

As found by GC–MS analysis, benzaldehyde was the main product of benzylamine conversion in the presence of a thiol and a copper–benzylamine complex. Benzonitrile was formed along with benzaldehyde; however, the amount of the former was lower by an order of magnitude (the mass spectra of these products are consistent with the corresponding mass spectra from the Wiley275 database). Thus, in thiol oxidation, the consecutive oxidation of the ligand occurs with the formation of the following products:



Water, which is required for the hydrolysis of an intermediate product, results from amine and thiol oxidation.

According to published data, the oxidation of amines in the presence of copper compounds in a nonpolar solvent occurs at elevated temperatures by a radical mechanism [11]. To determine the reaction mechanism at room temperature in the thiol–amine (benzylamine or cyclohexylamine)–copper complex system in isooctane, we studied the reaction by EPR spectroscopy using a spin trapping technique. In the presence of the radical trap MNP, two spin adducts were detected (Fig. 2). One of them was di-*tert*-butyl nitroxide, which was formed from MNP. The second spin adduct corresponds to a triplet of doublets in the spectrum. The constant of triplet splitting at nitrogen nuclei is $a_N = 14.3$ G, and the constant of doublet splitting is $a_{doublet} = 11.3$ G. This structure of the spectrum and the HFC constants correspond to a spin

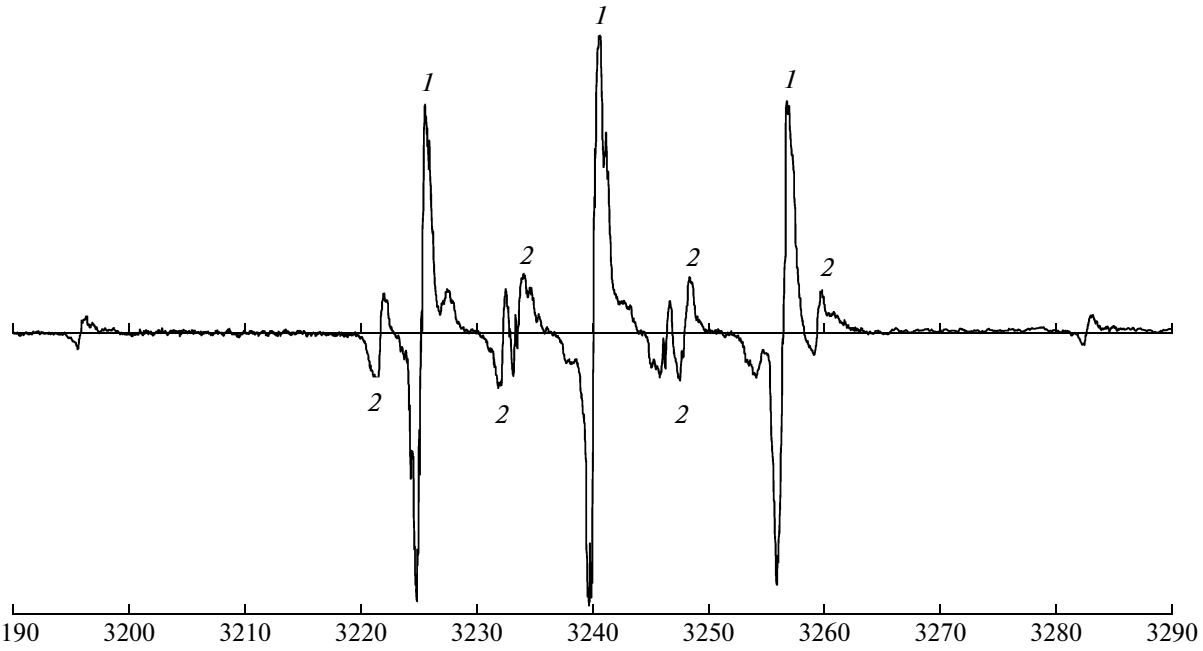


Fig. 2. EPR spectrum of the system containing copper chloride, benzylamine (or cyclohexylamine), dodecanethiol, and 2-methyl-2-nitrosopropane: signals of (*1*) di-*tert*-butyl nitroxide and (*2*) spin adduct with the hydrogen atom. The spectrum was recorded in the dark.

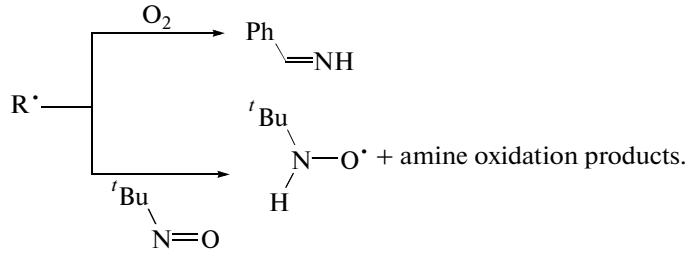
adduct with the hydrogen atom [12]. Adducts of this kind were described in the literature; for example, they were observed in systems containing transition metal carbonyls and methyl-substituted amides (dimethylformamide, hexamethylphosphotriamide) in isopropanol [12]. The experimental results are consistent with GC–MS data, and they suggest the consecutive oxidation of an amine with the formation of radical intermediates:

$$Ph{-}CH_2{-}NH_2 \xrightarrow{O_x} Ph{-}CH_2{-}\overset{+\cdot}{N}H_2;$$

$$Ph{-}CH_2{-}\overset{+\cdot}{N}H_2 \xrightarrow{-H^+} Ph{-}CH_2{-}\dot{N}H;$$

$$Ph{-}CH_2{-}\dot{N}H \longleftrightarrow Ph{-}\dot{C}H{-}NH_2(R^{\cdot}).$$

The radical $R^{\bullet}$ reacts with the trap to form the detected spin adduct:



Because the above processes were not observed in the absence of a thiol, these results are indirect evidence for the occurrence of the coupled radical oxidation of both the substrate and the amine in the simultaneous presence of thiols, amines, and a transition metal.

In the above example, amines reacted with an oxidizing substrate (O_2) playing the role of electron and hydrogen donors. Because a thiol exhibits clearly pronounced reducing properties, it was of interest to test a copper complex with an oxidizing ligand as a catalyst. The complex of copper with DMSO was chosen as a model because it is well known that DMSO can oxidize thiols [13]. In the absence of a catalyst, this reaction occurs at temperatures higher than 120°C:

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

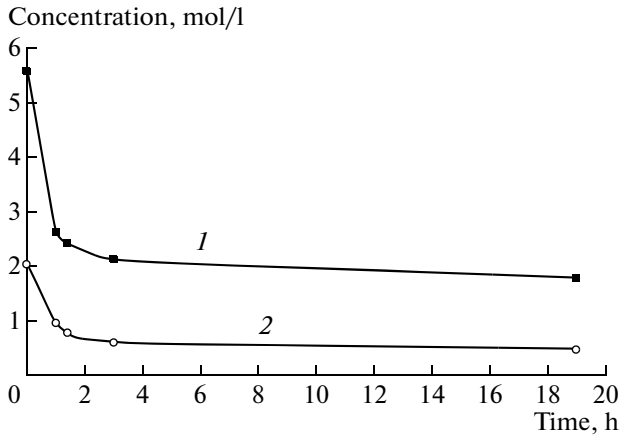


Fig. 3. Changes in the concentrations of (*1*) amylmercaptan and (*2*) DMSO with time. Initial concentrations, mol/l: $[Cu(DMSO)_2Cl_2] = 0.087$, [amylmercaptan] = 5.2, [DMSO] = 2.3, and [*n*-butanol] = 1.8 (internal standard). The reaction was performed at room temperature.

As well as the complex with benzylamine, $CuCl_2(DMSO)_2$ exhibits high catalytic activity in the reaction of mercaptan oxidation with atmospheric oxygen (10 (mol mercaptan) (mol Cu)$^{-1}$ h^{-1}) at a relatively low maximum conversion (26 mol of mercaptan per mole of copper) [14].

According to the results of chromatographic analysis, a simultaneous decrease in thiol and sulfoxide concentrations was observed in the $CuCl_2$–DMSO–amylmercaptan ternary system (Fig. 3). Taking into account the reaction stoichiometry and data given in Fig. 3, we can state that, in the presence of copper ions, the oxidation of the mercaptan by both DMSO (a molar ratio of 2 : 1) and atmospheric oxygen occurred simultaneously.

To check this conclusion, we studied interactions in the Cu(II)–mercaptan–DMSO system in the absence of oxygen. In the presence of the complex of copper with DMSO (0.005 g) in the reaction mixture containing dodecylmercaptan in isooctane (5 ml; fraction of mercaptide sulfur, 0.2 wt %), thiol underwent oxidation in a vacuum. In this case, on average, 2.5 ± 0.5 mol of mercaptan per mole of the copper complex was consumed. Upon mixing the same amount of a solution of dodecylmercaptan with individual $CuCl_2$ in a vacuum, the mercaptan consumption was 1 mol per mole of copper; in this case, copper was reduced to Cu(I). Consequently, we can state that DMSO oxidizes thiols in the presence of copper ions at room temperature. In the absence of Cu ions, the reaction did not occur under analogous conditions.

On the other hand, the formation of dimethyl sulfide was detected by chromatography upon mixing univalent copper chloride with DMSO in a vacuum. Mashkina [15] obtained an analogous result.

The set of experimental data allowed us to propose the following reaction scheme for mercaptan oxidation with DMSO in the presence of Cu(II):

$$Cu^{2+} + RSH \longrightarrow Cu^{+} + 0.5RSSR + H^{+};$$

$$2Cu^{+} + (CH_3)_2SO + 2H^{+} \longrightarrow 2Cu^{2+} + (CH_3)_2S + H_2O.$$

Note that this scheme satisfactorily describes the observed stoichiometry of the interaction of the copper complex with DMSO (2 mol of mercaptan per mole of DMSO).

Published data indicate that Cu^{2+} complexes oxidize dimethyl sulfide to DMSO in accordance with the following reaction scheme [15, 16]:

$$Me_2S + Cu^{2+} \longrightarrow [Me_2S\cdots Cu^{2+}] \longrightarrow [Me_2\overset{+\bullet}{S}\cdots Cu^{+}],$$

$$[Me_2\overset{+\bullet}{S}\cdots Cu^{+}] + O_2 \longrightarrow [Me_2\overset{2+}{S}{-}OO^{-}\cdots Cu^{+}]$$

$$\xrightarrow{+Me_2S} 2Me_2SO + Cu^{2+}.$$

Summarizing the above equations, we can construct a general reaction scheme for mercaptan oxidation with oxygen in the presence of the test copper complex. In the presence of DMSO, the consecutive reduction of copper ions with thiol occurred followed by metal reoxidation to a bivalent state by sulfoxide and the reduction of this latter to dimethyl sulfide. The catalytic effect can be explained by the partial reoxidation of dimethyl sulfide to DMSO by atmospheric oxygen with the participation of copper ions. Thus, a catalytic cycle is produced, the lifetime of which is restricted by the low efficiency of dimethyl sulfide oxidation to DMSO. As a consequence, the complexes of copper with DMSO exhibit low stability (the reaction TON is no higher than 23).

Note that the addition of an excess of a ligand had different effects on the catalytic properties of the test systems. In this case, the activity and stability of systems containing benzylamine increased, whereas an opposite behavior was observed in systems containing DMSO (Fig. 4). The inhibiting effect of an excess of DMSO was due to the heterogenization of the system. The solubility of DMSO in isooctane is low; therefore, the sulfoxide is separated as an individual phase if it occurs in an excess. The reaction rate considerably decreases because the metal complex mainly occurs in the phase of DMSO, as can be observed visually based on the appearance of a characteristic color, and the mercaptan substrate occurs in the phase of isooctane. The activity of the system can be increased by homogenization; for this purpose, aqueous alcohol additives are used [14].

Thus, in the test radical reactions catalyzed by copper complexes, reactive ligands undergo various transformations, which considerably affect the reaction rate and mechanism. In spite of generally accepted concepts, these transformations are not always undesirable, resulting in catalyst decay. The above examples indicate that, in a number of cases, they are necessary components of a catalytic cycle. This allows us to solve a practically important problem of the removal of mercaptans from hydrocarbon materials in a new way. The results of the study of the combined effect of reactive ligands and metal complexes based on these ligands made it possible to develop new active catalytic systems for the oxidation of organic sulfur compounds under mild conditions [14, 17].

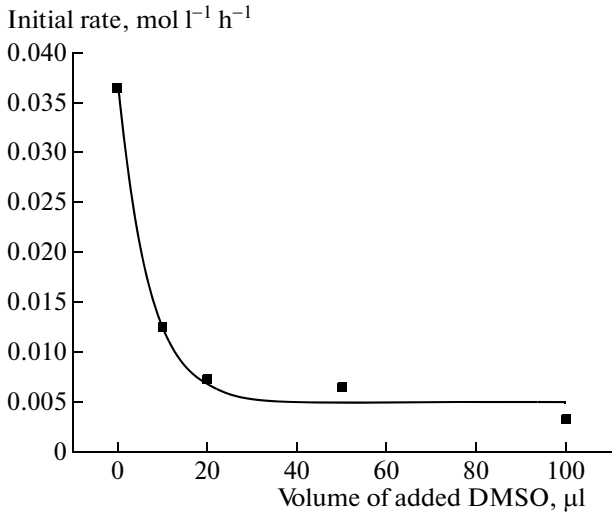


Fig. 4. Dependence of the initial rate of mercaptan oxidation in the presence of the complex of copper with DMSO on the volume of added DMSO. The initial concentration of the complex was 2×10^{-3} mol/l, and the thiol concentration was 5×10^{-2} mol/l. The reaction temperature was 25°C.

ACKNOWLEDGMENTS

This study was supported by the Russian Foundation for Basic Research (project no. 09-03-00128).

REFERENCES

1. Tarkhanova, I.G., Gantman, M.G., Chizhov, A.O., and Smirnov, V.V., *Izv. Akad. Nauk, Ser. Khim.,* 2006, no. 9, p. 1565.
2. Tarkhanova, I.G., Gantman, M.G., Zelikman, V.M., and Smirnov, V.V., *Kinet. Katal.*, 2007, vol. 48, p. 761 [*Kinet. Catal.* (Engl. Transl.), vol. 48, p. 711].
3. *Toplivo dlya dvigatelei. Metod opredeleniya merkaptidnoi i serovodorodnoi sery potentsiometricheskim titrovaniem. GOST 17323-71* (Engine Fuel: Method for the Determination of Mercaptan and Hydrogen Sulfide Sulfur Content by Potentiometric Titration—Soviet Standard GOST 17323-71), Moscow: Gos. Komitet SSSR po Standartam, 1980.
4. *Comprehensive Coordination Chemistry: The Synthesis, Reactions, Properties, and Application of Coordination Compounds*, Wilkinson, G., Ed., New York: Pergamon, 1985, vol. 5, p. 577.
5. Gutmann, V. and Hubner, L., *Mh. Chem*, 1961, vol. 92, p. 1261.

6. Nakamoto, K., *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, New York: Wiley, 1986, p. 269.
7. Kundo, N.N. and Keier, N.K., *Kinet. Katal.*, 1967, vol. 8, p. 796.
8. Gilbert, B.C., Silvester, S., and Walton, P.H., *J. Chem. Soc., Perkin Trans.*, 1999, vol. 2, p. 1115.
9. Tarkhanova, I.G., Gantman, M.G., and Smirnov, V.V., *6th World Congr. on Oxidation Catalysis*, Lille, France, 2009, p. 44.
10. Tarkhanova, I.G., Gantman, M.G., Smirnov, V.V., and Chizhov, A.O., *React. Kinet. Mech. Catal.*, 2010, vol. 101, p. 267.
11. Clifton, J.R. and Yoke, J.T., *Inorg. Chem.*, 1968, vol. 7, p. 39.
12. Gasanov, R.G., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, no. 5, p. 322.
13. Oae, S., *Khimiya organicheskikh soedinenii sery* (Chemistry of Organic Sulfur Compounds), Moscow: Khimiya, 1975.
14. RF Patent 2358004, 2009.
15. Mashkina, A.V., *Kinet. Katal.*, 1986, vol. 27, p. 860.
16. Brownstein, S., Han, N.F., Gabe, E., and Lee, F., *Can. J. Chem.*, 1989, vol. 67, p. 551.
17. RF Patent 2398735, 2010.