

Mixed-valence copper complexes with the organic donors as catalysts for dichlorobutene isomerization

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Abstract

The formation of mixed-valence copper complexes with dialkyl sulfides or triphenylphosphine in the catalytic isomerization of dichlorobutenes was investigated kinetically and spectroscopically (UV–Vis, IR, EPR, NMR). These species were prepared both starting from Cu(I) and Cu(II) compounds. The complexes containing 3 or 4 copper ions in different oxidation states, substrate and donor molecules were found to play a key role in catalysis. Chlorolefins with allylic chlorine atom may stabilize mixed-valence complexes as bridging ligand between Cu(I) and Cu(II). The EPR spectra of these complexes provide the five-coordinated Cu(II) with a trigonal–bipyramidal geometry of coordination sphere. The simultaneous presence of Cu(I) and Cu(II) in polynuclear structure is proposed to favor the electron transfer step in the reaction mechanism. © 1998 Elsevier Science B.V.

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1. Introduction

Mixed-valence copper complexes with the organic donors open up new possibilities in the creation of effective catalysts for chemical reactions. The presence of metal ions in different oxidation states can favor the processes of electron transfer which are limitation stages of many catalytic reactions. The energy of an electron transfer appears minimum if it proceeds between the centers of one complex without significant change of its geometry. The importance of copper complexes including mixed-valence

ones was established for oxidation of organic compounds [1,2] and for some alkynes reactions [3]. The mechanism of catalytic action of polynuclear copper complexes with the organic donor compounds (e.g. with N, S and P-heteroatoms) may be close to that of natural Cu-containing enzymes and proteins. Many of them are known to consist of more than one type of copper ions as a polynuclear structure [4]. Some low weight copper complexes with organic donors could be considered as analogues of related biological systems [5]. Therefore studies of the structures and the catalytical properties of these complexes are of great importance.

It is known, that the organic donors including triphenylphosphine and dialkyl sulfides form

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with CuCl a number of solid and liquid complexes with different ratio of ligand to copper depending on a nature and concentration of donor compounds [6,7]. With the decrease of donor excess polynuclear copper complexes with the ratio of components close to 1:1 predominate. These complexes have been found to be the most common tetranuclear species with the cubane structure. Our preliminary studies [8–11] of the dichlorobutene (DCB) isomerization according to the equation:



have demonstrated that this type of polynuclear copper complexes with dialkyl sulfides or triphenylphosphine are the most active catalysts for the process. The CuCl₂ complexes with dialkyl sulfides and triphenylphosphine are less investigated because the latter reduce Cu(II) to Cu(I) [6,7]. The Cu(II) reduction by the organic donor is a necessary step for making a mixed-valence catalytic complex. Here we report a detailed investigation of this process by spectroscopic methods.

Eq. (1) is one of the stages of chloroprene production, its mechanism based on π -allylcopper intermediates has been discussed [12], but the evidence for such a mechanism is scant. Taking this reaction as an example the following aspects of polynuclear catalysis are considered in the present work: the formation of active catalytic complexes in situ, the evidences of the existence of mixed-valence complexes under the catalytic process conditions, the structure of these complexes and their role in the reaction mechanism.

2. Experimental

The anhydrous copper (I) and (II) chlorides were used. The solid Cu(I) complexes with (CH₃)₂S and PPh₃ were synthesized by methods [6,7]. The purification of starting substances and solvents as well as the method of a kinetic

study have been described previously [8–11]. Initial reaction rates were determined in accordance with the tangents to the kinetic curve of product accumulation in the initial stage. To eliminate the induction period in these cases the reaction solutions were previously allowed to stand in air for 2–3 h. Products were analyzed by GCS on Chrom-5 gas chromatograph with FI detector (SE-30 column at temperature from 373 K up to 453 K).

The optical spectra were recorded in the 250–1200 nm range using UV–3100 and Specord M-40 spectrophotometers.

The EPR spectra of liquid and frozen solutions were detected at room temperature and at 77 K with the X-band Varian E-3 and Varian E-4 radiospectrometers. A magnetic field was graduated by the standards of DPPH ($g = 2.0036$) and Mn(II) ions in the MgO matrix. The Cu(II) concentrations were determined by a comparison of integral intensities of spectra of known volume samples with the standard Cu(II) signal. To determine the EPR parameters the computerized simulation of the experimental EPR spectra was performed according to Refs. [13,14].

3. Results and discussion

3.1. General observations

Eq. (1) proceeds in a liquid phase at temperatures 363–393 K with detectable rate only in the presence of catalysts. In DCB solution the process could be described by a kinetic equation of the pseudo-first order, therefore the sum of constants ($k_1 + k_{-1}$) as well as the initial rate may be used as the quantitative characteristics of a catalytic activity [8,9]. The reaction is rather selective, in all cases the main product of isomerization was *trans*-1,4-dichlorobutene-2. The amount of *cis*-isomer did not exceed 3%. The small quantity (0.1%) of chloroprenes was found. Only traces (0,005%) of dichlorobutene oligomers were observed.

Copper (I) and (II) chlorides have a low catalytic activity in the absence of the organic donors. The yield of the isomerization product did not exceed several percents in 3 h at 373 K. The addition of donor compounds such as dialkyl sulfides or triphenylphosphine resulted in a sharp increase of catalytic activity of copper chlorides. Catalytic systems were prepared by

three various methods: (1) mixing only CuCl or CuCl₂ with the organic donor at various ratios directly in DCB solution; (2) carrying out a preliminary synthesis of solid CuCl complexes with the organic donors of a desired structure and then dissolving these complexes in DCB solution; (3) mixing CuCl with CuCl₂ and organic donor in DCB solution without O₂. All

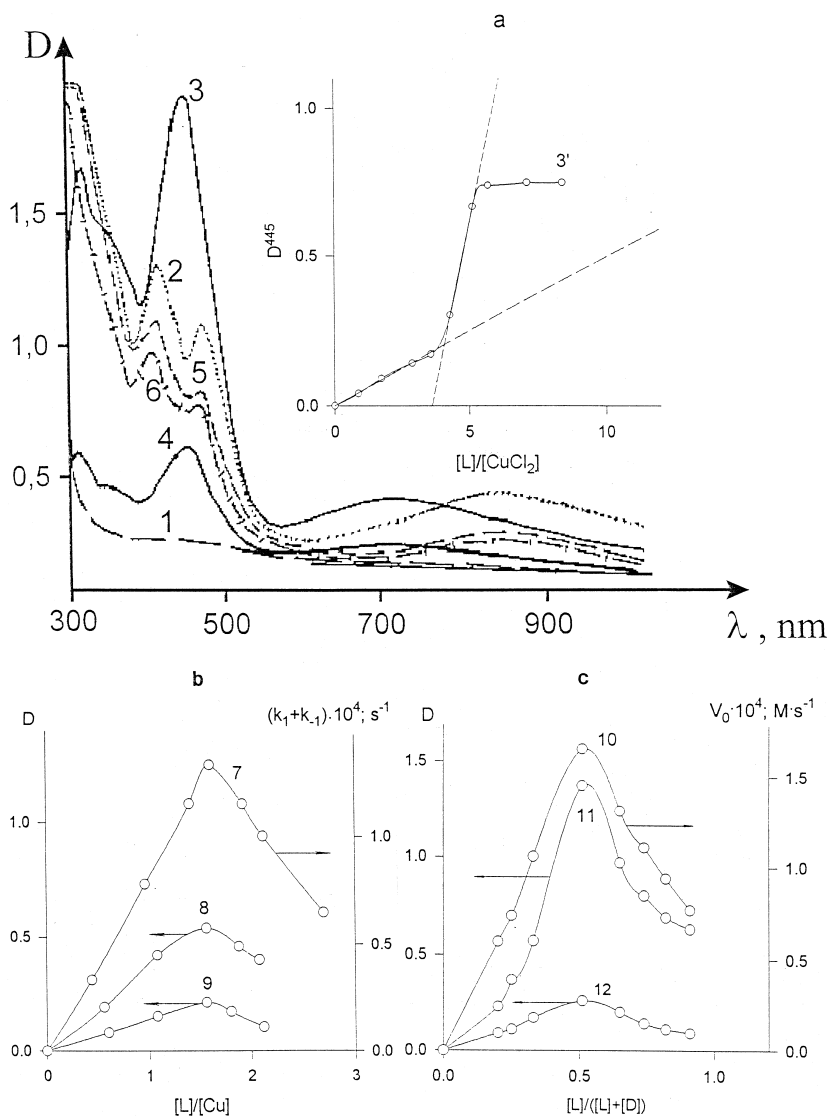


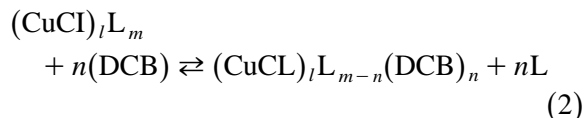
Fig. 1. (a) Absorption spectra of reaction solutions for the diheptyl sulphide as ligand: 1, CuCl in DCB; 2, the same after heating; 3, CuCl₂ in DCB or in chlorobenzene (CB); 3, curve of spectroscopic titration for the system 3 at 445 nm; 4, CuCl₂ in CB after heating; 5, the same in DCB; 6, CuCl and CuCl₂ in DCB. (b) Ratio of ligand/copper dependences of the rate constant at 373 K (7) and the optical density of absorption bands at 470 nm (8) and at 826 nm (9). (c) Ratio of ligand/DCB dependences of the reaction rate at 373 K (10) and the optical density of absorption bands at 470 nm (11) and at 826 nm (12).

methods have been found to give the same final result. The equilibrium composition of isomers (for example, at 373 K – 77% 1,4-DCB-2 and 23% 3,4-DCB-1) has been reached in most cases in 2 or 3 h. However, the initial activity depended on a method of the catalytic system preparation (see below). It manifested itself as an induction period in kinetic curves of accumulation of the isomerization product.

3.2. Copper (I) chloride-donor systems

In the case of a catalytic system being obtained from a mixture of CuCl and an organic donor without preliminary synthesis of the complex the reaction rate was found to strongly depend on a ratio of the organic donor and copper chloride. The maximum of the rate constant of the isomerization was achieved at 1,5 fold excess of the donor (Fig. 1). It could be explained by the assumption that the excess of the organic donor promotes the destruction of active polynuclear species and favors the formation of a mononuclear copper complex with a low catalytic activity. This assumption is in a good agreement with the data of Table 1 obtained for those systems where solid complexes of a certain structure have been previously prepared. We can see that the initial rate of isomerization essentially increases with the growth of the complex nuclearity. The high activity of polynuclear complexes is probably connected with their capability to transform into more

active ones. This transformation has been found to be a complicated many-steps process. In our opinion the first stage of active species formation consists in the replacement of some donor molecules in copper coordination sphere for DCB molecules according to:



where $n = 1$ or 2 .

We have investigated such reaction for $(\text{CuCl} \cdot \text{PPh}_3)_4$ complexes in DCB solution, where replacement of triphenylphosphine molecules for DCB molecules has been observed by NMR and IR-spectroscopical methods [10,11]. The signals of ^{31}P in free PPh_3 and in its addition product with DCB molecule ($\delta = -8.4; +31.3$ ppm) have been found in the solution. In addition the solid complex with the following stoichiometry: 4 Cu: (2–2.5) PPh_3 : (2–1.5) DCB has been isolated from the reaction mixture. IR-spectra (the absorption bands with $\bar{\nu} = 2974, 2948, 2922, 1636, 1616, 724$ cm^{-1}) provided the evidence of DCB molecule participation in it. Contrary to air-stable copper (I) complexes with only triphenylphosphine molecules the latter easily reacted with oxygen to produce a mixed-valence complex and triphenylphosphine oxide [10,11]. Using this complex as a catalyst resulted both in a disappearance of the induction period in the accumulation of the isomerization product and in an increase of the initial rate of process to ten times as much (Fig. 2).

Similar processes may spontaneously occur in a reaction solution in the presence of oxygen. The presence of both DCB and oxygen is essential to the transformation of initial complexes into more active species and to the following reaction stages [8–11]. The low rate of this transformation gives rise to the induction period of the catalytic reaction. Furthermore it manifests itself in the dependence of an initial rate of the reaction catalyzed by Cu(I) compounds on a time of the system exposure to the air. It fol-

Table 1

The catalyst nuclearity dependence of the initial rate (V_0) of Eq. (1)

Catalyst	Added compound	[DCB] (M)	$V_0 \cdot 10^4$ (M/s)
$\text{Cu}_4\text{Cl}_4[(\text{CH}_3)_2\text{S}]_4$	—	9.44	23
$\text{Cu}_4\text{Cl}_4[(\text{CH}_3)_2\text{S}]_4$	chlorobenzene	7.55	16
$\text{Cu}_4\text{Cl}_4[(\text{CH}_3)_2\text{S}]_4$	allylchloride	7.55	22
$\text{Cu}_4\text{Cl}_4[(\text{CH}_3)_2\text{S}]_4$	acetonitrile	7.55	12
$\text{Cu}_4\text{Cl}_4[(\text{CH}_3)_2\text{S}]_4$	dimethylformamide	7.55	11
$\text{Cu}_4\text{Cl}_4[(\text{CH}_3)_2\text{S}]_4$	diheptyl sulfide	7.55	11
$\text{Cu}_4\text{Cl}_4[(\text{C}_2\text{H}_5)_2\text{S}]_3$	—	9.44	20
$\text{Cu}_4\text{Cl}_4(\text{PPh}_3)_4$	—	9.44	15
$\text{Cu}_2\text{Cl}_2(\text{PPh}_3)_3$	—	9.44	1.0
$\text{CuCl}(\text{PPh}_3)_3$	—	9.44	0.2

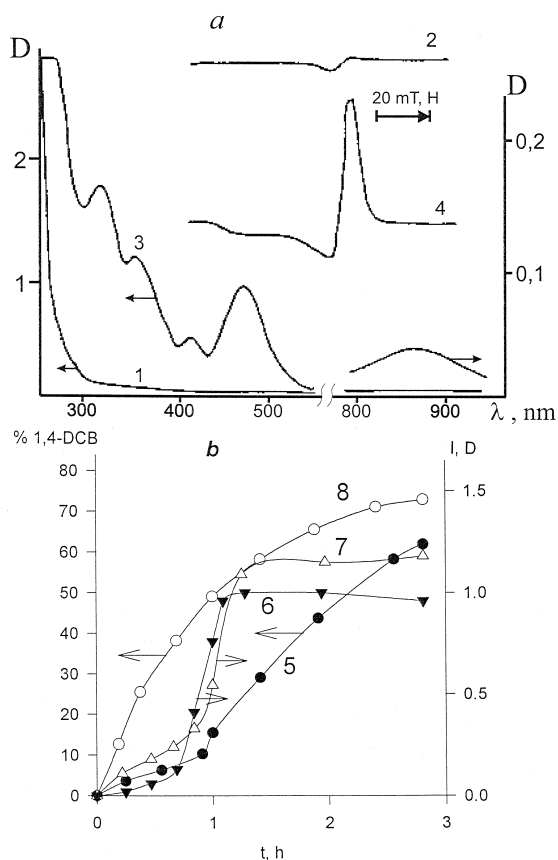


Fig. 2. (a) Absorption and EPR spectra of reaction solutions for the PPh_3 ligand (L): 1, 2 – CuCl in DCB; 3, 4 – after heating. (b) Kinetic curves for accumulation of 1,4-DCB at 373 K in the presence of CuCl_4L_4 (5) and of $\text{Cu}_4\text{Cl}_3\text{L}_{2.5}\text{D}_{1.5}$ (8); changes of intensities of the EPR signal (6) and the absorption band at 476 nm (7).

lows from the data obtained for the solution of 0.01 M CuCl and 0.075 M R_2S in DCB (Table 2).

Thus we can conclude that the second stage of the active species formation is DCB-promoted partial oxidation of Cu(I) which results in mixed-valence complexes. Some further evidences for this conclusion are following: (1)

new signals characteristic for Cu(II) species appeared in EPR- and absorption spectra of CuCl solutions with n-donor only in the simultaneous presence of DCB and O_2 , their parameters are given in Figs. 1 and 2 and in Table 3. They differ from the ones typical for only Cu(II) complexes; (2) the integral intensities of these signals correlated with a kinetic curve for the product accumulation. One can see it from the example data shown in Fig. 2 for the system CuCl –triphenylphosphine; (3) the catalytic activities of systems varied with the solution composition together with the intensities of new absorption bands. It is shown in Fig. 1 for the CuCl – $(\text{C}_7\text{H}_{15})_2\text{S}$ system.

The quantitative determination of Cu(II) concentration performed on the basis of data given in Fig. 2 has shown that only a quarter of copper content had valency (II). These observations permitted to suggest that reasonably strong mixed-valence complexes of copper (I) and (II) were formed in a solution preventing further Cu(I) oxidation.

From the spectroscopic data summarized in Table 3 it is clear that there are absorption bands at 470–480 nm and in the 800–900 nm range of wavelength in all reaction solutions independent of a ligand. Similar absorption bands are characteristic for mixed-valence complexes [15]. It has been found by Job's method that for the CuCl –diheptyl sulfide system (an example is shown in Fig. 1) the complexes with a stoichiometry $3\text{Cu}:2\text{L}:2\text{DCB}$ (where – L is a dialkyl sulfide) are responsible for absorption at these wavelengths. The data given in Table 4 demonstrate the dependence of catalytic activity on the ratio of Cu(I) to Cu(II) together with the changes of an optical density for the absorption bands mentioned above. It is seen that activity of a mixture of copper compounds in different

Table 2

	Condition			
	Fresh solution	After 24 h exposure	Without O_2	With CuCl_2
$(k_1 + k_{-1}) \cdot 10^5 \text{ s}^{-1}$	2.0	9.5	1.5	10.0

Table 3
Parameters of spectra of Cu(II) complexes

Complex	λ_{\max} (nm)	$g_{\parallel} \pm 0.005$	$g_{\perp} \pm 0.005$	$A_{\parallel} \pm 0.3$ (mT)	$A_{\perp} \pm 0.3$ (mT)	Remarks
CuCl ₂ + (iso-C ₃ H ₇) ₂ S + DCB		2.195	2.06 ± 0.01	17.8	—	$a_o = 1.3$ mT
CuCl ₂ + (<i>n</i> -C ₇ H ₁₅) ₂ S	308, 455, 710	2.193	~ 2.053	13.4	—	
CuCl ₂ + (<i>n</i> -C ₇ H ₁₅) ₂ S + DCB	308, 455, 710	2.175	2.057	14.4	—	$g_R = 2.03,$ $a_o = 1.8$ mT
CuCl ₂ + (<i>n</i> -C ₇ H ₁₅) ₂ S + 1,2,3 -trichloropropene		2.175	~ 2.05	14.7	—	$g_R = 2.033,$ $a_o = 1.8$ mT
CuCl ₂ + (<i>n</i> -C ₇ H ₁₅) ₂ S + DCB ^a	290, 417, 470, 826	2.004	2.160	5.8	9.2	$g_2 = 2.060$
CuCl + (<i>n</i> -C ₇ H ₁₅) ₂ S + DCB + O ₂ ^a	290, 417, 470, 826	2.004	2.160	5.8	9.2	
CuCl + (CH ₃) ₂ S + DCB + O ₂ ^a	360, 470, 800–900	2.004	2.160			
CuCl ₂ + PPh ₃ + DCB ^a	310, 365, 476, 870	2.14	2.07			
CuCl + PPh ₃ + DCB + O ₂ ^a	310, 365, 476, 870	2.14	2.07			
[Cu(bpy) ₂ Cl]ClO ₄		2.01	2.19	—	—	[19]
Cu(bpy) ₂ Cl ₂		2.02	2.19	—	—	[19]
[Cu(bpy) ₂ SC(NH ₂) ₂](ClO ₄) ₂		2.020	2.168	—	—	$g_2 = 2.141$ [20]
[CuN(CH ₂ CH ₂ NH ₂) ₃ OH] ⁺		2.006	2.210	7.2	10.7	[21]
CuN(CH ₂ CH ₂ N(CH ₃) ₂) ₃ Br ₂		1.956	2.182	8.7	9.8	[26]
[CuN(CH ₂ CH ₂ SC ₂ H ₅) ₃ Cl]ClO ₄		2.005	2.128	—	—	[22]

^aThe spectrum was registered after 1 h heating at 373 K.

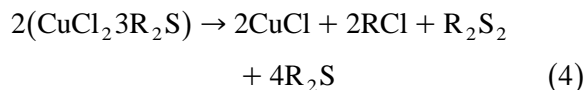
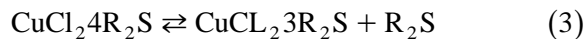
oxidation states is higher than for complexes of only one type, both the activity maximum and the absorption maximum are reached in the same excess of Cu(I).

3.3. Copper (II) chloride-donor systems

Another way for making mixed-valence copper complexes was a partial reduction of Cu(II) by donor compounds such as triphenylphosphine or dialkyl sulfide in DCB solution. The size of the alkyl group in dialkyl sulfide affected the reduction rate. For dimethyl sulfide the Cu(II) reduction went to completion already at room temperature, the other sulfides reacted with Cu(II) only on heating.

The reaction path strongly depended on a DCB presence. In the absence of DCB the

copper (II) reduction resulted in a complete disappearance of Cu(II) signals in optical and EPR-spectra of systems probably due to reactions:



Eq. (3) has been proposed according to the data [16]. The results of spectroscopic titration of CuCl₂ solution in CHCl₃ with diheptyl sulfide (Fig. 1) were in an agreement with a predominance of complexes with 1:4 stoichiometry, the titration curve obtained at $\lambda = 445$ nm had a clear-cut bend under this ratio. The parameters of the EPR spectrum (Table 3) are typical for complexes with octahedral geometry. Products

Table 4

The Cu(I)/Cu(II) ratio dependences of the catalytic activity of copper complexes with diheptyl sulfide in Eq. (1) at 373 K and of the optical density (*D*) of reaction solutions at 826 nm

	0.013	0.011	0.010	0.009	0.0086	0.0068	0.0044	—
CuCl (M)	0.013	0.011	0.010	0.009	0.0086	0.0068	0.0044	—
CuCl ₂ (M)	—	0.002	0.003	0.004	0.0043	0.0063	0.0086	0.013
$(k_1 + k_{-1}) \cdot 10^5$ (s ⁻¹)	1.5	7.2	8.4	9.8	11.8	8.1	4.9	0.6
<i>D</i>	0	0.21	0.28	0.33	0.35	0.26	0.17	0.02

of Eq. (4) have been identified by chromatography technique. According to our kinetic studies carried out in diheptyl sulfide excess Eq. (4) can be described by kinetic equation of second order with respect to copper concentration with $k_2 = (3 \pm 0.3) \cdot 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ at 373 K.

The process of Cu(II) reduction in the presence of DCB proceeded otherwise. Features of this reaction are described in detail below for the CuCl_2 -diheptyl sulfide-DCB system as an example. In the EPR spectra at room temperature four well resolved lines with parameters: $g_o = 2.095 \pm 0.003$ and $a_o = (5.7 \pm 0.2) \text{ mT}$ were observed. In Figs. 3 and 4 spectra of the frozen solutions at 77 K are indicated before and after heating. The parameters of the EPR spectrum before heating (Table 3) are typical for Cu(II) complexes with axial symmetry of a coordination sphere for the distorted octahedral geometry in the b_{1g} ground state with the unpaired electron localization at the $3 d_{x^2-y^2}$ orbital ($g_{\parallel} > g_{\perp} > 2$). It was confirmed by the EPR spectrum simulation (Fig. 3) performed for

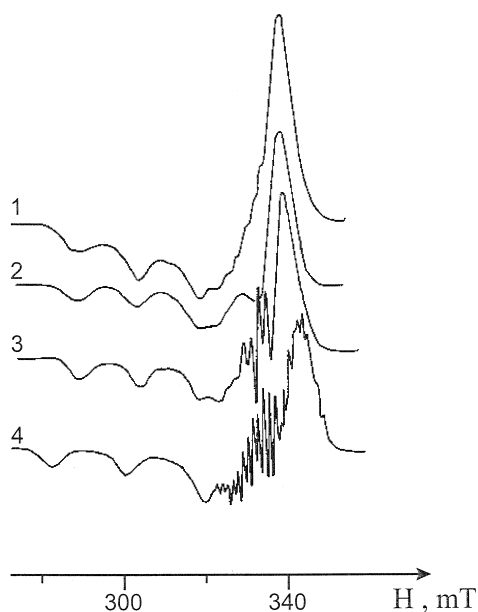


Fig. 3. EPR spectra of CuCl_2 -dialkyl sulfide complexes at 77 K: 1, diheptyl sulfide in CB; 2, theoretical spectrum with parameters given in the text; 3, the same in DCB; 4, diisopropyl sulfide in DCB.

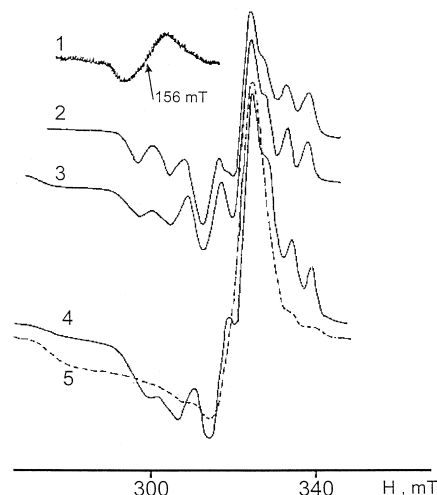


Fig. 4. EPR spectra of CuCl_2 -diheptyl sulfide complexes (after heating) at 77 K: 1, forbidden transition in a half magnetic field; 2, theoretical spectrum with parameters given in the text; 3, 0.01 M CuCl_2 in DCB; 4, 0.05 M CuCl_2 and CuCl without heating; 5, the same after heating.

the values $g_x = g_y = 2.027$; $g_z = 2.165$; $A_x = A_y = 3.2 \text{ mT}$; $A_z = 15.0 \text{ mT}$ at linewidths of Gaussian shape components $D_x = D_y = 2.86 \text{ mT}$; $D_z = 2.56 \text{ mT}$. According to a good agreement of the values measured experimentally g_o and $g'_o = (g_{\parallel} + 2g_{\perp})/3$ it is possible to assume that structures of Cu(II) complexes are identical in a solution at 295 K and in a solid state at 77 K.

Moreover a well resolved spectrum of an organic radical or cation-radical [17] is imposed on the Cu(II) spectrum in frozen solution. From the comparison of spectra of diheptyl and diisopropyl sulfide complexes (Fig. 3) it is seen that these spectra are depending on the dialkyl sulfide structure. The concentration of these species does not exceed 0.01–0.1% from the copper (II) content.

Heating of solutions of the Cu(II) complexes with dialkylsulfide as well as with triphenylphosphine [8,9] in the presence of DCB results both in an essential change of the type of EPR spectrum and in a decrease of the intensity of Cu(II) signals, i.e. a concentration of paramagnetic centers. The spectral changes indicate a

transformation in the coordination sphere of a metal, the type of spectrum at 77 K (Fig. 4) for diheptyl sulfide is characteristic for the five-coordinated Cu(II) complex in the D_{3h} ground state with the unpaired electron localization at the $3 d_z^2$ orbital and with values $g_{\parallel} < g_{\perp}$ [18–21]. From the analysis of structural data for similar complexes [19,22–24] it is known, that they generally have some distorted trigonal–bipyramidal geometry. Three-axis anisotropy of the EPR spectrum could be expected for these complexes. The theoretical calculation of this type of spectra really proved it, the description of the spectrum shape only with usage of g_{\parallel} , A_{\parallel} , g_{\perp} and A_{\perp} does not characterize the system completely. The spectrum indicated on Fig. 4 was designed at: $g_x = 2.007$, $g_y = 2.094$, $g_z = 2.163$; $A_x = 5.53$, $A_y = 3.0$, $A_z = 9.0$ mT and at following linewidths: $D_x = 1.69$, $D_y = 1.52$, $D_z = 2.16$ mT. One can see that the calculated and observed spectra at 77 K are in a good agreement at 290–350 mT.

Changes of the integral intensities of EPR spectra in liquid and frozen solutions of diheptyl sulfide Cu(II) complexes in the course of heating at 373 K in DCB solution are indicated in Fig. 5 in comparison with the inert solvent. Contrary to the inert solvent these values are strongly distinct from one another in the presence of DCB. The Cu(II) concentration calculated from the spectra of the liquid solution is close to zero while that one calculated for the frozen solution is close to half of the initial Cu(II) content. Therefore, the spectrum of the solution after heating was not observed at room temperature or owing to a strong change of relaxation properties (a decrease of a spin–lattice relaxation time T_1 up to 10^{-10} s and below at 295 K contrasting to $T_1 \sim 10^{-8}$ s at 77 K), or owing to thermodynamic instability of this type of Cu(II) complexes at 295 K. The latter seems more probable.

In accordance with the fact that Cu(II) reduction in the presence of DCB stopped after reaching the ratio Cu(I):Cu(II) of about 1:1, the resulting spectrum of the system studied can be

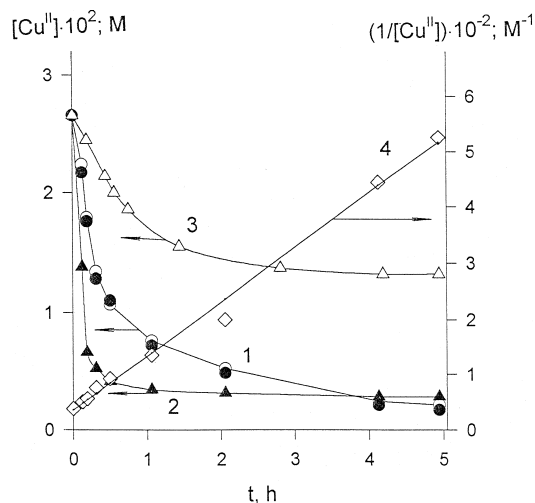


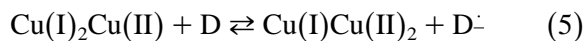
Fig. 5. Kinetic curves of Cu(II) reduction by diheptyl sulfide at 373 K measured from integral intensities of the EPR spectra of solutions at 293 and 77 K in CB (1) and in DCB at 293 K (2) and 77 K (3) and the fit of the curve (1) in coordinates of the second order kinetic equation (4).

attributed to a mixed-valence complex. This suggestion is strongly proved by our synthesis of a mixed-valence complex. Mixing CuCl and CuCl₂ with dialkyl sulfide in the DCB solution produced as a result the absorption and EPR spectra similar to those described earlier without heating (Figs. 1 and 4).

Some more EPR signals were observed for frozen solutions: the broad line at 280 mT (Fig. 4) and a signal with small intensity in a half-field (a forbidden transition) with $g = 4.21 \pm 0.02$ and the linewidth equal to 12 ± 1.5 mT (Fig. 4) increased with growing concentrations. The increase of the copper concentration results both in the growth of the intensities of these signals and in the primary formation of structures of the one type. The type of spectrum (5) given in Fig. 4 prevails after heating the solution, containing simultaneously high concentrations of CuCl and CuCl₂. One can assume that the broad line at 280 mT concerns the components of parallel orientation of monomeric Cu(II) complexes with tetragonal bipyramidal geometry with characteristic ratio $g_{\parallel} > g_{\perp}$. It is not possible to determine their parameters in view of poorly resolved lines of the spectrum, but

they are probably close to those obtained for the triphenylphosphine system under similar conditions (Fig. 1, Table 3).

At the same time the observation of the EPR signal in a half-field shows the existence of polynuclear complexes containing at least two Cu(II) ions. Superposition of the EPR signals does not permit to calculate a concentration of this complex strictly; it is only possible to confirm that it is not the only one and its content in a solution is not high. The probable description of the process at increased temperature could be:

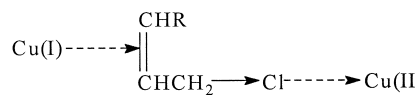


where D may be DCB molecule or any product of its conversion.

3.4. The key role of DCB in catalyst evolution

The data given above have shown the great difference of reaction ways in the presence of DCB and without it. Moreover, the replacement of 3,4-DCB or 1,4-DCB for allylchloride did not change the system properties, however, other alkenes such as hexen-1 and vinylidene chloride acted as inert solvents (chlorobenzene or chloroform). The feature of allylic chlorolefins is their ability to construct the best catalyst for the further conversion. As stated above the most highly active complexes could be prepared both starting from Cu(I) complexes with the organic donor in the presence of oxygen and DCB and starting from Cu(II) complexes by reduction by donor excess in DCB presence proceeding in accordance with Scheme 1.

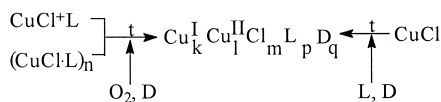
The spectroscopic properties of the reaction solution after heating are identical in both cases, besides they are close to that obtained for the solution of both CuCl and CuCl₂ without heat-



Scheme 2.

ing. The presence of DCB molecules was determining significance in the oxidation way as well as in the reduction one. DCB molecules have been found to play a role of the catalyst for partial oxidation of low active Cu(I) complexes to more active mixed-valence ones, while the Cu(I) complexes with the organic donors did not react with oxygen in the DCB absence. The presence of DCB is also necessary for the production of mixed-valence complexes starting from Cu(II), it prevents the Cu(II) reduction from going to completion and favors the formation of stable Cu(I,II) complexes. So we can conclude that a specificity of chlorolefins is connected with their ability to stabilize mixed-valence species. It is possible if the ligand plays the role of a bridging bond between two metal atoms in the different oxidation states. Allyl chloride and its derivatives are specific bidental ligands with two centers of coordination: (1) the chlorine atom in allyl position with notable negative charge capable to coordinate with a middle strength Lewis acid such as Cu(II); (2) the electron deficit double bond according to effect of the substituents to which a soft Lewis acid Cu(I) can be coordinated. A complex formation can be described with Scheme 2.

Thus, the catalytic DCB isomerization in the presence of copper complexes is a very complicated process with great number of stages. The most important steps are the following: (1) the insertion of DCB molecule into coordination sphere of a metal in Cu(I) or Cu(II) complexes, probably the breaking of one of the Cu–S or Cu–P donor–acceptor bonds preceded this process; (2) the geometrical reorganization of a coordination sphere of Cu, tetrahedral Cu(II) complexes with triphenylphosphine [8–11] and octahedral Cu(II) complexes with dialkyl sulfide have been shown to be both inactive in cataly-

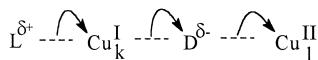


Scheme 1.

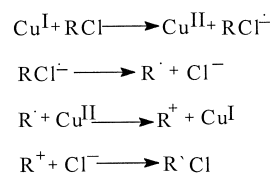
sis. The active species were formed through the complexes with trigonal bipyramidal geometry or at least compounds contained such fragments in their structure; (3) the partial oxidation (or reduction) of Cu(I) (or Cu(II)) complexes and polynuclear complex formation; (4) the catalytic reaction itself. The importance of geometry of the copper coordination sphere in a polynuclear complex is clear from the data of reaction rates obtained for added compounds (Table 1). Using such ligands as dimethylformamid or acetonitrile, as is seen from Table 1, results in the reduction of the process rate, that probably is connected with occupation of the sixth coordination place by these molecules to produce low active octahedral complexes. On the contrary, addition of allylchloride into a reaction system results in an increase of the rate, which can be connected with capability of this compound like DCB to stabilize the five-coordinated structure of Cu(II) complexes. Lesser steric hindrances of allylchloride in comparison with DCB to form bridging bonds could be of importance.

The simultaneous presence of copper ions of different valency in the active complex permits to assume a possibility of an electron transfer stage. Delocalization of the electron density in the system involving 3–4 or more ions promotes a charge transfer process according to Scheme 3.

The structural features of the DCB molecule make such an electron transfer process rather possible, the presence of chlorine atoms in allylic position should lead to an increase of the electron affinity A_E compared with unsubstituted alkenes. Our calculations by semi empirical MNDO method gave an A_E value of about 0.9 eV. This is much greater than those for unsubstituted olefins (< 0). The DCB anion-radical should have a low stability, the enthalpy of the production of Cl^- anion and a radical



Scheme 3.



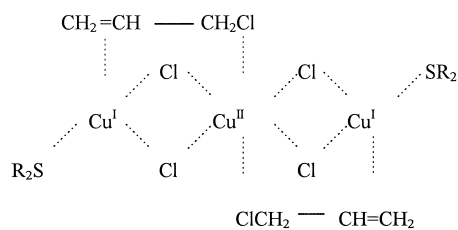
Scheme 4.

from DCB anion-radical is equal to 46 kJ/mol according to MNDO calculations [9]. The mechanism of isomerization is not fully understood but it seems that Eq. (1) can be probably represented as a chain of several processes (Scheme 4).

All the processes shown above proceed most likely in a coordination sphere of copper ions in the mixed-valence polynuclear complex, its high activity can be explained within this mechanism by providing better conditions for delocalization of electron density in these species. As the evidence of intermediate formation of species of an ion-radical nature in a catalytic system the observation of superhyperfine structure of EPR-spectra of Cu(II) complexes with dialkyl sulfides in DCB solutions may be considered, that shows a possibility of electron transfer according to Scheme 3.

From our results it may be noted that the most active complexes in catalytic DCB isomerization contain at least 3–4 copper atoms in the different oxidation states, only the part of which has valency (II). According to their stoichiometry a structure with many bridging bonds could be expected for this type of complexes. The DCB molecule is suggested to be one of the bridging ligands. Taking into account both the structural data published for mixed-valence trinuclear copper complexes with bidentate ligands [25] and our observations the following scheme for the complex formed in the reaction solution can be assumed (Scheme 5).

Such a structure may be considered as a precursor of an active catalyst with five-coordinated Cu(II) geometry. The rate of formation of these complexes determines the isomerization rate. It is possible to suppose the great impor-



Scheme 5.

tance of similar processes in some other reactions with copper complexes as catalysts. The charge delocalization in large electronic systems involving metals in the different oxidation states and organic molecules provides great scope for chemical processes.

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References

- [1] M.A. El-Sayed, G. Davies, *Inorg. Chem.* 29 (1990) 4891.
- [2] F.J. Viersen, J. Reedijk, *Recl. Trav. Chim. Pays-Bas* 109 (1990) 97.
- [3] H. Hoan, O.N. Temkin, *Kinet. Catal.* 35 (1994) 367.
- [4] W. Kaim, J. Rall, *Angew. Chem.* 35 (1996) 43.
- [5] J.M. Downes, J. Whelan, B. Bosnich, *Inorg. Chem.* 20 (1981) 1081.
- [6] D.J. Fife, W. Moore, K.W. Morse, *Inorg. Chem.* 23 (1984) 2581.
- [7] J.S. Filippo, L.E. Zyontz, J. Potenza, *Inorg. Chem.* 14 (1975) 1667.
- [8] T.N. Rostovshchikova, E.V. Vovk, E.N. Golubeva, *Kinet. Catal.* 33 (1992) 251.
- [9] T.N. Rostovshchikova, V.V. Smirnov, E.V. Vovk, *Kinet. Catal.* 33 (1992) 682.
- [10] T.N. Rostovshchikova, V.I. Pergushov, *Zh. Obshch. Khim.* 64 (1994) 12.
- [11] T.N. Rostovshchikova, V.I. Pergushov, *Zh. Obshch. Khim.* 64 (1994) 985, in Russian.
- [12] G.W. Parshall, S.D. Ittel, *Homogeneous Catalysis. The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes*, 2nd edn., Wiley, New York, NY, 1992, p. 301.
- [13] G.M. Zhidomirov, Ja.S. Lebedev, S.N. Dobrjakov, *Interpretation of the complicated EPR spectra*, Moscow, 1975 (in Russian).
- [14] A.I. Kkorin, A.A. Shubin, *Sov. J. Chem. Phys.* 7 (1991) 1770.
- [15] W.K. Musker, C.H. Neagley, *Inorg. Chem.* 14 (1975) 1728.
- [16] A.A. Shkljaev, N.A. Geraseva, V.F. Ahufrienko, *Coord. Khim.* 5 (1979) 1156, in Russian.
- [17] D.N. Ramakrishna Rao, M.C.R. Symous, B.W. Wren, *J. Chem. Soc. Perkin Trans.*, (1984) 1681.
- [18] H.E. Elliot, B.J. Hathway, R.C. Slade, *J. Chem. Soc.*, (1966) 1443.
- [19] K.T. McGregor, W.E. Hatfield, *J. Chem. Soc. Dalton Trans.*, (1974) 2448.
- [20] G.A. Senyukova, I.D. Micheykin, K.I. Zamaraev, *Zh. Strukt. Khim.* 11 (1970) 23.
- [21] R. Barbucci, A. Bencini, D. Gatteschi, *Inorg. Chem.* 16 (1977) 2127.
- [22] R. Barday, B.F. Hoskins, C.H. Kennard, *J. Chem. Soc.*, (1963) 5691.
- [23] P.C. Jain, E.C. Lingafeller, *J. Am. Chem. Soc.* 89 (1967) 724.
- [24] M. Ferrari, *Acta Cryst. B* 29 (1973) 1808.
- [25] C. Bellitto, F. Bigoli, P. Deplano, M.L. Mercuri, M.A. Pellinghlli, G. Staulo, E.F. Trogu, *Inorg. Chem.* 33 (1994) 3005.
- [26] M. Suzuki, H. Kanatomi, H. Koyama, I. Murase, *Bull. Chem. Soc. Jpn.* 53 (1980) 1961.