Role of chloroolefins in the formation of copper complexes catalytically active in isomerization of dichlorobutenes*

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Tetranuclear copper(I) complexes with organic donor ligands were found to be the best precursors of a catalyst for dichlorobutene isomerization. The products of interaction between allyl chloride and a tetranuclear triphenylphosphine complex of copper bromide were investigated by diffraction and spectral analysis. This reaction yields $[Cu(PPh_3)Br_nCl_{1-n}]_4$ and complexes containing the products of transformation of both triphenylphosphine and allyl chloride.

Key words: copper, dichlorobutenes, allyl chloride, dialkyl sulfide, triphenylphosphine, mixed-valence complexes, isomerization, homogeneous catalysis.

Polynuclear mixed-valence copper complexes with organic ligands are of interest as low-molecular-weight models of the active sites of some enzymes.[1] The high activity of the complexes was demonstrated using nonbiochemical reactions such as allylic isomerization of chloroolefins[2] and some oxidation processes with the participation of alkynes[3] as examples. An increase in the catalytic activity of Cu^{II} complexes in the presence of Cu^I in oxidation processes, which is likely of the same nature, has been observed[4—6].

The data available suggest that active complexes are often formed *in situ* with the participation of reagents. Both oxidizing agents (for example, dioxygen) and organic reagents with pronounced reducing properties (organic sulfides and phosphines) can play an important role in the formation of the active complexes[7,8]. The catalytic isomerization of dichlorobutenes (DCBs)[2,7,8]

$$CH_2ClCHClCH{=}CH_2 \rightleftharpoons CH_2ClCH{=}CHCH_2Cl, \quad (1)$$

is an example of this reaction. In this reaction, the substrate itself, which is not a strong oxidizing or reducing agent, seems to play a key role in the formation of a mixed-valence complex, an isomerization catalyst. Spectral data and the results of studies of the activity of polynuclear mixed-valence complexes of different compositions, synthesized from Cu^I and Cu^{II} compounds, unambiguously indicate that the catalytically active complex contains no less than 3—4 Cu atoms in different oxidation states. The catalytic activity of homovalent copper complexes is inferior to that of the heterovalent analogs by an order of magnitude or more.

The following is evidence of the complicated nature of the catalytically active complex and the participation of chloroolefins in its formation[2,7,8]:

— an induction period is observed in the DCB isomerization in the presence of homovalent Cu^I or Cu^{II} complexes with sulfide or phosphine ligands. For the Cu^I complexes, the reaction rate increases in the presence of dioxygen, and the effect of dioxygen is insignificant for the Cu^{II} complexes;

— the induction period is shortened with the use of tetranuclear copper(I) complexes as the catalyst precursors. The induction period virtually disappears on repeated addition of a solution of complexes used previously in the isomerization to dichlorobutenes. The induction period also disappears with the use of a solid heteroligand complex (probably, a mixture) with the empirical formula $Cu_4Cl_x(PPh_3)_{1.5-2}(DCB)_{2.5-2}$ ($x <$ 7), which was isolated from the reaction solution, as the catalyst;

— a new complex is formed in solutions of Cu^I complexes in the presence of dioxygen or Cu^{II} complexes with donor ligands in DCB. This complex exhibits an electronic absorption spectrum and an EPR spectrum that are typical of mixed-valence $Cu^{I,II}$ compounds. The complex was not found in the absence of the chloroolefin. The catalytic activity of the system agrees with the concentration of this complex.

The results cited suggest that DCB stabilizes catalytically active mixed-valence copper complexes. It is likely that structurally analogous olefins that are incapable of isomerizing will possess the same properties. Allyl chloride (AC) is the simplest example of these compounds.

In this work, the effect of AC on the rate of the DCB isomerization was studied in the presence of tetranuclear copper(I) complexes in order to refine the nature of the

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catalytically active complexes and the role of a chloroolefin in the formation of these complexes. The products of interaction between AC and the copper(I) bromide complex with triphenylphosphine $[CuBr(PPh_3)]_4$ were examined. We decided on triphenylphosphine as a ligand because there are reliable data on the structure of tetranuclear triphenylphosphine complexes of copper halides[9,10].

Experimental

IR spectra of complexes were measured on a Specord M80 spectrophotometer in pellets with KBr and CsI and in mineral oil.

Chromatographic analysis of the reaction products was performed on a Chrom-5 chromatograph with a flame-ionization detector on columns packed with SE-30 and PEG-1000 (5%) stationary phases on Silochrome. Compounds were identified by determining the Kovats retention indices and comparing with reference substances.

Anhydrous Cu^I and Cu^{II} halides and thoroughly purified and dried reagents and solvents were used for preparing complexes. Procedures for purifying the reagents and performing kinetic and spectral measurements have been described previously[2,7,8]. In most cases, the reactions of DCB isomerization proceeded in the presence of dioxygen. For comparison, particular experiments were performed in the absence of dioxygen in evacuated ampules.

Solid copper halide complexes with PPh_3, Me_2S, and Et_2S were prepared according to well-known procedures[9—11]. To examine the role of a chloroolefin, the same syntheses were performed with AC in place of inert chloroform at the concentration $Cu^I = L = 0.005$ mol L^{-1}. An excess solvent was slowly evaporated for 3—4 weeks.

X-ray diffraction analysis was performed on a CAD-4 automatic diffractometer in the scanning mode; the structure was determined using the DIRDIF and SHELXL-93 software programs.

Results and Discussion

Effect of allyl chloride on the rate of isomerization. Tetranuclear copper complexes with dialkyl sulfides and triphenylphosphine are the best catalysts in reaction (1). This is readily apparent from a comparison of the initial rates of isomerization in the presence of complexes of various nuclearity (Table 1). Table 1 demonstrates the effect of additives of different nature (the volume ratio DCB : additive = 4 : 1) on the rate of the isomerization of 3,4-DCB to 1,4-DCB with tetranuclear copper(I) complexes as examples. Under experimental conditions, the process is adequately described by a pseudo-first-order equation with respect to DCB. We used the initial rates related to the initial substrate concentration for comparison with consideration of the reversibility of reaction (1). The experimental error of determining the rate constant was ±15%. As can be seen in Table 1, allyl chloride is an optimum medium for running the reaction. Comparable results were obtained on performing the reaction in the pure substrate. Complex-forming compounds (MeCN, DMF, and diheptyl sulfide) inhibit the reaction; organochlorine solvents have a lesser effect on its rate. The effects observed cannot be explained by a change in nonspecific solvation properties of the medium on introducing additives because the amounts added are small, and the capability of the additives for nonspecific solvation is similar in many cases (AC, chloroform, and chlorobenzene). It is likely that the catalytic activity of complexes in the isomerization is primarily affected by the capability of the added compounds for specific interaction with them. These compounds are favorable (AC) for the formation of species more active in catalysis or inhibit (MeCN, DMF, and excess diheptyl sulfide) the formation of these species.

Table 1. Initial rates of 3,4-DCB isomerization to the 1,4-isomer (100 °C; $[Cu^I] = 0.01$ mol L^{-1})

Catalyst	Additive	[DCB] /mol L^{-1}	$\frac{V_0 \cdot 10^4}{[DCB]}/s^{-1}$
$Cu_4Cl_4[Me_2S]_4$	—	9.44	2.4
$Cu_4Cl_4[Me_2S]_4$	Chlorobenzene	7.55	2.1
$Cu_4Cl_4[Me_2S]_4$	Allyl chloride	7.55	2.9
$Cu_4Cl_4[Me_2S]_4$	Acetonitrile	7.55	1.6
$Cu_4Cl_4[Me_2S]_4$	Dimethylformamide	7.55	1.5
$Cu_4Cl_4[Me_2S]_4$	Diheptyl sulfide	7.55	1.5
$Cu_4Cl_4[Et_2S]_3$	—	9.44	2.1
$Cu_4Br_4(PPh_3)_4$	—	9.44	1.8
$Cu_4Br_4(PPh_3)_4$	Chloroform	7.55	1.2
$Cu_4Br_4(PPh_3)_4$	Allyl chloride	7.55	1.9
$Cu_4Cl_4(PPh_3)_4$	—	9.44	1.6
$Cu_2Cl_2(PPh_3)_3$	—	9.44	0.11
$CuCl(PPh_3)_3$	—	9.44	0.02

Spectral investigation of solutions of the complexes. UV and visible spectra of complexes in the $AC—CuCl_m—PPh_3$ and $AC—CuCl_m—R_2S$ (m = 1 or 2) systems are identical to that described previously for analogous systems with DCB.[2,7,8] When Cu^I solutions in AC with donor additives are left to stand in air, absorption bands in the regions of 420—470 and 800—900 nm appear, as distinct from the case of inert organochlorine solvents. As is the case with DCB, Cu^I in sulfide and phosphine complexes is partially oxidized by dioxygen in the presence of allyl chloride, and Cu^{II} is partially (rather than completely, as without chloroolefin) reduced by the ligands mentioned. In both cases, the complexes have identical spectra in the UV and visible regions and similar EPR spectra (Fig. 1) with parameters close to that described previously for DCB.[2,8,12] The same spectra and processes occurring in the system indicate that the nature of complexes with the participation of AC is identical to that of the DCB complexes, namely, they are mixed-valence copper chloride complexes that include an organic donor ligand and a chloroolefin (or products of transformation of the latter). Note that these complexes are not formed without a chloroolefin, and the spectra of solutions correspond to the spectra of homovalent analogs[2,7,8,11].

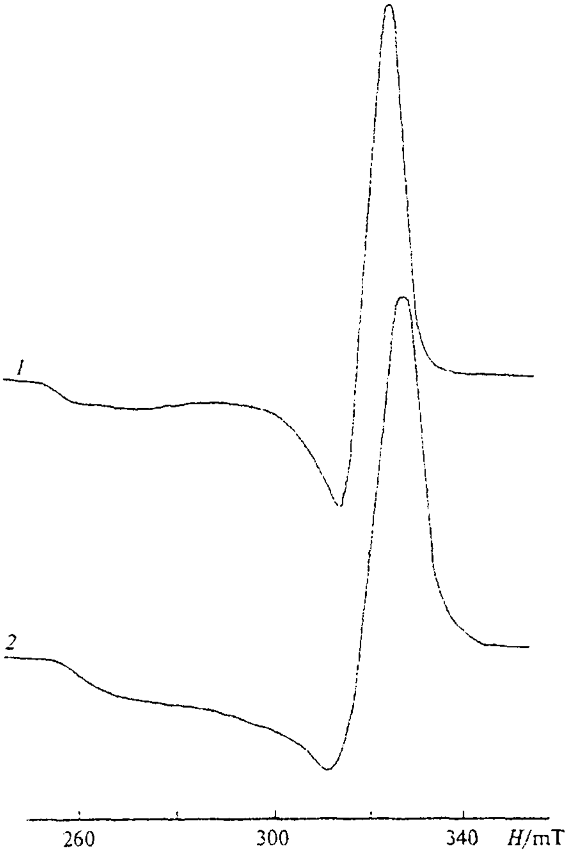
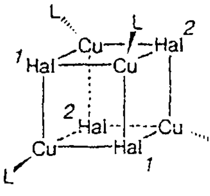


Fig. 1. EPR spectra of CuCl solutions in DCB in the presence of PPh_3 (*1*) and $(C_7H_{15})_2S$ (*2*) after standing in air for a day ($[Cu^I] = 0.01$ mol L^{-1}; $[Cu^{II}] = 0.0025$ mol L^{-1}).

In this work, the capability of the O_2^{2-} ion to participate as a ligand in mixed-valence complexes was additionally examined. It is well known[13] that oxidation of Cu^I complexes with organic ligands by dioxygen often results in the formation of adamantane-like oxygen-containing structures exhibiting absorption bands in the same spectral region as the systems under investigation. However, in this case, synthesis from $CuCl_2$, triphenylphosphine (or diheptyl sulfide), and AC (or DCB) in the absence of dioxygen resulted in complexes with the same spectral properties as that of complexes prepared in air. Thus, it is unreasonable to suggest the necessary participation of oxygen as a bridging ligand in the formation of mixed-valence complexes containing a chloroolefin. On the other hand, data published for Cu^I-based systems (see. Refs. 2, 7, and 8) indicate that dioxygen plays an important role as an activator of the catalytic system. In the absence of dioxygen, the rate of isomerization was lower, and both absorption bands and EPR signals typical for Cu^{II} were not observed in the spectra of the solutions even after prolonged heating.

Isolation of complexes from solutions. Slow evaporation of excess AC from a CuX solution with triphenylphosphine results in a complex mixture containing crystals of several types and a red oily substance. In the case of CuBr, this latter can be washed off with CCl_4; then, the crystals were sorted out into two types under a microscope. The first type (complex **1**) comprises coarse yellowish crystals (to 1—2 mm) having a prismatic habit with good faces. The second (complex **2**) comprises fine crystals (less than 0.5 mm) of the same color and irregular shape. It is not inconceivable that complex **2** is a mixture of different complexes rather than an individual substance. The oily substance washable with CCl_4 also contains copper, which has a typical EPR spectrum similar to that given in Fig. 1, and is a solution of complexes in the products of transformation of AC (see below). Washing the oil with ether results in its decomposition into a copper-containing solid precipitate and a solution of organic components in ether.

X-ray diffraction analysis. A well-defined diffraction pattern was not obtained on attempting to examine complex **2** by X-ray analysis. An isometric crystal of linear size no greater than 0.3 mm in all dimensions was selected for analyzing complex **1**. Complex **1** is an adduct of copper halides with triphenylphosphine of the composition $[Cu(PPh_3)Br_nCl_{1-n}]_4$, where $n = 0.83 \pm 0.02$ (**1**). Complex **1** is isostructural to the corresponding chloro analog $[Cu(PPh_3)Cl]_4$ with somewhat greater unit cell parameters and has a cubane-type geometric structure as distinct from the initial bromide complex $[CuBr(PPh_3)]_4$.



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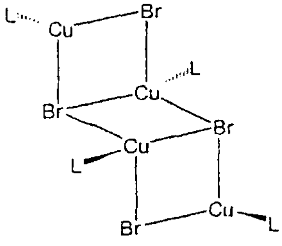


$[CuBr(PPh_3)]_4$

Complex **1** contains 50.84% Br and 49.16% Cl in the *1* position and 31.90% Br and 68.10% Cl in the *2* position.

Vibrational spectra of the complexes. Complex 1. Table 2 summarizes the fundamental vibrational frequencies of this complex in comparison with the literature data[14] on triphenylphosphine, triphenylphosphine oxide, and the initial complex $[CuBr(PPh_3)]_4$. It can be seen that the observed bands correspond to coordination-bonded triphenylphosphine, except for a group of weak bands in the region <300 cm^{-1}, which are not given in Table 2. These weak bands are likely attributed to the copper-halide stretching vibrations in terminal and bridging units. In general, the spectrum obtained is in complete agreement with the X-ray diffraction data

Table 2. IR spectra (ν) of triphenylphosphine, triphenylphosphine oxide, the $[CuBr(PPh_3)]_4$ complex, and complexes 1 and 2 (only medium-intensity and strong bands are given)

Compound	ν/cm^{-1}
PPh_3	1480, 1435, 1095, 1074, 760, 750, 696 vs, 515, 500
PPh_3O	3059, 1440, 1193 vs, 1122 vs, 1072, 998, 760, 727 vs, 695 vs, 542 vs, 505
$[CuBr(PPh_3)]_4$	1480, 1440, 1096, 736, 688 vs, 520, 496
1	1480, 1440, 1096, 1072, 744 vs, 696 vs, 520, 504
2	3056, 2928, 1792, 1720, 1616, 1592, 1480, 1440, 1160, 1120 vs, 1096, 1072, 1000, 744, 720, 696 vs, 544 vs, 520, 504

and can be unambiguously attributed to the tetranuclear triphenylphosphine complex of copper(I) halides.

Complex 2. The spectrum of complex 2 is considerably more complicated. As follows from the data in Table 2, intense bands of PPh_3O are prominent in the spectrum along with a set of bands corresponding to PPh_3. In particular, these are a band at near 720 cm^{-1} (this band is extremely weak in PPh_3) and intense bands at 1120 and 1160 cm^{-1} (PPh_3 has no bands of measurable intensity in this region) and in the region of 3056 cm^{-1} (PPh_3 exhibits absorption in this region; however, the intensity of the bands is low). Generally, it is believed that coordination-bonded triphenylphosphine oxide is present in complex 2. The fact that PPh_3O is present in the complex rather than in a free state is supported by a significant shift of the band of the stretching vibration P=O (1193 → 1160 cm^{-1}). Moreover, absorption bands of the vibrations of aliphatic groups (ν(C—H) 2928, 1792, and 1720 cm^{-1} and a number of bands with intermediate intensity in the region 1500—1600 cm^{-1} where PPh_3 and PPh_3O do not absorb or exhibit bands of extremely low intensity) are present in the spectrum of complex 2.

The attribution of the bands mentioned above is not completely clear. They cannot be assigned to triphenylphosphine, the products of its transformation, and AC because there is no intense bands of AC at 3088, 2960, 1412, and 1256 cm^{-1}; however, additional bands at 1792 and 1720 cm^{-1} are present. The position of the latter bands is typical of carbonyl compounds (acids and ketones); thus, they can be supposedly assigned to the products of AC oxidation.

Red oil. It is likely that this product is a mixture of several substances. Typical bands of AC and the entire set of bands of complex 2 are observed in its spectrum. The above bands supposedly assigned to the products of AC oxidation have higher relative intensity, as compared with other bands, than that in crystalline complex 2. This fact suggests that the oily substance is a solution of complex 2 and free or coordinated allyl chloride in the products of AC transformation. Chromatographic analysis confirmed the presence of AC and unidentified heavy organic compounds (the Kovats index ~1800 on PEG at 150 °C) that are not identical to PPh_3 and its oxide in this oil.

Tentative conclusions on the role of chloroolefin in the course of formation of catalytically active complexes. The results presented demonstrate that a number of competitive reactions occur in the test system, and further examinations are required in order to obtain a complete pattern. However, some conclusions can be drawn even at this stage as follows:

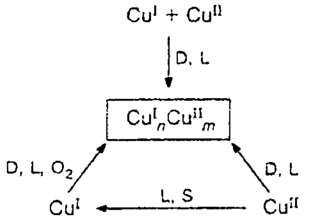
— redox processes with the formation of mixed-valence complexes exhibiting high catalytic activity occur in solutions of copper halide complexes with triphenylphosphine in the presence of chloroolefins with a Cl atom in the allyl position. Comparative experiments with vinylidene chloride in place of AC demonstrated that vinylidene chloride behaves as an inert solvent. The formation of mixed-valence complexes takes place on both oxidation of Cu^I complexes and reduction of Cu^{II} complexes;

— the haloolefin is coordinated to copper ions at the stage preceding the formation of the complex. This is also evidenced by the fact that the predominantly bromine (in composition) complex crystallized from AC was found to be isostructural to the purely chloro rather than purely bromo analog with a chair-like structure;

— on separation of complexes from solutions in AC, if not at the preceding stages, partial oxidation of the complexes occurs followed by the formation of products of triphenylphosphine and chloroolefin oxidation supposedly producing carbonyl compounds. These processes result in the formation of complex 2, which is probably the closest analog of a mixed-valence structure. It is important to note that Cu^I complexes can be obtained from Cu^{II} in an inert solvent as a result of quantitative reduction with an organic donor compound. This reduction was studied in detail with dialkyl sulfides taken as an example[2]. In the absence of a chloroolefin, oxidation of the Cu^I complexes does not take place even on prolonged standing of solutions or the solid complexes in air. The role of a chloroolefin consists in the activation of partial oxidation of a tetrameric copper(I) complex and the coordinated ligands by dioxygen.

— the results obtained together with the literature data[8,12] suggest that tetranuclear copper(I) complexes are precursors of a catalytically active species. This is indicated by the presence of an induction period. The rate of isomerization correlates with the degree of conversion of the complex (an analog of complex 1) into a mixed-valence polynuclear complex. It is likely that this complex, formed only with the participation of a chloroolefin, is transformed to complexes 1 and 2 in the course of separation from a solution;

— the results of this work support in principle a simplified scheme suggested previously[2] for the formation of mixed-valence copper complexes active in catalytic isomerization:



where L is the organic donor; D is the substrate; and S is the solvent.

This scheme ignores the effects of the products of transformation of chloroolefins and dioxygen. A great body of data on the role of oxygen and its metal complexes[13,15,16] in catalytic transformations indicate the importance of these processes to the reaction mechanisms.

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