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Formation of Active Catalysts in the System: Chlorocuprates$-$CCl$_4$$-$$n$-C$_{10}H_{22}$

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Transformations of anionic Cu^{II} chlorocomplexes have been studied under conditions of catalytic exchange reactions between carbon tetrachloride and *n*-alkanes. It was shown that chlorocuprates are just precursors and are easily reduced to the genuine catalysts, that is, to the respective Cu^{I} complexes. Both the composition and the geometric structure of the precursor ($CuCl_4^{2-}$) and, probably, the active site ($CuCl_3^{2-}$) have been investigated by several techniques (UV$-$vis spectroscopy, electron spin resonance (ESR), extended X-ray absorption fine structure (EXAFS), X-ray absorption near-edge structure (XANES), and static magnetic measurements). The dependence of the metathesis velocity on the [Cl$^-$]/[Cu] ratio was found to exhibit a maximum most likely corresponding to the highest content of trichlorocuprite $CuCl_3^{2-}$.

Introduction

Complexes of copper ions with halide anions are known to be catalysts or catalyst precursors for many single electron transfer (SET) processes: the addition of carbon tetrachloride to alkenes,[1,2] the "living" radical polymerization,[3,4] the radical cyclization,[5] and various other applications.[6−8] The key steps of the reactions are proposed to be

$$\{Cu^{II}Cl\} + Red \rightarrow \{Cu^{I}Cl\} + Ox \qquad (1)$$

$$\{Cu^{I}Cl\} + RCl \rightleftarrows \{Cu^{II}Cl_2\} + R\cdot \qquad (2)$$

The first reaction may take place when Cu^{II} complexes are used as precursors. Red is a reducing agent (e.g., a substrate, ligand, counterion, or impurity). In the second step, an active unit designated as {Cu^{I}Cl} reversibly attacks the halohydrocarbon RCl forming a radical R· that may take part in further transformations.

Copper chlorocomplexes are easily formed in solutions containing Cu$^+$ or Cu^{2+} and Cl$^-$ ions.[9−13] In noncomplexing solvents, for example, in chlorohydrocarbons, chlorocuprates(II) exist as mononuclear ($CuCl_4^{2-}$), binuclear ($Cu_2Cl_6^{2-}$), and, possibly, polynuclear species.[14] Cu$^+$ forms with Cl$^-$ anions $CuCl_2^-$, $CuCl_3^{2-}$, and polynuclear complexes (e.g., $Cu_2Cl_4^{2-}$). The ratio in which these complexes are formed depends on [Cl$^-$]/[Cu^{2+}] ([Cl$^-$]/[Cu$^+$]).[15,16]

The relationship between the properties and the activity of copper complexes in SET processes is a subject of active discussion. In some cases, an addition of chloride anions to the reaction mixture promotes the reactions.[17,18] Other examples demonstrate the high activity of polynuclear copper complexes with chloride anions.[19] The aim of our research was to establish connections between composition, structure, and nuclearity of copper chloride complexes and their catalytic activity for the C$-$Cl bond metathesis as one example of a SET process.

$$RCl + R'H \rightarrow RH + R'Cl \qquad (3)$$

The following scheme governs the main steps of this reaction and includes at least four SET processes (1, 4, 7, and 8).[20]

$$\{Cu^{II}Cl\} + Red \rightarrow \{Cu^{I}Cl\} \qquad (1)$$

$$\{Cu^{I}Cl\} + CCl_4 \rightarrow \{Cu^{II}Cl_2\} + CCl_3\cdot \qquad (4)$$

$$CCl_3\cdot + RH \rightarrow CHCl_3 + R\cdot \qquad (5)$$

$$R\cdot + CCl_4 \rightarrow RCl + CCl_3\cdot \qquad (6)$$

$$\{Cu^{II}Cl_2\} + CCl_3\cdot \rightarrow \{Cu^{I}Cl\} + CCl_4 \qquad (7)$$

$$\{Cu^{II}Cl_2\} + R\cdot \rightarrow \{Cu^{I}Cl\} + RCl \qquad (8)$$

$$2CCl_3\cdot \rightarrow C_2Cl_6 \qquad (9)$$

This paper analyzes the main peculiarities of the first step, which is the precursor reduction to Cu^{I} species. {Cu^{II}Cl} are anionic mono-, bi-, and polynuclear chlorocuprates in chlorobenzene. Tris-tributylbenzylammonium cation was used as a counterion. Amines and ammonium cations are known to reduce Cu(II) easily[21−23] and could participate in step 1.

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Experimental Methods

Free-radical processes are highly influenced by the presence of even small amounts of oxygen. At the same time, water can alter the coordination sphere and even the oxidation state of the copper ion. Therefore, special attention was devoted to avoid even traces of water and oxygen in the samples.

Anhydrous cupric chloride and tributylbenzylammonium chloride (TBBAC) were obtained as described in refs 24 and 25. Chlorobenzene was purified by distillation under argon with subsequent drying by 4 Å molecular sieves. The reagents (carbon tetrachloride and *n*-decane) and the catalyst (different proportions of $CuCl_2$ and TBBAC have been used to obtain various $[Cl^-]/[Cu^{2+}]$ ratios and nuclearities of chlorocuprates in the solutions) were dissolved in chlorobenzene at ambient temperature. The concentration of copper ions varied between $2 \cdot 10^{-4}$ and $1 \cdot 1^{-2}$ M, and the concentration of TBBAC varied between $5 \cdot 10^{-4}$ and $3 \cdot 10^{-2}$ M. The initial concentrations of CCl_4 and *n*-decane were 0.1 and 1 M, respectively. The solutions for kinetic measurements were placed into glass ampules, were degassed, and were sealed. Then, they were sustained at 423 K for a fixed period The reaction products were analyzed by gas chromatography (GC).

UV−vis spectra of the solutions were obtained employing the spectrophotometer Shimadzu C-160. Spectra of the initial solutions were detected in open 1 mm cuvettes. Spectra of the previously degassed reaction solutions were recorded in sealed 10 mm cuvettes.

Electron paramagnetic resonance (EPR) spectra were detected employing the radiospectrometer Varian E-3 at 77 K. The standards for the estimation of the **g**-tensor values were Mn^{2+} in MgO matrix and 10^{-3} M $Cu(NO_3)_2$ in 50% mixture CD_3OD-D_2O ($\mathbf{g}_{\|} = 2.424 \pm 0.005$ and $\mathbf{g}_{\perp} = 2.092 \pm 0.005$, $A_{\|} = 117 \pm 3$ G[26]). The content of paramagnetic centers in the samples was measured by double integration of the spectra with subsequent comparison with the standard ($CuCl_2 \cdot 2H_2O$ monocrystal with a known number of spins) as has been described in ref 27.

Magnetic susceptibility was measured by the Faraday method at 77−300 K and at a magnetic field of 10 kOe. For each measurement of the magnetic susceptibilies, the solutions were put into quartz ampules under argon and were sealed off.

The extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) spectra of the Cu−K edge for all samples were obtained at the EXAFS Station of Siberian Synchrotron Radiation Centre. The storage ring VEPP-3 with an electron beam energy of 2 GeV and an average stored current of 90 mA was used as the source of radiation. The X-ray energy was monitored with a channel cut Si(111) monochromator. All spectra were recorded under fluorescent mode. For the EXAFS and XANES measurements, a special cell (with inert gas flushing) was used to avoid the destruction of the samples (solutions). XANES spectra were recorded with stepwidths of about ∼0.2 eV. The EXAFS spectra were treated using standard procedures.[28] The background was removed by extrapolating the pre-edge region onto the EXAFS region in the form of Victoreen polynomials. Three cubic splines were used to construct the smooth part of the adsorption coefficient. The inflection point of the edge of the X-ray adsorption spectrum was used as the initial point ($k = 0$) of the EXAFS spectrum. The radial distribution of the atoms (RDA) function was calculated from the EXAFS spectra in $k^3\chi(k)$ by Fourier transformation at wavenumber intervals of 3.8−12 Å^{-1}. A curve-fitting procedure employing the EXCURV92 code[29] was employed to determine the distances and coordination numbers.

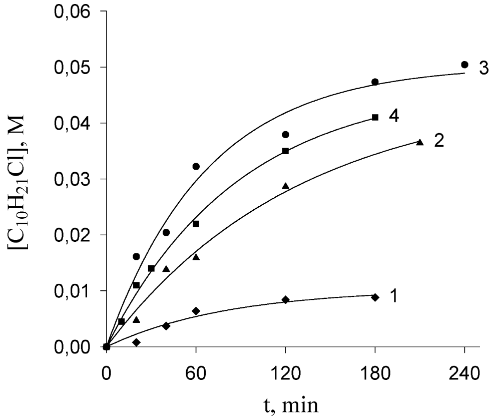

Figure 1. The kinetic curves of the formation of chlorodecanes in C−Cl bond metathesis: 1, $[CuCl_2] = 0$ M; 2, $[CuCl_2] = 2.5 \times 10^{-4}$ M; 3, $[CuCl_2] = 2.0 \times 10^{-3}$ M; 4, $[CuCl_2] = 3.0 \times 10^{-3}$ M; [TBBAC] $= 2.0 \times 10^{-2}$ M.

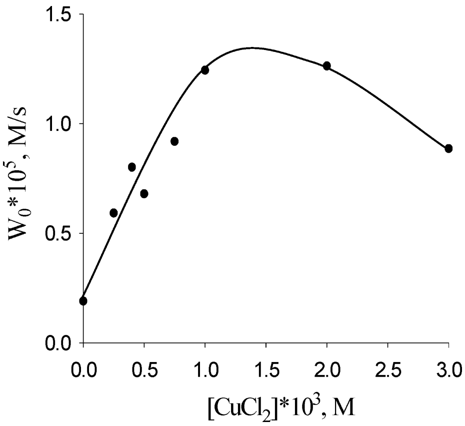

Figure 2. The dependence of the initial velocity of C−Cl bond metathesis on the Cu^{2+} concentration: [TBBAC] $= 2.0 \times 10^{-2}$ M.

This was realized for $k^3\chi(k)$ in similar wavenumber intervals after preliminary Fourier filtering using the known data for copper compounds. The values of the Debye−Waller factors were fixed (0.005 Å^2).

Results

It was shown earlier that the main products of the reaction between carbon tetrachloride and *n*-decane in the presence of copper complexes are chloroform and secondary monochlorodecanes:[30]

$$CCl_4 + C_{10}H_{22} \rightarrow CHCl_3 + C_{10}H_{21}Cl \qquad (10)$$

The same composition of products was obtained when chlorocuprates(II) were used as catalysts. Only small amounts of 1-chlorodecane (less than 5% of all chlorodecanes) and hexachloroethane (<1%) were detected by GC. The kinetic curves of the chlorodecane formation are given in Figure 1.

Induction periods which had been observed when complexes with N,N-dimethylformamide (dmf) were used[31] were not observed in the present investigation. The dependence of the initial velocity on Cu^{2+} concentration at fixed $[Cl^-]$ concentration exhibits a maximum at a $[Cl^-]:[Cu^{2+}]$ ratio around 7 (Figure 2). This value one can explain by the existence of two or more types of copper chlorocomplexes with different reactivity in solutions. In fact, Cu^{II} and Cu^{I} are known to form various types of mono- ($CuCl_4^{2-}$, $CuCl_2^-$, $CuCl_3^{2-}$), bi- ($Cu_2Cl_6^{2-}$, $Cu_2Cl_3^-$,

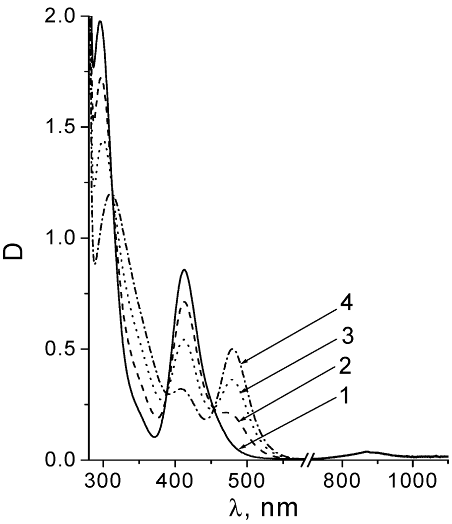

Figure 3. UV−vis spectra of chlorobenzene solutions containing 3×10^{-3} M $CuCl_2$ and different quantities of TBBAC: 1, $[Cl^-]/[Cu^{2+}] = 20$; 2, $[Cl^-]/[Cu^{2+}] = 4$; 3, $[Cl^-]/[Cu^{2+}] = 3.6$; 4, $[Cl^-]/[Cu^{2+}] = 3.2$.

$Cu_2Cl_4^{2-}$), and polynuclear ($Cu_3Cl_8^{2-}$, $Cu_3Cl_4^-$, $Cu_5Cl_7^{2-}$) complexes with Cl^-.[14,31−34] $[Cu^{2+}]$ ions participating in active sites, as well as the right descending part corresponding to high Cu^{2+} concentration, could be explained by the formation of bi- or polynuclear chlorocuprates, which are probably less active in steps 1 and 2. The 7-fold excess of chloride ion probably is necessary to shift the equilibrium to the formation of chlorine-reach complexes ($CuCl_4^{2-}$, $CuCl_3^{2-}$) at high temperatures. To explain this interesting fact and to support our suggestions, it was necessary to compare the reactivity of copper complexes in separate redox reactions (1, 2) representing the Cu^{II} reduction and the generation of radicals, respectively.

Several physical methods (UV−vis, electron spin resonance (ESR), EXAFS, XANES, and static magnetic measurements) were used for the comparison of the activity of the complexes and the study of the dynamics of their transformations in the reaction conditions.

Figure 3 shows the typical UV−vis spectra of the solution of the reagents and the chlorocuprate catalyst in chlorobenzene. Several adsorption bands, corresponding to n→d and d→d transitions,[14,15] were observed.

The transition at 410 nm belongs to the tetrachlorocuprate anion, and the band with a maximum at 480 nm refers to the $Cu_2Cl_6^{2-}$ complex.[15] The broad and complicated absorption structure in the near-infrared (NIR) region corresponds to the d−d transitions in both anions. When heating the reaction system, the intensity of all bands decreases and becomes negligible after 5−10 min.

A typical ESR spectrum of the reaction mixture is given in Figure 4. The spectrum has a biaxial anisotropy of the **g**-tensor ($\mathbf{g}_{\|} = 2.458 \pm 0.005$ and $\mathbf{g}_{\perp} = 2.06 \pm 0.01$) and a nonresolved hyperfine structure. It was shown earlier that such spectra correspond to $CuCl_4^{2-}$ complexes with D_{2d} symmetry.[35] The absence of hyperfine structure may result from strong magnetic dipole−dipole or spin-exchange interactions because of association of quaternary ammonium salts in frozen solutions. Furthermore, the superimposition of ESR spectra of tetrachlorocuprates with different geometry (e.g., with different Cl−Cu−Cl angles) and, consequently, with strongly different **g**-tensor values may take place.[14] Bi- and polynuclear chlorocuprates are usually known to be ESR-silent.[36] Under the reaction conditions used here, the intensity of the ESR spectra diminishes in a similar fashion as the electronic ones.

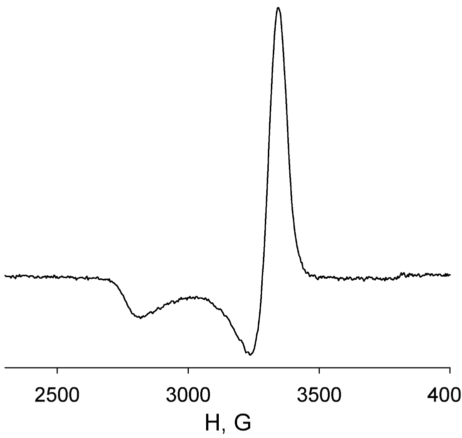

Figure 4. ESR spectrum of the $CuCl_2$ and TBBAC solution in chlorobenzene (77 K); $[Cl^-]/[Cu^{2+}] = 10$.

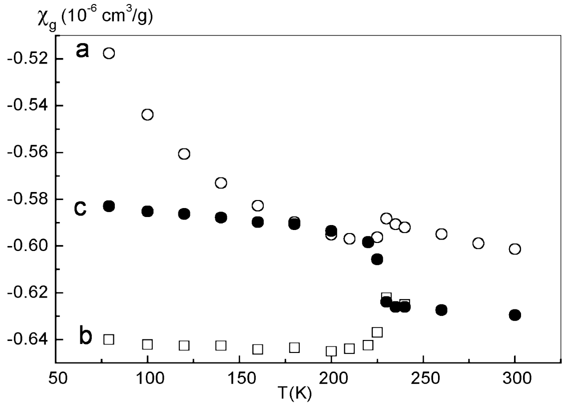

Figure 5. Temperature dependencies of the magnetic susceptibility of the solutions before (a) and after 5 min (b) and 60 min (c) upon heating at 150°.

The most plausible explanation of these experimental results lies in the reduction of Cu^{II} to Cu^{I} of which the complexes exhibit neither an ESR spectrum nor any d→d and n→d transitions. At the same time, one could not exclude the formation of polynuclear Cu^{II} complexes which may also be ESR-silent[36] and which should exhibit the electronic spectra in different spectral regions. This is why other techniques, first of all static magnetic measurements, were to be used for the definitive proof of the proposed reduction of cupric ions. However, this method is seldom used in studies of diluted solutions because of its rather low sensitivity. Nevertheless, attempts were made here to receive accurately and to analyze thoroughly the data of static magnetic measurements.

Consequently, reliable and reproducible data have been obtained when $[Cu^{2+}]$ exceeded 0.01 M. Only tetrachlorocuprates can be dissolved at this concentration ($[Cl^-]/[Cu^{2+}] = 10$).

Dependencies of the magnetic susceptibilities of the tested samples on the external magnetic field were not detected. The temperature dependency of the magnetic susceptibility of the solutions before (a) and after 5 (b) and 60 (c) min of the process is presented in Figure 5.

The Curie−Weiss law is obeyed for system a down to 77 K, as expected for d^9 systems,[14] but after heating, the temperature-dependent paramagnetism was no longer observed. This is another strong evidence for the proposed $Cu^{II} \rightarrow Cu^{I}$ transformation under the reaction conditions.

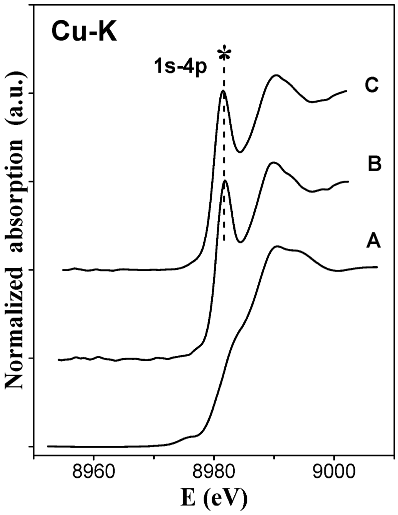

Figure 6. XANES of the system containing $CuCl_2$, TBBAC, and reagents (a) before heating, (b) 5 min heating at 150°, and (c) 60 min heating at 150°.

The above techniques can only be used to detect the disappearance of Cu^{II} complexes. The XANES (X-ray absorption near-edge structure) spectroscopy provides direct information about an oxidation state of a metal ion.[37−40] An oxidation state is generally characterized by the electronic transition from the inner core (1s) to highly excited states near the ionization threshold. For example, Cu^{I} presents a narrow, intense peak corresponding to the $1s \rightarrow 4p$ Cu^{I} electronic transition.[40,41] Even though XANES is rarely used for the study of diluted solutions of metal complexes, we succeeded in the measurement of XANES spectra of the solutions A−C as displayed in Figure 6.

It is obvious that in the spectra B and C the $1s \rightarrow 4p$ transition is clearly apparent, while this peak is absent in the case of the initial mixture A containing only $CuCl_4^{2-}$ units. Thus, these results can be taken as firm evidence for the reduction of tetrachlorocuprate anions under the reaction conditions. The active species, containing Cu^{I}, form rapidly in the solutions. This is in good agreement with the absence of induction periods in the kinetic curves of the metathesis. However, both the composition and the geometry of the active catalysts still need to be identified.

The Fourier transform analysis of the extended X-ray absorption fine structure (EXAFS) oscillations allows a quantitative estimation of the local order as well as of the structure of the immediate vicinity of the central absorber atom in noncrystalline species.[28,37,38] Figure 7 presents the Fourier transformed EXAFS data for the reaction mixtures A−C. Each curve only exhibits one maximum; thus, apparently only one structure prevails in these solutions. However, the geometric parameters of these complexes are different. The Cu−Cl distances and the effective coordination numbers of the copper complexes in the samples are given in Table 1.

The geometry of the dissolved copper complex before the reaction is typical for the mononuclear tetrachlorocuprate anion $Cu^{II}Cl_4^{2-}$,[14,42−44] which is in good agreement with the UV−vis and EPR spectroscopy data obtained here. Following the heat treatment of a new complex under the reaction conditions, complexes with different geometric parameters of their coordination sphere arose instantly and did not change during prolonged reation time. Shorter Cu−Cl distances and the lower coordination numbers are specific for copper ^{I}complexes[46,47] to which the formula $Cu^{I}Cl_3^{2-}$ has been attributed.

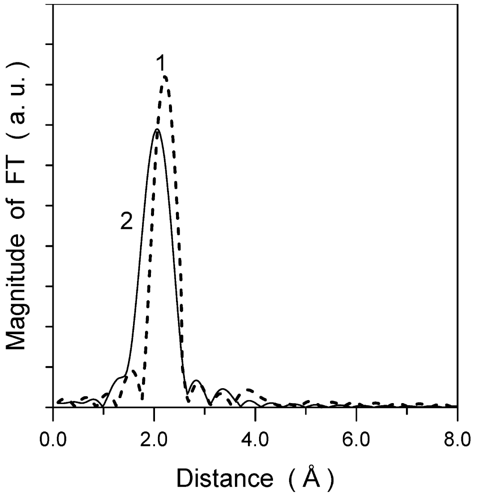

Figure 7. EXAFS of the system containing $CuCl_2$, TBBAC, and reagents (1) before heating and (2) 5 and 60 min heating at 150°.

TABLE 1

sample	*r*(Cu−Cl), Å	effective coord. number	complex
A	2.25	4	$CuCl_4^{2-}$
B	2.11	3	$CuCl_3^{2-}$
C	2.11	3	$CuCl_3^{2-}$

Conclusion

Under the employed reaction conditions, tetrachlorocuprate anions are rapidly reduced to Cu^{I} complexes within a few minutes. These cupric complexes are proposed to be the active species in the catalysis of the C−Cl bond metathesis.

The composition and the geometry of the precursor ($CuCl_4^{2-}$) and of the active site ($CuCl_3^{2}$) have been established by many techniques (UV−vis, ESR, EXAFS, XANES, and static magnetic measurements). The deserved maximum of the dependence of the catalytic activity on the $[Cl^-]/[Cu^{2+}]$ ratio is proposed to correspond to the highest content of active trichlorocuprite $CuCl_3^{2-}$. $CuCl_3^{2-}$ probably is most likely the active species $\{Cu^{I}Cl\}$ in eqs 1, 4, 7, and 8.

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