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Dimerization of Chlorocuprates in Weakly Polar Solvents

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Abstract—The solutions of $CuCl_2$ and tributylbenzylammonium chloride in chlorobenzene, which are used as catalysts for a number of processes with the participation of halogenated hydrocarbons, were studied by electronic spectroscopy in visible and UV regions. It was found that copper(II) ions occurred as two anionic chlorocuprate species ($CuCl_4^{2-}$ and $Cu_2Cl_6^{2-}$), which were in equilibrium, in solutions over wide ranges of concentrations and temperatures. The individual spectra of the two above chlorocuprate species were distinguished. The thermodynamic parameters of the equilibrium $2CuCl_4^{2-} \rightleftarrows Cu_2Cl_6^{2-} + 2Cl^-$ were calculated.

INTRODUCTION

Copper(II) ions in complexes containing halide anions can be reduced to copper(I) with weak reducing agents, such as unsaturated compounds [1], aldehydes and ketones [2], other C–H acids [3], and organic radicals [4, 5]:

$$\{Cu^{2+}Hal\} + Red \rightleftarrows \{Cu^{+}\} + RedHal,$$

where $\{Cu^{2+}Hal\}$ is a copper(II) complex with halide ions, Red is a reducing agent, $\{Cu^+\}$ is a copper(I) complex, and RedHal is a product (or products) of the oxidation of the reducing agent.

It was found that the reactivity of copper(II) complexes depends on the following two main factors: the number of halide anions in the coordination sphere and the nuclearity, that is, the number of metal ions in the complex. An increase in the Hal^- content usually resulted in an increase in the rate of reduction [3, 6]; tetrahalocuprate anions are the most active. In contrast, binuclear and polynuclear copper complexes practically do not enter redox reactions under comparable conditions [7].

The reduction of the chloride complexes of copper(II) is the most important step in many catalytic processes with the participation of hydrogen halides, such as the telomerization of olefins with carbon tetrachloride, the radical polymerization of olefins, the metathesis of C–Hal bonds, etc. [8, 9]. The product of the reduction reaction is a catalytically active halide complex of copper(I):

$$R\text{–}Hal + \{Cu^{+}\} \rightleftarrows R^{\bullet} + \{Cu^{2+}Hal\},$$

$$R^{\bullet} + S \longrightarrow R'^{\bullet} + P,$$

$$R'^{\bullet} + \{Cu^{2+}Hal\} \longrightarrow \{Cu^{+}\} + R'Hal$$

(S is a reagent, and P is a product (or products)).

The thermodynamic characteristics of equilibria in solutions containing halogenated hydrocarbons, Cu^{2+} ions, and halide anions should be known for the optimization of catalytic reaction conditions. However, until recently, the structure and composition of the halide complexes of copper(II) and the parameters of equilibria between various chlorocuprate species have been studied only in polar solvents; as a rule, these solvents are not inert under conditions of catalysis [10, 11]. It is well known that $[CuCl_nL_{4-n}]^{2-n}$ ions, where $n = 0$–4, are formed in water, DMSO, DMF, acetonitrile, etc. At $n < 4$, solvent (L) molecules occupy vacant sites in the coordination sphere of copper [12].

Halogenated hydrocarbons such as chlorobenzene, which do not form complexes with the Cu^{2+} ion, are optimum solvents for performing the above catalytic reactions. For a number of reasons, primarily, because of the low solubility of the halide complexes of copper, the structure, composition, and equilibria between the chloro complexes of copper(II) have practically not been studied. Recently, because of the development of physicochemical techniques, monomeric ($CuCl_4^{2-}$) and dimeric ($Cu_2Cl_6^{2-}$) chlorocuprates were detected in a chlorobenzene medium, and their structural and spectroscopic characteristics were obtained [13]. However, reliable thermodynamic characteristics of equilibrium reaction (I) between these complexes were not found.

$$2CuCl_4^{2-} \rightleftarrows Cu_2Cl_6^{2-} + 2Cl^{-}. \tag{I}$$

The aim of this study was to determine the equilibrium constant, the free energy, the enthalpy, and the entropy of reaction (I).

EXPERIMENTAL

Solutions with different concentration ratios between the dimeric and monomeric chlorocuprates

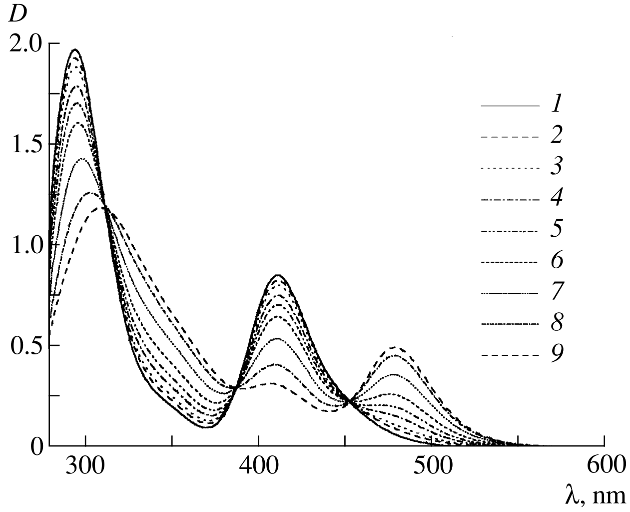

Fig. 1. Electronic spectra of the solutions of $CuCl_2$ and tributylbenzylammonium chloride in chlorobenzene at γ = (*1*) 10.0, (*2*) 5.0, (*3*) 4.5, (*4*) 4.2, (*5*) 4.0, (*6*) 3.8, (*7*) 3.6, (*8*) 3.4, and (*9*) 3.2; $[Cu^{2+}] = 3.2 \times 10^{-3}$ mol/l; l = 1 mm.

were prepared by dissolving anhydrous $CuCl_2$ and tributylbenzylammonium chloride in chlorobenzene [13]. The concentration of $CuCl_2$ was varied within a range from 1.0×10^{-3} to 8.3×10^{-3} mol/l. The concentration of tributylbenzylammonium chloride was varied from 3.6×10^{-3} to 8.3×10^{-2} mol/l. In this case, the ratio $\gamma = [Cl^-]/[Cu^{2+}]$ changed within the range 3.2–20 (at $\gamma < 3.2$, copper(II) chloride dissolved incompletely).

The electronic spectra of chlorocuprate solutions were measured on Shimadzu UV-2401 PC and C-160 spectrophotometers within the wavelength range 280–650 nm at 293–343 K. A hermetically sealed quartz cuvette with an optical path length (l) of 1 mm was used in the experiments. The cuvette was heated with a Nichrome spiral filament directly in the cuvette compartment of the instrument. The accuracy of thermostating was 2 K.

The number of absorbing components was determined using an algorithm [14] based on the calculation of the rank of a light-absorption matrix taking into account the experimental error. The calculation was performed with the use of the MATLAB program. To calculate the concentration of each absorbing species ($CuCl_4^{2-}$ and $Cu_2Cl_6^{2-}$), the measured spectra were represented as a superposition of two spectra corresponding to individual components. In this case, the spectrum of a solution with the maximum value $\gamma = 20$ was taken as the spectrum of the $CuCl_4^{2-}$ anion because at $10 \le \gamma \le 20$ the spectrum of the solution remained almost unchanged. The spectrum of the $Cu_2Cl_6^{2-}$ anion was chosen so that the superposition of two individual spectra showed the best description of the entire set of experimental data. The concentrations of $CuCl_4^{2-}$ and $Cu_2Cl_6^{2-}$ anions were found as corresponding coefficients in the superposition. The molar absorption coefficient at an absorption maximum at 412 nm for a solution with $\gamma = 10$ was calculated by the least-squares technique as the slope of a straight line on the D/l–$[Cu^{2+}]$ coordinates. The total concentrations of copper(II) ions in solutions were additionally refined with the use of molar absorption coefficients at isosbestic points, which were precalculated for a solution with $\gamma = 10$. The calculation was performed by minimizing the sum of squared differences between the experimental and calculated values of optical absorption (D) with the use of Microsoft Excel. The maximum error in the determination of concentrations was 4%.

The equilibrium constant of reaction (I) at temperature T was calculated from the equation

$$K_T = \frac{[Cu_2Cl_6^{2-}][Cl^-]^2}{[CuCl_4^{2-}]^2}\ (\text{mol/l}), \qquad (1)$$

based on the calculated concentrations of the monomeric and dimeric chlorocuprates. The equilibrium constant K_{293} was found as the average of values for different γ ratios.

RESULTS AND DISCUSSION

Figure 1 demonstrates the spectra of the solutions of $CuCl_2$ and tributylbenzylammonium chloride in chlorobenzene with different ratios $\gamma = [Cl^-]/[Cu^{2+}]$ at T = 295 K. It can be seen that the absorption at 480 nm decreased and the absorption at 410 nm increased with γ; the shape of the spectrum in the region 300–400 nm also changed. At $\gamma > 10$, the spectrum remained almost unchanged; according to published data [10], it belongs to the absorption of the $CuCl_4^{2-}$ anion. The absorption band with a maximum at 480 nm corresponds to the dimeric chlorocuprate $Cu_2Cl_6^{2-}$ [15].

To determine the molar absorption coefficient of the $CuCl_4^{2-}$ anion at the absorption maximum at 412 nm, we prepared a series of solutions with variable Cu^{2+} concentration but with a constant γ ratio equal to 10. Figure 2 illustrates the dependence of the absorption of solutions at 412 nm on the molar concentration of copper. The value of ε_{412} calculated by the least-squares technique was equal to $(2.7 \pm 0.1) \times 10^3$ l mol^{-1} cm^{-1}.

As can be seen in Fig. 1, three isosbestic points at 313, 388, and 454 nm can be distinguished in the spectra. Because the optical absorption at these points is independent of the γ ratio, the determination of the molar absorption coefficients of absorbing species at

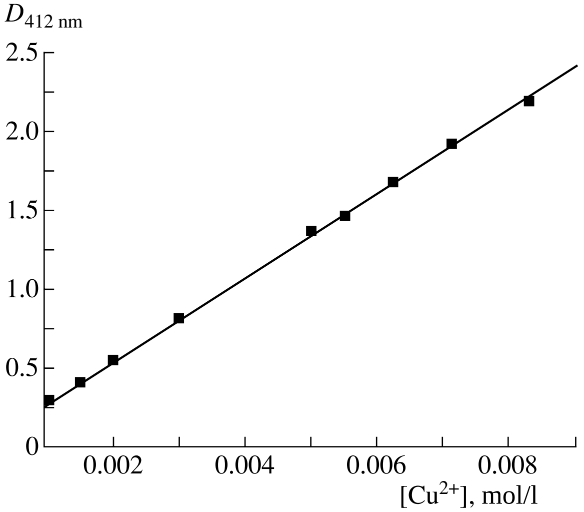

Fig. 2. The dependence of the absorbance at 412 nm on $[\mathrm{Cu}^{2+}]$ at $\gamma = 10.0$; $l = 1$ mm.

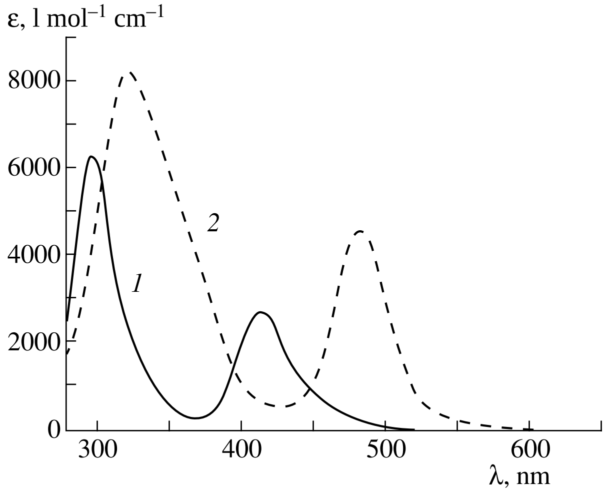

Fig. 3. Individual spectra of the (*1*) $\mathrm{CuCl_4^{2-}}$ and (*2*) $\mathrm{Cu_2Cl_6^{2-}}$ anions.

isosbestic points can be helpful for the accurate calculation of the total copper(II) concentration in solution:

$$\varepsilon_{\text{iso, CuCl}_4^{2-}} = \frac{1}{2}\varepsilon_{\text{iso, Cu}_2\text{Cl}_6^{2-}} = \frac{D_{\text{iso}}}{l[\mathrm{Cu}^{2+}]},$$

where ε_{iso} (l mol^{-1} cm^{-1}) is the molar absorption coefficient at an isosbestic point, D_{iso} is the absorbance at the isosbestic point, and l (cm) is the optical path length. Table 1 summarizes the molar absorption coefficients, which were calculated as described above, of the chlorocuprates $\mathrm{CuCl_4^{2-}}$ and $\mathrm{Cu_2Cl_6^{2-}}$ at the isosbestic points.

The series of spectra shown in Fig. 1 was also used to determine the dependence of the composition of solutions containing $\mathrm{CuCl_2}$ and tributylbenzylammonium chloride on the γ ratio. Previously [13], it was believed that, in addition to the monomeric and dimeric species, which occur in equilibrium (I), complexes with a higher nuclearity ($\mathrm{Cu}_n\mathrm{Cl}_{2n+2}^{2-}$), which absorb in the same spectral range, can be present in the solutions of chlorocuprates in chlorobenzene:

$$\mathrm{Cu_2Cl_6^{2-} + CuCl_4^{2-} \rightleftharpoons Cu_3Cl_8^{2-} + 2Cl^-}\ \text{etc.}$$

However, the calculation of the number of absorbing species at the chosen values of γ demonstrated that all the data (Fig. 1) can be described by the superposition of two individual spectra. This result corresponded to an absolute error in absorption measurements equal to 0.005 [14]. Thus, under experimental conditions, the formation of chlorocuprates with nuclearity higher than 2 can be ignored, and only equilibrium (I) can be considered.

Taking into account the following equations for material balance and the additivity of spectra:

$$[\mathrm{Cu}^{2+}]_{\text{tot}} = [\mathrm{CuCl_4^{2-}}] + 2[\mathrm{Cu_2Cl_6^{2-}}],$$

$$[\mathrm{Cl}^-]_{\text{tot}} = [\mathrm{Cl}^-] + 4[\mathrm{CuCl_4^{2-}}] + 6[\mathrm{Cu_2Cl_6^{2-}}],$$

$$D_\lambda = \varepsilon_{\lambda,\,\mathrm{CuCl_4^{2-}}} l[\mathrm{CuCl_4^{2-}}] + \varepsilon_{\lambda,\,\mathrm{Cu_2Cl_6^{2-}}} l[\mathrm{Cu_2Cl_6^{2-}}],$$

we calculated the concentrations of the $\mathrm{CuCl_4^{2-}}$ and $\mathrm{Cu_2Cl_6^{2-}}$ chlorocuprates in each of the test solutions. Simultaneously, we obtained the individual spectrum of the $\mathrm{Cu_2Cl_6^{2-}}$ anion. Figure 3 demonstrates the spectra of the anions. Figure 4 shows the dependence of the concentrations of the monomeric and dimeric chlorocuprates in the γ ratio in solutions. Based on these data, the equilibrium constant at 293 K was found to be equal to $(5 \pm 3) \times 10^{-6}$ mol/l.

The thermodynamic parameters of equilibrium (I) were determined from the temperature dependence of electronic spectra for solutions with different γ ratios (3.5, 4.0, and 4.2). For each of the solutions, the concentration of copper was refined using the calculated molar absorption coefficients at the isosbestic points (Table 1). We found that the qualitative composition of solutions remained unchanged over a wide range of temperatures. In this case, the entire set of spectra can also be described by the superposition of two individual spectra of the $\mathrm{CuCl_4^{2-}}$ and $\mathrm{Cu_2Cl_6^{2-}}$ anions. The values of K_T calculated for each temperature were linearized on the $\ln(K) - 1/T$ coordinates (Fig. 5); this fact addi-

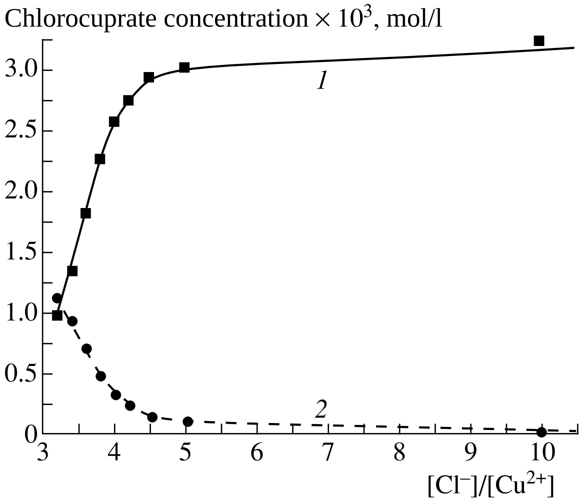

Fig. 4. The dependence of the concentrations of (*1*) $CuCl_4^{2-}$ and (*2*) $Cu_2Cl_6^{2-}$ anions on the γ ratio at T = 293 K; $[Cu^{2+}] = 3.2 \times 10^{-3}$ mol/l.

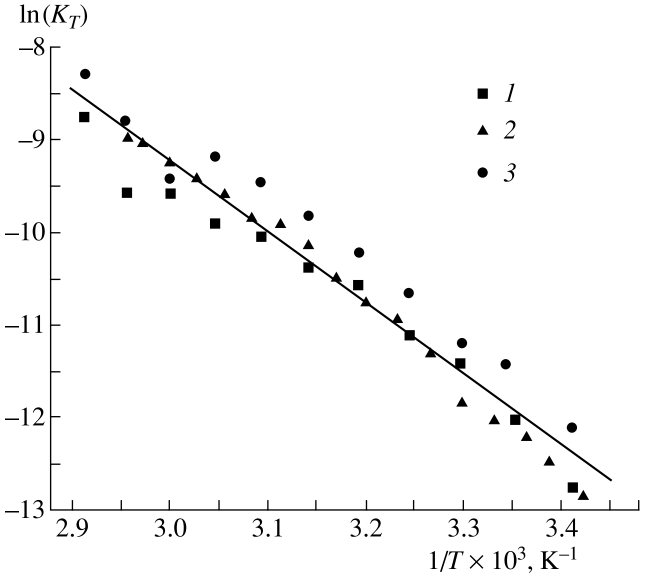

Fig. 5. The temperature dependence of the equilibrium constant K_T (mol/l) of reaction (I) for solutions with γ = (*1*) 3.5, (*2*) 4, and (*3*) 4.2.

tionally supported the occurrence of a unique equilibrium (reaction (I)) in the system. Table 2 summarizes the thermodynamic parameters of this equilibrium. It can be seen that equilibrium (I) is characterized by positive free-energy values up to 556 K. Consequently, the $CuCl_4^{2-}$ were predominant under these conditions. As the temperature was increased, the equilibrium was shifted to the formation of $Cu_2Cl_6^{2-}$.

Table 1. Molar absorption coefficients at isosbestic points for the $CuCl_4^{2-}$ and $Cu_2Cl_6^{2-}$ chlorocuprates in chlorobenzene

λ, nm	$\varepsilon_{iso} \times 10^{-2}$, l mol^{-1} cm^{-1}	
	$CuCl_4^{2-}$	$Cu_2Cl_6^{2-}$
313	37.2 ± 0.6	74 ± 1
388	9.2 ± 0.2	18.4 ± 0.4
454	7.2 ± 0.2	14.4 ± 0.4

Table 2. Thermodynamic parameters of equilibrium (I)

$\log K_{293}$, [mol/l]	ΔH, kJ/mol	ΔS, J mol^{-1} K^{-1}	ΔG_{293}, kJ/mol
−5.4 ± 0.3	64.0 ± 0.8	115 ± 3	30 ± 2

Thus, we found that two types of copper(II) complexes with chloride anions ($CuCl_4^{2-}$ and $Cu_2Cl_6^{2-}$) were present in the Cu^{2+}–Cl^- system in a chlorobenzene solvent over wide concentration and temperature ranges. The individual spectra of the complexes in ultraviolet and visible regions were obtained. The thermodynamic parameters of equilibrium (I) were determined.

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