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Kinetics and Mechanism of the Reaction of Carbon Tetrachloride with Copper in Dimethylacetamide

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Abstract—The reaction of copper with carbon tetrachloride in dimethylacetamide was studied. In the absence of atmospheric oxygen, the oxidative dissolution of copper occurred by the mechanism of single-electron transfer with the formation of C_2Cl_6 and copper(I) complexes. The kinetic and thermodynamic parameters of the reaction were found. The reaction mechanism is discussed.

INTRODUCTION

Complex compounds of copper are in considerable industrial use as selective catalysts in various chemical processes. The direct oxidative dissolution of copper metal in systems containing CCl_4 (a coordinating solvent), which occurs under mild conditions, is one of the most promising methods for the synthesis of these compounds [1].

For the development of optimum conditions for the target-oriented synthesis of the complex compounds of copper halides with organic ligands, the kinetics and mechanism of the reaction of copper with CCl_4 in the presence of dimethylacetamide (DMAA) were studied in detail. In this solvent, copper undergoes oxidation at a high rate [2], and the resulting copper complexes are of interest as catalysts for various chemical processes.

EXPERIMENTAL

The EPR spectra were measured on a Radiopan radiospectrometer at 293 K according to a well-known procedure [3, 4]. 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO) free radical was used as a radical trap.

The low-frequency IR spectra were measured on a Perkin-Elmer 325 spectrophotometer; the samples were prepared as suspensions in mineral oil.

The purity of starting substances was monitored and the quantitative analysis of organic reaction products was performed using gas–liquid chromatography (GLC). The conditions of GLC analysis were described previously [5].

Inorganic reaction products (copper cations) were determined by ion chromatography on a Tsvet-3006 chromatograph with the use of Diacat-3 columns (Elsiko, Moscow; $l = 150$ mm, $d = 3$ mm). An aqueous 4 mM ethylenediamine, 5 mM citric acid, and 5 mM tartaric acid solution was used as an eluant. The rate of elution was 15 ml/min. The sample volume was 100 μL (after 1 : 1000 dilution with water).

Reaction products were analyzed by chromatography–mass spectrometry on a Hewlett-Packard GC–MS instrument (USA) (HP 5972 mass-selective detector, HP 5890 chromatograph) using a chromatographic capillary column ($l = 30$ m, $d = 0.25$ mm) with a diphenyl (5%) stationary phase supported on polydimethylsiloxane. The column temperature was 40–250°C; the heating rate was 30 K/min. Helium was the carrier gas (the carrier-gas flow rate was 1 ml/min). The injector temperature was 250°C, and the detector temperature was 280°C.

Copper powder of >99.99% purity was prepared by the reduction of $CuSO_4$ (analytical grade) with magnesium powder (MP-1) in an atmosphere of argon free from O_2.

A copper wire (GOST 72625-4, Cu content of 99.99%) 0.2 mm in diameter was held in DMF for 24 h. Just before the experiment, the sample was mechanically purified to remove the swollen insulating film, exposed to concentrated nitric acid for 5–10 s, and washed with water, acetone, and then DMAA.

Copper(II) bromide was dried in a vacuum at 60°C according to a published procedure [6].

All of the organic compounds were obtained from commercial sources.

3-Methylpyridine (Janssen) was dried with fused KOH and twice distilled over KOH in an inert gas atmosphere; $T_b = 143.7–144°C$, $n_D^{20} = 1.5067$. Published data: $T_b = 144.0°C$, $n_D^{20} = 1.5068$ [7].

Dimethylacetamide was purified by slow double vacuum distillation over a large amount of P_2O_5 [6].

Carbon tetrachloride, acetone, and other solvents were purified in accordance with standard procedures [8]. All of the solvents were freed from dissolved gases

Table 1. Product composition in the oxidative dissolution of copper in CCl_4–DMAA systems in the absence and in the presence of radical traps

Entry	DCPH/Cu, mol/mol	Yield, mol %	
		$CHCl_3$	C_2Cl_6
1	0	0	100
2	2	67	33
3	3	80	20
4	6	100	0

by repeatedly freezing and thawing at a reduced pressure and stored in ampules in the absence of air.

The procedures used for preparing copper complexes are described below.

A 1-g portion of Cu powder was dissolved in 10 ml of DMAA and 10 ml of CCl_4 in an argon atmosphere at 50°C. After 1 h, the white precipitate formed (which rapidly became green in air) was filtered off in an atmosphere of argon freed from oxygen. The recrystallization from 3-MePy afforded 3.8 g (72%) of yellow crystals, which were stable in air [7]. Found (%): Cu, 16.50; Cl, 9.32; C, 56.88; H, 5.68; N, 11.06. For $C_{18}H_{21}N_3CuCl$ anal. calc. (%): Cu, 16.49; Cl, 9.37; C, 57.14; H, 5.59; N, 11.10. IR spectrum (mineral oil), ν (cm^{-1}): 475 (Cu–N), 420 (Cu–N), 350 (Cu–N), 320 (Cu–N), 292 (Cu–N), 230 (Cu–N).

Organic reaction products were extracted with diethyl ether (20 ml). The ether layer was separated, and the residue was dissolved in 5 ml of an acetone–hexane mixture (1 : 1). After a day, green crystals precipitated from the solution; these crystals were a mixture of two copper(II) complexes that are difficult to separate. The crystals were dissolved in 6 ml of a DMF–CCl_4 mixture (2 : 1, by volume). A 0.2-g portion of 1,2,4-triazole (TA) was added to the solution, and the mixture was heated at 70°C for 10 min. After the solution was cooled, finely crystalline green powder of dichloro(1,2,4-triazole)copper(II) $[CuCl_2(TA)]$ precipitated; this precipitate was separated using standard procedures. The yield was 0.64 g (20%); T_m = 288–290°C. Published data: T_m = 288–290°C [9]. Found (%): Cu, 31.00; Cl, 34.70; C, 11.70; H, 1.50; N, 21.1. Anal. calcd. (%): Cu, 31.23; Cl, 34.85; C, 11.80; H, 1.48; N, 20.64. IR spectrum (mineral oil), ν (cm^{-1}): 319 (Cu–Cl_t), 275 (Cu–Cl_b), 243 (Cu–Cl_b), 253 (Cu–N), where Cu–Cl_t and Cu–Cl_b denote terminal Cu–Cl bonds and bridge bonds, respectively.

Unreacted CCl_4 and DMAA, as well as hexachloroethane (C_2Cl_6), were detected in the ether solution. The isolated yield of C_2Cl_6 was 3.6 g (95%); T_m = 186.5–187.5°C. Published data: T_m = 186.8–187.4°C [10]. Found (%): C, 10.20; Cl, 89.80. For C_2Cl_6 anal. calcd. (%): C, 10.15; Cl, 89.85. Mass spectrum (EI, 70 eV), m/z (I_{rel}, %): 199 $[M–Cl]^+$ (51), 164 $[M–2Cl]^+$ (33), 129 $[M–3Cl]^+$ (13), 117 $[M–CCl_3]^+$ (100), 94 $[M–4Cl]^+$ (33), 82 $[M–CCl_3–Cl]^+$ (22), 70 $[Cl_2]$ (1.3), 59 $[M–5Cl]^+$ (13), 47 $[M–CCl_3–2Cl]^+$ (27).

The reaction in the presence of a radical trap was studied analogously to the above procedures. Dicyclohexylphosphine (DCPH) was used as the radical trap.

Unreacted CCl_4 and DMAA, as well as C_2Cl_6 and $CHCl_3$, were detected in the ether solutions. Table 1 summarizes the yields of organic reaction products.

Chloroform. T_b = 61–61.3°C; n_D^{20} = 1.4458. Published data: T_b = 61.1°C; n_D^{20} = 1.4459 [10]. Found (%): C, 10.05; H, 0.84; Cl, 89.11. For $CHCl_3$ anal. calc. (%): C, 10.06; H, 0.84; Cl, 89.10. Mass spectrum (EI, 70 eV), m/z (I_{rel}, %): 118 $[M]^+$ (1), 117 $[M–H]^+$ (0.7), 83 $[M–Cl]^+$ (100), 82 $[M–H–Cl]^+$ (4), 70 $[Cl_2]$ (1), 47 $[M–H–2Cl]^+$ (36), 36 [HCl] (1).

The preparation of copper complexes in the presence of anhydrous $CuBr_2$ was performed analogously to the above procedures. The Cu : $CuBr_2$ molar ratio was equal to 1 : 1. Unreacted CCl_4 and DMAA, as well as C_2Cl_6 and CCl_3Br, were detected in the ether solution.

Bromotrichloromethane. The yield was 0.16 g (5%); T_b = 104–105°C; n_D^{20} = 1.5064. Published data: T_b = 104.7°C; n_D^{20} = 1.5063 [10]. Found (%): C, 6.10; Cl, 53.63; Br, 40.27. For CCl_3Br anal. calcd. (%): C, 6.06; Cl, 53.64; Br, 40.30. Mass spectrum (EI, 70 eV), m/z (I_{rel}, %): 163 $[M–Cl]^+$ (51), 128 $[M–2Cl]^+$ (5), 117 $[M–Br]^+$ (100), 93 $[M–3Cl]^+$ (5), 82 $[M–Cl–Br]^+$ (41), 81 $[Br]^{\bullet}$ (17), 70 $[Cl_2]$ (0.6), 47 $[M–2Cl–Br]^+$ (31), 35 $[Cl]^{\bullet}$ (15).

Study of the reaction kinetics. The reactions of copper with CCl_4 in DMAA were studied by the resistometric method [11] in accordance with a well-known procedure [2] in an atmosphere of water-free argon freed from oxygen.

The reaction was studied in the kinetic mode, as evidenced by the independence of the rate of copper dissolution in the test media from the rate of stirring. Table 2 summarizes the results of this study.

RESULTS AND DISCUSSION

We studied the reaction kinetics of the oxidative dissolution of Cu in the CCl_4–DMAA system using the resistometric method. This method provides an opportunity to study various kinetic features of fast heterogeneous reactions; it is characterized by high accuracy and reproducibility of results [11, 12].

To determine the kinetic characteristics of the process, the reaction was performed in an indifferent solvent of nonane and *para*-xylene in a ratio of 1 : 1 by volume (DN_{SbCl_5} = 0 kJ/mol for nonane and *para*-xylene) [2].

Table 2. Kinetic and thermodynamic parameters of the oxidative dissolution of copper in the CCl_4–DMAA system calculated using the Langmuir–Hinshelwood mechanism from the adsorption of the reagent and the solvent at different active centers of the metal surface

Parameter	T, K	$k_3 \times 10^3$, g cm^{-2} min^{-1}	K_1, l mol^{-1}	K_2, l mol^{-1}
	313	0.42	0.54	1.54
	323	1.04	0.52	1.04
	333	2.47	0.50	0.71
	343	5.52	0.47	0.50
R*		0.999	0.997	0.999
ΔE_a, kJ/mol		76.6		
$\Delta H^\circ_{CCl_4}$, kJ/mol			−4.0	
ΔH°_{DMAA}, kJ/mol				−33.1
$\Delta S^\circ_{CCl_4}$, J mol^{-1} K^{-1}			−17.9	
ΔS°_{DMAA}, J mol^{-1} K^{-1}				−102.3

* Sample correlation coefficient for the function $\ln K = f\left(\frac{1}{T}\right)$.

The figure demonstrates the dependences of the rate of oxidative dissolution of copper on the concentrations of CCl_4 and DMAA. An increase in the concentration of DMAA from 0.2 to 2 mol/l did not change the shape of curves for the dependence of the reaction rate on the concentration of CCl_4. This fact indicates that the process occurs by the Langmuir–Hinshelwood mechanism with the adsorption of the reagent and the solvent at different active centers of the metal surface [13]:

$$CCl_4 + S_1 \overset{K_1}{\rightleftharpoons} (CCl_4)S_1, \quad \text{(I)}$$

$$L + S_2 \overset{K_2}{\rightleftharpoons} (L)S_2, \quad \text{(II)}$$

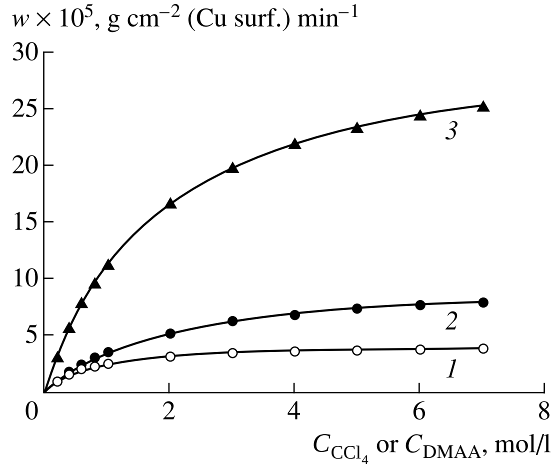
$$(CCl_4)S_1 + (L)S_2 \xrightarrow{k} \text{products}, \quad \text{(III)}$$

where L is DMAA; K_1 and K_2 are the equilibrium constants of CCl_4 and DMAA adsorption, respectively; k is the rate constant of the chemical process; and S_1 and S_2 are the active centers at which the adsorption of CCl_4 and DMAA, respectively, takes place.

In this case, surface coverages derived from the Langmuir isotherms for the adsorption of individual components appear in the rate equation, and an expression for w has the form

$$w = k\frac{K_1K_2[CCl_4][L]}{1 + K_1[CCl_4] + K_2[L] + K_1K_2[CCl_4][L]}. \quad (1)$$

The treatment of the experimental relations (figure) using the set of Eqs. (I)–(III) allowed us to determine the equilibrium constants of CCl_4 and DMAA adsorption on the surface of copper (K_1 and K_2, respectively) and the rate constant k of the chemical reaction. The study of the reaction kinetics at different temperatures allowed us to find E_a of the chemical reaction and the enthalpies and entropies of adsorption of the reactants on the surface of copper. Table 2 summarizes the results.



The dependence of the rate of oxidative dissolution of copper in the CCl_4–DMAA system on the initial concentrations of mixture components in the presence of an indifferent solvent (nonane–*para*-xylene; 1 : 1, by volume) at 313 K: (*1*) C_{CCl_4} = 0.2 mol/l, (*2*) C_{DMAA} = 0.2 mol/l, and (*3*) C_{DMAA} = 2 mol/l. *x*-Axis: C_{CCl_4} for curve *1* and C_{DMAA} for curves *2* and *3*.

A comparison of the results with published data [2] on the oxidative dissolution of copper in the CCl_4–DMSO system demonstrated that $\Delta H^{\circ}_{CCl_4}$ on the surface of copper remained almost unchanged (–4 kJ/mol) on the replacement of DMSO by DMAA, whereas the corresponding values for a coordinating solvent changed considerably (from –46 to –33 kJ/mol). This fact is indicative of the selective adsorption of a dipolar aprotic solvent, which participates in the reaction, on the surface of copper.

The Langmuir–Hinshelwood scheme for the test process suggests that the interaction of adsorbed reactant molecules with the oxidized metal surface, that is, a surface chemical reaction, is a rate-limiting step of the reaction.

A detailed study of the mechanism of any chemical reaction is a challenge. It has recently been found that, as a rule, the reactions of various reagents with metals in dipolar aprotic solvents occur by radical [14], radical–ion [14, 15], or carbanion [16] mechanisms, the ratio between which depends on the nature of the metal, the reagent, and the solvent [14, 17].

The analysis of reaction products demonstrated that, in the absence of atmospheric oxygen (including oxygen adsorbed on the metal surface), the dehalogenation of CCl_4 with copper in DMAA occurred with the formation of C_2Cl_6 and copper(I) complexes, which were identified as tris(trimethylpyridine)copper(I) chloride $[CuCl(3\text{-}MePy)_3]$ [7]:

$$2nCCl_4 + 2nCu + 2mL \longrightarrow nC_2Cl_6 + 2[Cu_nCl_nL_m],$$

$$[Cu_nCl_nL_m] + 3n3\text{-MePy} \longrightarrow n[CuCl(3\text{-MePy})_3] + mL,$$

where L = DMAA, 3-MePy is 3-methylpyridine, $1 \le n \le 4$, and $1 \le m \le 4$.

With the use of ion chromatography, we found that only copper(I) complexes were formed in the course of the process. These complexes slowly reacted with the CCl_4–DMAA system to form copper(II) complexes by the reaction [18]

$$[Cu_nCl_nL_m] + 2nCCl_4 + (2n - m)L \longrightarrow n[CuCl_2 \cdot 2L] + nC_2Cl_6,$$

or they very readily oxidized when the reaction products were isolated in air.

The formation of C_2Cl_6 in the reaction mixture allowed us to assume that the oxidative dissolution of copper in the CCl_4–DMAA system occurs by a radical mechanism.

The disappearance of the EPR signals of the added TEMPO radical, which can react with radical intermediates, suggests that the mechanism of oxidative copper dissolution in CCl_4–DMAA systems has a radical nature, because the EPR signals of TEMPO did not appear after the oxidation of copper and the reduction of the mixtures by KI in an acetate buffer solution [3, 4].

The radical species in solutions were detected and identified with the use of radical traps.

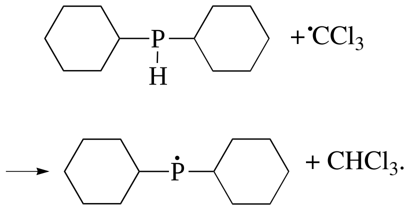
As a chemical trap of radicals, we used DCPH, which previously showed a good performance. It provides an opportunity not only to detect radical intermediates but also to determine their concentration in solution [15].

In the dehalogenation of CCl_4 with copper in DMAA in the presence of DCPH, the composition of reaction products changed depending on the CCl_4 : DCPH molar ratio (Table 1). At the CCl_4 : DCPH molar ratio equal to 1 : 6, the formation of C_2Cl_6 was not observed (Table 1), but an equivalent amount of $CHCl_3$ was detected instead:

$$2CCl_4 + Cu + 2L \xrightarrow{DCPH} [CuCl_2 \cdot 2L] + 2CHCl_3,$$

where L = DMAA.

Analysis of reaction products in the presence of radical traps and in the absence of them indicates that the process occurs by a radical mechanism via the formation of the trichloromethyl radical



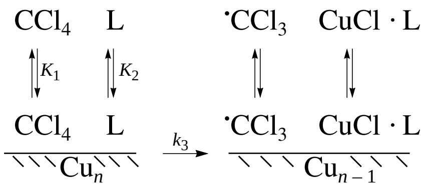
It is well known that ${}^{\bullet}CCl_3$ radicals are readily oxidized by $CuBr_2$ solutions in dipolar aprotic solvents with the formation of CCl_3Br [6]. When the test process was performed in the presence of anhydrous $CuBr_2$ (the Cu : $CuBr_2$ molar ratio was equal to 1 : 1), CCl_3Br (7 mol %) was detected in the reaction products. This fact suggests that the low yield of Cu(II) complexes in the reaction mixture in the course of the process is associated with their reduction by ${}^{\bullet}CCl_3$ radicals to form complex compounds of Cu(I) and CCl_4 [6]. The resulting complexes of Cu(I) slowly interact with CCl_4; therefore, the following equilibrium was established in the system [6, 18]:

$$(n - 1)[CuCl_2 \cdot 2L] + (n - 1){}^{\bullet}CCl_3 \rightleftharpoons [Cu_{n-1}Cl_{n-1}(m - 2)L] + (n - 1)CCl_4 + (2n - m)L,$$

where L = DMAA; $1 \le n \le 4$; $1 \le m \le 4$.

The results of this work indicate that the dehalogenation process occurs on the surface of copper by a radical mechanism via the formation of ${}^{\bullet}CCl_3$ radicals, which undergo colligation in solution. The adsorption of the reagent and the solvent occurs by the Langmuir–

Hinshelwood mechanism at different active centers of the metal surface in accordance with the scheme



The $^{\bullet}CCl_3$ radicals undergo dimerization in solution to form hexachloroethane:

$$^{\bullet}CCl_3 + {}^{\bullet}CCl_3 \longrightarrow C_2Cl_6.$$

The complex compounds of copper(I) with organic ligands in solutions form di- or tetramers [18]:

$$CuCl \cdot L + Cu_{n-1}Cl_{n-1} \cdot L_{n-1} \longrightarrow Cu_nCl_n \cdot L_n,$$

$$Cu_nCl_n \cdot L_n + (m-n)L \longrightarrow [Cu_nCl_n \cdot mL]\downarrow,$$

where L = DMAA, $2 \le n \le 4$, and $2 \le m \le 4$.

The resulting copper(I) complexes very slowly react with the CCl_4–L system in accordance with the following reaction scheme [6, 18]:

$$[Cu_nCl_n \cdot mL] + CCl_4 \rightleftarrows [Cu_nCl_n \cdot mL]^{+}CCl_4^{\overline{\bullet}}$$

$$\longrightarrow {}^{\bullet}CCl_3 + [Cu_nCl_{n+1} \cdot mL],$$

$$^{\bullet}CCl_3 + {}^{\bullet}CCl_3 \longrightarrow C_2Cl_6,$$

$$[Cu_nCl_{n+1} \cdot mL]$$

$$\longrightarrow [Cu_{n-1}Cl_{n-1} \cdot (m-2)L] + [CuCl_2 \cdot 2L],$$

$$[Cu_{n-1}Cl_{n-1} \cdot (m-2)L] + (n-1)CCl_4$$

$$+ (2n-m)L \rightleftarrows (n-1)[CuCl_2 \cdot 2L]$$

$$+ (n-1){}^{\bullet}CCl_3, \text{ etc.}$$

Moreover, copper(II) complexes can be reduced by copper metal [3] with the formation of copper(I) complexes:

$$n[CuCl_2 \cdot 2L] + nCu + 2(m-n)L$$

$$\longrightarrow 2[Cu_nCl_n \cdot mL].$$

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