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Kinetics and Mechanism of Reaction of Carbon Tetrachloride with Copper(0) in Dimethylformamide

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Abstract—Reaction of copper(0) with carbon tetrachloride in DMF was studied. In the absence of atmospheric oxygen, the oxidative dissolution of copper(0) occurs as one-electron transfer and gives rise to C_2Cl_2 and copper(I) complexes. Kinetic and thermodynamic parameters of the process are determined, and its mechanism was considered.

One of the most perspective synthetic approaches to copper(I) complexes invoves direct oxidative dissolution of metallic copper in carbon tetrachloride–coordinating solvent systems, that occurs in mild conditions [1].

The aim of the present work was to study the mechanism and kinetic regularities of the reaction of copper(0) with CCl_4 in the presence of DMF, since the latter solvent favors fast oxidation [2], and the resulting copper(I) complexes are of interest as catalysts.

The kinetics of the oxidative dissolution of copper(0) in the CCl_4–DMF system were studied by resistometry, since this method provides highly accurate and reproducible kinetic characteristics of fast heterogeneous reactions [3, 4]. The reaction was performed in an inert solvent, such as a mixture of nonane and *p*-xylene, 1:1 by volume [for nonane and *p*-xylene, *DN*($SbCl_5$) 0], the showed itself nicely previously [2].

The resulting kinetic curves are shown in the figure. Their analysis shows that the process occurs by the Langmuir–Hinshelwood or Eley–Rideal [5]. The Langmuir–Hinshelwood mechanism relates to reaction of equibrially and independently adsorbed reagent and solvent molecules with metal surface with subsequent formation of intermediates and products. In this case, there are two possible schemes of the process. The first suggests reagent and solvent adsorption of active centers of metal surface [2, 5].

$$CCl_4 + S_1 \overset{K_1}{\rightleftarrows} (CCl_4)S_1, \qquad (1)$$

$$L + S_2 \overset{K_2}{\rightleftarrows} (L)S_2, \qquad (2)$$

$$(CCl_4)S_1 + (L)S_2 \xrightarrow{k} \text{Reaction products.} \qquad (3)$$

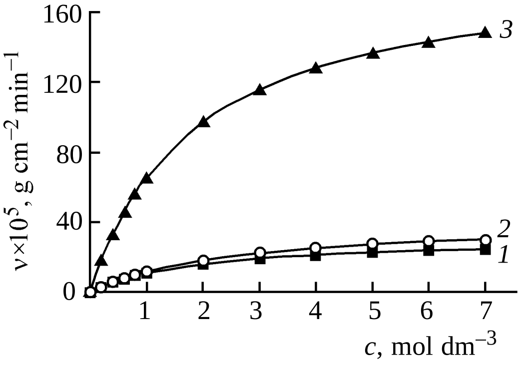
Here and hereinafter, L is DMF; K_1 and K_2, equilibrium adsorption constants of CCl_4 and DMF, respectively; *k*, rate constant of reaction (3); and S_1 and S_2, CCl_4- and DMF-adsorbing active centers of metal surface, respectively.

In this case, the kinetic equation includes the surface concentrations of the components, obtained from their Langmuir isotherms, and takes the form

$$v = k' \frac{K_1K_2[CCl_4][L]}{1 + K_1[CCl_4] + K_2[L] + K_1K_2[CCl_4][L]}. \qquad (4)$$

$k' = KN_1N_2$, where N_1 and N_2 are the numbers of CCl_4- and DMF-adsorbing active centers of metal surface, respectively.

The second scheme suggests formation on metal surface of intermediate compounds $(CCl_4)_x(DMF)_yS$ [2].



Rate of oxidative dissolution of copper(0) in the CCl_4–DMF system vs. initial concentrations of the components of the system at 343 K in the presence of an inert solvent (nonane–*p*-xylene, 1:1 by volume). (*1*) c_{DMF} 0.2, (*2*) c_{CCl_4}, and (*3*) c_{DMF} 2 M.

$$CCl_4 + S \underset{}{\overset{K_1}{\rightleftarrows}} (CCl_4)S, \quad (5)$$

$$L + S \overset{K_2}{\rightleftarrows} (L)S, \quad (6)$$

$$x(CCl_4)S + y(L)S \overset{K_3}{\rightleftarrows} (CCl_4)_x(L)_yS + (x + y - 1)S, \quad (7)$$

$$(CCl_4)_x(L)_yS \xrightarrow{k} \text{Reaction products.} \quad (8)$$

Here K_1, K_2, and K_3 are the equilibrium constants of reactions (5)–(7); k, rate constant of reaction (8); and S, CCl_4- and DMF-adsorbing active centers.

If the reaction occurs by the second scheme [Eqs. (5)–(8)], where $x = y = 1$, its rate has Eq. (9) [2].

$$v = k'\frac{K_1K_2K_3[CCl_4][L]}{1 + K_1[CCl_4] + K_2[L] + K_1K_2K_3[CCl_4][L]}. \quad (9)$$

$k' = KN$, where N is the number of CCl_4- and DMF-adsorbing active centers of metal surface.

The Eley–Rideal mechanism [5, 6] suggests that an oxidant molecule equilibrially adsorbed on metal surface reacts with the metal, when a molecule of the coordinating solvent approaches this oxidant molecule from solution. The nonlinear v–[L] dependence shows that DMF molecules, too, are adsorbed on metal surface [schemes (10)–(12)] [6].

$$CCl_4 + S \overset{K_1}{\rightleftarrows} (CCl_4)S, \quad (10)$$

$$L + S \overset{K_2}{\rightleftarrows} (L)S, \quad (11)$$

$$(CCl_4)_S + L \xrightarrow{k} \text{Reaction products.} \quad (12)$$

In this case, the reaction rate has Eq. (13) [k' is given by Eq. (9)] [6].

$$v = k'\frac{K_1[CCl_4][L]}{1 + K_1[CCl_4] + K_2[L]}. \quad (13)$$

As the concentration of DMF is increased from 0.2 to 2 M, the dependence of reaction rate on CCl_4 concentration preserves its shape, implying a Langmuir–Hinshelwood reaction mechanism [7, 8]. The fact that the reaction in hand follows the Langmuir–Hinshelwood scheme suggests that the limiting stage involves reaction of adsorbed reagent molecules with the surface of the metal to be oxidized, i.e. a surface chemical reaction.

However, we now have insufficient evidence to decide between these two schemes [Eqs. (1)–(3) and (5)–(8)] unambiguously.

Treatment of the experimental dependences (see figure) in terms of Eqs. (1)–(3) gave the equilibrium absorption constants of CCl_4 and DMF on copper(0) surface (K_1 and K_2) and the rate constant (k') of the chemical process. From the kinetic parameters at various temperatures we obtained the activation energy (E_a) of the chemical process, as well as the absorption enthalpy (ΔH) and entropy of the reagents (ΔS) on copper(0) surface (see table).

The resulting E_a value for the chemical process (79820 ± 324 J mol^{-1}) are nicely consistent with the value obtained by electrodialysis (83500 ± 300 J mol^{-1}) on the assumption that the reaction is first-order in CCl_4 [4].

Actually, at low degrees of copper surface covering, the reaction rate is proportional to the reagent concentrations to the first power [Eq. (14)] [2, 5].

$$v = KN_1N_2K_1K_2[CCl_4][L]. \quad (14)$$

The equation for the apparent activation energy (E_a^{ap}) of the overall process takes form (15).

$$E_a^{ap} = E_a + \Delta H^0_{ads}(CCl_4) + \Delta H^0_{ads}(DMF). \quad (15)$$

The E_a^{ap} calculated by Eq. (15) is 48500 ± 800 J mol^{-1} is nicely consistent with the experimental apparent reaction constant of the overall process (E_a^{ap} 45200 ± 500 J mol^{-1}).

Comparison of the resulting with those obtained in [2] for oxidative dissolution of copper(0) in the CCl_4–DMSO system showed that the $\Delta H^0_{ads}(CCl_4)$ on copper surface remains almost invariable in going from DMSO to DMF (–4 kJ mol^{-1}), whereas the respective values for the coordinating solvent vary rather strongly (from –46 [2] to –27 kJ mol^{-1}). This finding suggests selective adsorption of the dipolar aprotic solvent on copper(I) surface, which is consistent with published data [8] on adsorption of organic compounds on the surfaces of metals and their oxides.

Analysis of the reaction products led us to conclude that in the absence of atmospheric oxygen (including that adsorbed on metal surface) dehalogenation of CCl_4 with copper(0) in DMF gives rise C_2Cl_6 and Cu^+ and Cu^{2+} complexes.

In solutions, the Cu^+ complexes form di- or tetramers and are quite easily oxidized in air [schemes (16) and (17)] [9], and, therefore, they were identified by IR spectroscopy and elemental analysis as tris(3-methylpyridine)copper(I) chloride $[CuCl(3\text{-}MePy)_3]$ [10] prepared by their reaction with 3-methylpyridine [scheme (18)].

$$CuCl \cdot L + Cu_{n-11} \cdot L_{n-1} \longrightarrow Cu_nCl_n \cdot L_n, \quad (16)$$

Kinetic and thermodynamic parameters of oxidative dissolution of copper(0) in the CCl_4–DMF, calculated by the Langmuir–Hinshelwood scheme

Parameter	$k' \times 10^3$, g cm^{-2} min^{-1}	K_1, l mol^{-1}	K_2, l mol^{-1}
T, K			
313	0.28 ± 0.01	0.62 ± 0.01	1.00 ± 0.01
323	0.74 ± 0.02	0.60 ± 0.01	0.72 ± 0.01
333	1.78 ± 0.02	0.57 ± 0.01	0.53 ± 0.01
343	4.21 ± 0.02	0.54 ± 0.01	0.40 ± 0.01
R [a]	0.999	0.995	0.999
E_a, kJ mol^{-1}	79.80 ± 0.30	–	–
ΔH^0_{ads} (CCl_4), kJ mol^{-1}	–	–4.00 ± 0.30	–
ΔH^0_{ads} (DMF), kJ mol^{-1}	–	–	–27.30 ± 0.20
ΔS^0_{ads} (CCl_4), J mol^{-1} K^{-1} [b]	–	–16.90 ± 0.90	–
ΔS^0_{ads} (DMF), J mol^{-1} K^{-1} [b]	–	–	–87.10 ± 0.70

[a] Correlation coefficient for the $\ln K = f(1/T)$ dependence. [b] For 298 K.

$$Cu_nCl_n \cdot L_n + (n - m)L \longrightarrow [Cu_nCl_n \cdot mL], \quad (17)$$

$$2 \le n \le 4 \text{ and } 2 \le m \le 4,$$

$$[Cu_nCl_nL_m] + 3n\text{3-MePy} \rightarrow n[CuCl(\text{3-MePy})_3] + mL, \quad (18)$$

$$1 < n < 4 \text{ and } 1 < m < 4.$$

Ionic chromatography was used to show that the process involves initial formation of Cu^+ compounds that are further oxidized with the CCl_4–DMF system by the mechanism of oneelectron transfer [9]. The structure of the complexes depends on the reagent ratio [11] [schemes (19)–(21)].

$$2nCCl_4 + 2nCu + 2mL \longrightarrow nC_2Cl_6 + 2[Cu_nCl_nL_m], \quad (19)$$

$$2[Cu_nCl_nL_m] + 2nCCl_4 + (4n - 2m)L$$
$$\longrightarrow 2n[CuCl \cdot 2L] + nC_2Cl_6, \quad (20)$$

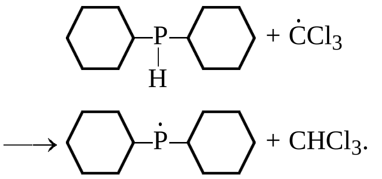
$$6[Cu_nCl_nL_m] + 6nCCl_4$$
$$2n[Cu_3Cl_6 \cdot 2L] + (6m - 4n)L + 3nC_2Cl_6, \quad (21)$$

$$1 \le n \le 4 \text{ and } 1 \le m \le 4.$$

The formation of C_2Cl_6 in the reaction mixture allows us to suggest the oxidative dissolution of copper(0) in the CCl_4–DMF system occurs as one-electron transfer.

Radical species in solutions were detected and identified by means of radical traps. The disappearance during reactions of the ESR signals of the stable 2,2,6,6-tetramethylpiperidine 1-oxide radical that is capable of reacting with radical intermediates provides further evidence for the radical nature of the process, since ESR signals of 2,2,6,6-tetramethylpiperidine 1-oxide do not appear after oxidation of Cu0 and reduction of mixtures with KI in acetate buffer and H_2O_2 in alkaline medium [12, 13].

As the chemical radical trap we applied dicyclohexylphosphine (DCHP) that not only allows one to detect radical intermediates, but also to determine their concentration in solution [14] [scheme (22)].


(22)

The product composition of the dehalogenation of CCl_4 with copper(0) in DMF in the presence of DCHP depends on the Cu^0–DCHP molar ratio. In the absence of DCHP, the major reaction product is C_2Cl_6. When the Cu^0–DCHP molar ratio is 1 : 1, $CHCl_3$ (67%) was found along with C_2Cl_6 (33%), whereas at Cu^0–DCHP = 1 : 5, no C_2Cl_6 was detected; instead, equivalent amount of $CHCl_3$ was formed.

$$CCl_4 + Cu + 2L \xrightarrow{\text{DCHP}} [CuCl_2 \cdot 2L] + 2CHCl_3. \quad (23)$$

Analysis of the reaction products in the absence and in the presence of radical traps established that stages (19)–(21) occur by a radical mechanism via formation of trichloromethyl radicals that recombine mostly in solution. Moreover, CCl_3 can reduce Cu^{2+} compounds to compounds with Cu^+ and CCl_4 [scheme (24)].

$$n[CuCl_2 \cdot 2L] + nCCl_3$$
$$\longrightarrow [Cu_nCl_n \cdot mL] + nCCl_4 + (2n - m)L. \quad (24)$$

Evidence for this suggestion comes from the fact the reaction in the presence of anhydrous $CuBr_2$ ($Cu^0:CuBr_2$ molar ratio is 1:1) gave CCl_3Br (5 mol%) among other products. This result is consistent with the results of oxidation of $(CCl_3)_2Hg$ with anhydrous $CuBr_2$ in DMF, that, too, involves CCl_3 formation [15].

Our present findings show that the process in hand occurs by the mechanism of one-electron transfer via formation of CCl radicals that recombine in solution; therewith, the reaction of CCl_4 and DMF with copper(0) surface occurs by the Langmuir–Hinshelwood scheme.

EXPERIMENTAL

The ESR spectra were recorded on a Radiopan SE/Œ-2543 spectrometer (9400 MHz) at 293 K by the procedure in [12, 13]; the radial trap was 2,2,6,6-tetramethylpiperidine 1-oxide. The low-frequency IR spectra were obtained on a Perkin–Elmer-325 spectrophotometer in mineral oil.

The purity of the starting materials was controlled and quantitative analysis of organic reaction products was performed by GLC (see [16]).

Inorganic reaction products (Cu^+ and Cu^{2+}) were analyzed by ionic chromatography on a Tsvet-3006 chromatograph on Diacat-3 columns (150 × 3 mm; Elsiko, Moscow). The eluent was aqueous solution of ethylenediamine (4 mM), citric acid (5 mM), and tartaric acid (5 mM); elution rate 15 ml/min; sample volume 100 μl (dilution 1:1000).

Gas chromatography–mass spectrometry was performed on a Hewlett–Packard instrument (HP-5972 mass-selective detector, HP-5890 chromatograph) using a an HP-5 capillary column (30 000 ± 25 mm); oven temperature 40–250°C, heating rate 30 deg min^{-1}, carrier gas helium (1 ml min^{-1}), injector temperature 250°C, detector temperature 280°C.

Cu^0 powder (purity >99.99%) was obtained by reduction of $CuSO_4$ (analytic grade) with magnesium powder (MP-1) under oxygen-free argon. Copper wire (State Stadard 7262-54, Cu 99.99 wt%) 0.2 mm in diameter was kept in DMF for 24 h. Immediately before use the sample was mechanically cleared of swollen isolation film, immersed for 5–10 s into concentrated nitric acid, washed with water, acetone, and DMF [2].

Copper(II) bromide was dried in a vacuum at 60°C as described in [15].

All organic compounds were purified as described in [17], solvent were degassed by repeated freezing–pumping–thowing cycles and handled in ampules.

The kinetics of the reaction of copper(0) with CCl_4 in DMF were studied by resistometry [3, 4] under dry oxygen-free argon, stirring speed was 2500 rpm. Beginning with 2000 rmp, the rate of copper(0) dissolution was independent of stirring speed, implying a kinetic regime of the process.

To study the reactions in the presence and in the absence of DCHP, copper(0) powder, 1 g, was dissolved in 10 ml of DMF and 10 ml CCl_4 with or with no DCHP addition (the DCHP:Cu molar ratio was varied from 0 to 5) at 50°C under argon with continuous stirring. When the metal had dissolved and a white precipitate of a Cu^+ compound formed, organic reaction products were extracted with 30 ml of ether, and the residue was dissolved in an acetone–hexane mixture, 1:1 by volume. Green crystals of $[Cu_2Cl_4(DMF)_4]$ precipitated and were filtered off and analyzed. The Cu^+ compound was recrystallized from 3-methylpyridine and analyzed as $[Cu(3\text{-}MePy)_3Cl]$. IR spectrum (mineral oil), ν, cm^{-1}: 475, 420, 350, 320 (Cu–N); 292 (Cu–Cl); 230 (Cu–N). Found, %: C 56.88; H 5.68; Cl 9.32; Cu 16.50; N 11.06. $C_{18}H_{21}N_3ClCu$. Calculated, %: C 57.14; H 5.59; Cl 9.37; Cu 16.49; N 11.10.

By GC–MS in the ether extracts we detected unreacted DMF and CCl_4, as well as C_2Cl_6 and/or $CHCl_3$.

The oxidative dissolution of copper(0) in the CCl_4–DMF system in the presence of dry $CuBr_2$ was performed in a similar way, Cu:CuBr2 = 1:1. The ether extract contained unreacted CCl_4 and DMF, as well as C_2Cl_6 and CCl_3Br.

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