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 C2Cl2 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 involves 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 CCl4 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 CCl4: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(SbCl5) 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 metalsurface 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].

Here and hereinafter, L is DMF; $K_1$ and $K_2$, equilibrium adsorption constants of CCl4 and DMF, respectively; $k$, rate constant of reaction (3); and $S_1$ and $S_2$, CCl4- 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

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

$k' = KN_1 N_2$, where $N_1$ and $N_2$ are the numbers of CCl4- and DMF-adsorbing active centers of metal surface, respectively.

The second scheme suggests formation on metal surface of intermediate compounds (CCl4)$_x$(DMF)$_y$S [2].

![Graph showing the relationship between rate of oxidative dissolution of copper(0) and initial concentrations of the components in the CCl4:DMF 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.](1070-3632/05/7507-1131©2005PleiadesPublishing,Inc.)
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. (10)–(12)], where $x = y = 1$, its rate has Eq. (9) [2].

$$v = k' \frac{K_1 K_2 K_3 [CCl_4][L]}{1 + K_1 [CCl_4] + K_2 [L] + K_1 K_2 K_3 [CCl_4][L]}$$

$k' = KN$, 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 equilibrally 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].

$$CCl_4 + S \overset{K_1}{\longrightarrow} (CCl_4)S,$$

$$L + S \overset{K_2}{\longrightarrow} (L)S,$$

$$(CCl_4)S + y(L)S \overset{K_3}{\longrightarrow} (CCl_4)_y(L)_yS + (x + y - 1)S,$$

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

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

$$v = k' \frac{K_1 [CCl_4][L]}{1 + K_1 [CCl_4] + K_2 [L]}$$

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 ($\Delta H$) and entropy of the reagents ($\Delta S$) on copper(0) surface (see table).

The resulting $E_a$ value for the chemical process (79820 ± 324 J mol$^{-1}$) is 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].

$$v = K_1 N_2 K_1 K_2 [CCl_4][L].$$

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

$$E_{ap}^a = E_a + \Delta H_{ads}^0 (CCl_4) + \Delta H_{ads}^0 (DMF).$$

The $E_{ap}^a$ calculated by Eq. (15) is 48500 ± 800 J mol$^{-1}$, which is nicely consistent with the experimental apparent reaction constant of the overall process ($E_{ap}^a$ 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 $\Delta H_{ads}^0 (CCl_4)$ 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$_2$Cl$_6$ and Cu$^+$ and Cu$^{2+}$ complexes.

In solutions, the Cu$^+$ complexes form di- or tetra- 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-MePy)$_3$] [10] prepared by their reaction with 3-methylpyridine [scheme (18)].

$$\text{CuCl} \cdot L + Cu_{n-11} \cdot L_{n-1} \longrightarrow Cu_n Cl_n \cdot L_n. \quad (16)$$