Oxidation of Cadmium with Dicarbonylcyclopentadienyliron Chloride in Dimethylformamide

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Abstract—The kinetic and activation parameters of oxidation of cadmium with dicarbonylcyclopentadienvliron chloride in dimethylformamide were determined. The apparent equilibrium constants, enthalpy, and entropy of adsorption of the reactants on the metal surface were evaluated. The reaction scheme was suggested.

In [1] we reported on the synthesis of an organometallic compound with a Mg–Fe bond by oxidation of Mg with dicarbonylcyclopentadienyliron chloride (I). In this study we examined the kinetics and products of the reaction of I with Cd.

The dependences of the reaction rate on the content of **I** and dimethylformamide (DMF, used as solvent) in the reaction mixture are shown in Figs. 1 and 2. The curves shown in Figs. 1 and 2 do not allow unambiguous conclusion on whether the adsorption centers on the metal surface are similar or different in nature. Therefore, we studied the dependences of the reaction rate on the concentration of **I** at different fixed concentrations of DMF in the reaction mixture (Fig. 3). The results, in line with the concept presented in [2], suggest that both compound **I** and DMF are adsorbed on reaction centers of similar nature on the Cd surface. In this case, the reaction course can be described by the scheme

$$Ox + S \xleftarrow[K^{ads}]{K^{ads}} OxS, \qquad (1)$$

$$L + S \xleftarrow{} LS,$$
 (2)

$$OxS + LS \xrightarrow{k} Products.$$
(3)

The expression for the reaction rate is as follows:

$$V = \frac{k' K_{Ox}^{ads} K_{L}^{ads} C_{Ox} C_{L}}{(1 + K_{Ox}^{ads} C_{Ox} + K_{L}^{ads} C_{L})^{2}}.$$
 (4)

where $k' = k(S_0)^2$, k is the rate constant, S_0 is the number of active centers on unit surface area of the metal, and K_{Ox}^{ads} and K_{L}^{ads} are the equilibrium constants of adsorption of the oxidant and ligand, respectively.

Treatment of the experimental data in the coordinates $(C_{\text{Ox}}/V)^{1/2} = f(C_{\text{Ox}})$ at $C_{\text{L}} = \text{const}$ and

 $(C_{\rm L}/V)^{1/2} = f(C_{\rm L})$ at $C_{\rm Ox}$ = const allowed calculation of the apparent equilibrium constants of adsorption of **I** and DMF and the reaction rate constants:

| <i>Т</i> , К | 278 | 288 | 293 |
|--|-------|------|------|
| $K_{\rm Ox}^{\rm ads}$ | 14.59 | 7.11 | 5.55 |
| K ^{ads} | 0.25 | 0.19 | 0.16 |
| $k \times 10^2$, g cm ⁻² min ⁻¹ | 1.17 | 4.65 | 5.70 |

From the temperature dependences of these quantities, we determined the apparent enthalpy and entropy of adsorption of the reactants on the metal surface: $\Delta H_{\text{Ox}}^{\text{ads}} -52\pm4 \text{ kJ mol}^{-1}$, $\Delta S_{\text{Ox}}^{\text{ads}} -164\pm12 \text{ J mol}^{-1} \text{ K}^{-1}$, $\Delta H_{\text{L}}^{\text{ads}} -21\pm2 \text{ kJ mol}^{-1}$, $\Delta S_{\text{L}}^{\text{ads}} -99\pm9 \text{ J mol}^{-1} \text{ K}^{-1}$, and activation energy of the process $E 75\pm5 \text{ kJ mol}^{-1}$. The latter value is indicative of the kinetic control of the reaction [3].

In accordance with [4], the electronegativity of the $Cp(CO)_2Fe$ fragment is appreciably lower than that of $Cp(CO)_3Mo$. This may be one of the factors responsible for the ~140 times higher rate constant of oxidation of Cd with I in DMF at 293 K, compared to that of the reaction of $Cp(CO)_3MoCl$ with Cd under identical conditions [5].

After completion of the oxidation of Cd with a solution of I (C_0 0.15 M) in THF at 20°C, the brown liquid phase was separated from the unchanged metal and light-colored precipitate. The amount of converted Cd was 0.85 mol per mole of consumed I. The precipitate was washed with diethyl ether and dried under reduced pressure. According to the analysis for Cd and Cl (1 : 2), the precipitate was CdCl₂. Its yield was 20.6% based on consumed I. The liquid phase was evaporated, and the residue was treated with diethyl ether to obtain a red solution and a yellow precipitate, which were separated. The solid phase insoluble in ether was (dicarbonylcyclopentadi-



Fig. 1. Rate of oxidation of Cd with dicarbonylcyclopentadienyliron chloride in DMF–toluene (C_{DMF} 3 M) as a function of the oxidant concentration. Temperature, K: (1) 293, (2) 288, and (3) 278.



Fig. 2. Rate of the reaction of dicarbonylcyclopentadienyliron chloride with Cd as a function of DMF concentration. Inert diluent toluene (C_{Ox} 0.05 M). Temperature, K: (1) 293, (2) 288, and (3) 278 K.



Fig. 3. Relative rate of oxidation of Cd in DMF-toluene as a function of the concentration of I at 278 K. DMF concentration, M: (1) 3 and (2) 9.

enyliron)cadmium chloride, as indicated by the results of its analysis: Fe : Cd : Cl = 1.00 : 1.05 : 1.11. The yield of CpFe(CO)₂CdCl was 53.6% based on **I**. Certain excess of Cd and Cl corresponds to the presence of a CdCl₂ impurity (2.6% based on **I**).

Thus, the first step of the oxidation of Cd with I is reaction (5):

$$Cd + Cp(CO)_2FeCl \longrightarrow Cp(CO)_2FeCdCl.$$
 (5)

The ether was partially evaporated under reduced pressure, and pentane was added in small portions to the residue cooled to -5° C. In so doing, a violet crystalline substance precipitated; it was washed with cold pentane and dried under reduced pressure. The product was identified as bis(dicarbonylcyclopentadienyliron) (**II**) by the decomposition point (194°C) and analysis for Fe. Found, %: Fe 31.0. Calculated, %: Fe 31.5. Published data [6]: decomposition point 195°C. The yield of **II** was 14.0% based on **I**.

It is known [7] that, in oxidation of Cu with I in DMF, the (dicarbonylcyclopentadienyliron)copper chloride formed in the first step reacts with I to form complex II. Similar reaction occurs in the case of Cd:

$$Cp(CO)_2FeCdCl + Cp(CO)_2FeCl \longrightarrow [Cp(CO)_2Fe]_2 + CdCl_2.$$
(6)

According to [8], polynuclear organometallic halides can occur in the Schlenk equilibrium with the corresponding symmetrical species:

$$2Cp(CO)_2FeCdCl \xrightarrow{\rightarrow} [Cp(CO)_2Fe]_2Cd + CdCl_2.$$
 (7)

However, in the products of cadmium oxidation with \mathbf{I} , bis(dicarbonylcyclopentadienyliron)cadmium was not detected even in trace amounts. This fact indicates that equilibrium (7) is strongly shifted to the left. This conclusion is consistent with the results of our experiments [5] on oxidation of cadmium with tricarbonylcyclopentadienylmolybdenum chloride.

EXPERIMENTAL

Cadmium [TU (Technical Specifications) 6-09-3095–78] in the form of turnings and 0.5-mm wire was used without additional surface treatment. Dicarbonylcyclopentadienyliron chloride was prepared according to [6]. The main substance content in the product, according to the results of the analysis for Cl and Fe [9], was no less than 99%; decomposition point 89°C (published data [6]: decomposition point 88–89°C). Analysis for cadmium was performed according to [9]. Organic solvents were purified by standard procedures [10]. All manipulations with organometallic compounds and their solutions were performed under reduced pressure or in an Ar atmosphere. The reaction kinetics was monitored resistometrically with an installation modified for experiments with readily oxidizable and readily hydrolyzable substances [11].

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