Russian Journal of General Chemistry, Vol. 73, No. 7, 2003, pp. 1051–1053. Translated from Zhurnal Obshchei Khimii, Vol. 73, No. 7, 2003, pp. 1110–1113.
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Oxidation of Copper with Dicarbonylcyclopentadienyliron Chloride in Polar Solvents

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Received June 27, 2001

Abstract—Dicarbonylcyclopentadienyliron chloride oxidizes copper in dimethylformamide and dimethyl sulfoxide to give copper(II) chloride and dicarbonylcyclopentadienyliron dimer. The apparent kinetic characteristics of the process and the thermodynamic parameters of adsorption of reactants on the metal surface were determined. The reaction scheme was proposed.

In [1], we studied oxidation of magnesium with η^5-$C_5H_5Fe(CO)_2Cl$ (**I**) in dimethylformamide (DMF). We found that compound **I**, in contrast to the related molybdenum and tungsten compounds [2], oxidizes in dimethyl sulfoxide (DMSO) and DMF not only magnesium, but also copper.

In reaction of **I** with copper in these solvents, the reaction stops at 20–30% conversion of the oxidant. This is probably due to shielding of the metal surface with the reaction products. The color of the reaction mixture changes from red to red-brown. Monitoring of the consumption of copper (gravimetrically) and **I** (by a decrease in the intensity of the IR absorption band ν_{CO} 2048 cm^{-1}) shows that 2 mol of the oxidant is consumed per mole of the metal.

A study of copper oxidation with ethyl iodide in DMSO [3] showed that the starting alkyl halide rapidly reacts with the solvent [4]. As a result, molecular iodine is accumulated, which is actually the reactive species. Adsorption of I_2 and DMSO molecules occurs on metal surface centers of different nature.

Compound **I** used in this work as an oxidant does not react with DMSO or, at least, its reaction with DMSO is much slower than oxidation of the metal. This is indicated, firstly, by the fact that the concentration of **I** in the reaction mixture in the course of the process does not noticeably differ from the concentration calculated assuming that the oxidant is spent exclusively for copper oxidation. Secondly, chlorine that could be formed in the reaction of DMSO with **I** by the scheme given in [3] is considerably less soluble in DMSO than I_2, and it would evolve into the gas phase. This would distort the chlorine balance [5] in the reaction products, which disagrees with the experiment (initial Cl^- concentration 0.100 M, concentration in the reaction products 0.102 M). Furthermore, Ali *et al*. [6] detected no reaction of DMSO with **I** at 300 K within a month in the absence of UV radiation.

After reaction completion, the unchanged copper was removed, and the major fraction of the solvent was distilled off at reduced pressure. The residue was treated with chloroform. The precipitate that formed was identified by chemical analysis as $[CpFe(CO)]_4$ [5, 7] (found Fe, %: 36.9. $C_{24}H_{20}Fe_4O_4$. Calculated Fe, %: 37). When heated to 210°C, the compound decomposes without melting. A similar result was obtained in [7]. The structure of this compound is also confirmed by spectral analysis. Its IR spectrum contains no bands at 1955 and 1995 cm^{-1} characteristic of terminal coordinated CO groups in $[CpFe(CO)_2]_2$, and the band of bridging CO groups at 1776 cm^{-1} is well pronounced.

Our results suggest the following mechanism of copper oxidation with **I** in DMF or DMSO.

$$CpFe(CO)_2Cl + Cu \xrightarrow{L} \underset{\mathbf{II}}{CpFe(CO)_2CuCl}. \qquad (1)$$

The product of copper oxidation passes into the solution and reacts therein with the second oxidant molecule:

$$\mathbf{II} + CpFe(CO)_2Cl \longrightarrow CuCl_2 + \underset{\mathbf{III}}{[CpFe(CO)_2]_2}. \qquad (2)$$

The kinetic relationships of the reaction, given below, support the suggested reaction scheme.

Formation of **II** is confirmed by the following experiment. When $HgCl_2$ was added to the starting mixture in the concentration comparable with that of the oxidant, bis(dicarbonylcyclopentadienyliron)mer-

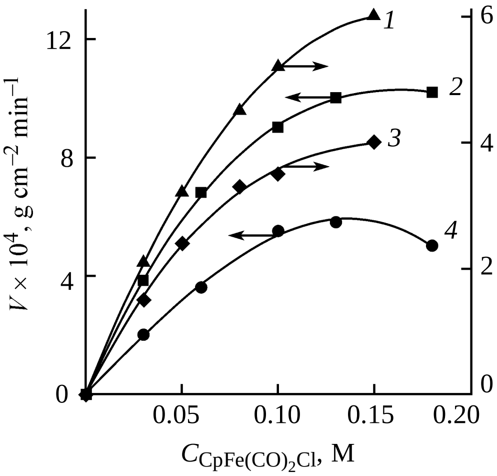

Fig. 1. Rate of copper oxidation with $CpFe(CO)_2Cl$ in (*1, 3*) DMSO (C_{DMSO} 14 M) and (*2, 4*) DMF (C_{DMF} 13 M) as a function of the oxidant concentration. Temperature, K: (*1, 2*) 333 and (*3, 4*) 323.

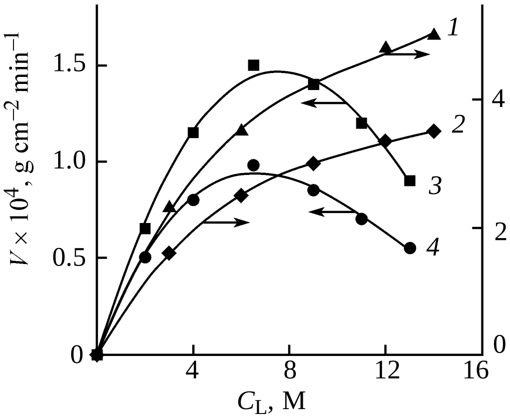

Fig. 2. Rate of copper oxidation with $CpFe(CO)_2Cl$ as a function of the ligand concentration. Inert solvent *p*-xylene; $C_{CpFe(CO)_2Cl}$ 0.1 M. Ligand: (*1, 2*) DMSO and (*3, 4*) DMF. Temperature, K: (*1, 3*) 333 and (*2, 4*) 323.

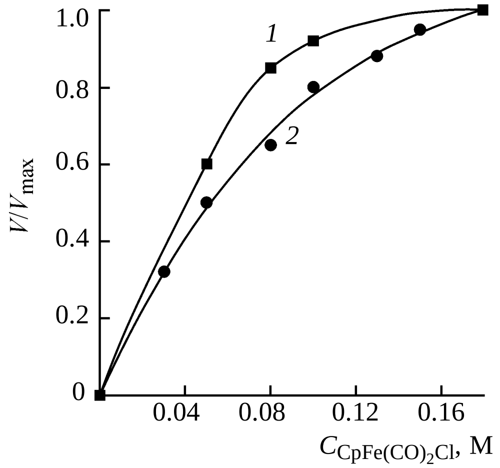

Fig. 3. Oxidation of copper with $CpFe(CO)_2Cl$ in DMSO: plot of V/V_{max} vs. oxidant concentration (333 K). C_{DMSO}, M: (*1*) 9 and (*2*) 14.

cury was isolated from the reaction products as yellow-orange crystals, mp 145.9°C (published data [8]: mp 146°C).

$$\mathbf{II} + HgCl_2 \longrightarrow CuCl_2 + [CpFe(CO)_2]_2Hg. \quad (3)$$

Dimer **III** formed by reaction (2) in accordance with [7] transforms into the tetramer:

$$\mathbf{III} \longrightarrow [CpFe(CO)]_4 + 4CO. \quad (4)$$

The presence of CO in the reaction products was proved by chromatographic analysis.

The plots of the rate of copper oxidation with **I** in DMF as a function of oxidant concentration C_{Ox} at constant ligand concentration C_L and as a function of C_L at constant C_{Ox} pass through a maximum (Figs. 1, 2), suggesting that the reactants are adsorbed on the copper surface centers of similar nature. As for the reaction in DMSO, the shapes of the kinetic curves $V = f(C_{ox})$ at C_L = const and $V = f(C_L)$ at C_{Ox} = const (Figs. 1, 2) do not allow unambiguous conclusion on whether the oxidant and ligand are adsorbed on the active surface centers of similar or different nature. However, the plots of the reaction rate vs. oxidant concentration at different (but constant during the process) ligand concentrations (Fig. 3) unambiguously show that in this case also the reactants are adsorbed on similar reaction centers of the copper surface.

Thus, in both DMF and DMSO, oxidation of copper with compound **I** is described by the Langmuir–Hinshelwood scheme [9]:

$$\mathrm{Ox} + \mathrm{S} \overset{K_{Ox}}{\rightleftarrows} \mathrm{OxS}, \quad (5)$$

$$\mathrm{L} + \mathrm{S} \overset{K_L}{\rightleftarrows} \mathrm{LS}, \quad (6)$$

$$\mathrm{OxS} + \mathrm{LS} \xrightarrow{k'} \mathrm{Products}. \quad (7)$$

Here, Ox is the oxidant; L, ligand; S, active center of the metal surface; K_{Ox} and K_L, equilibrium constants of adsorption of the oxidant and ligand, respectively.

In accordance with (5)–(7), the reaction rate is described as follows:

$$V = k'\frac{S_0^2[\mathrm{Ox}][\mathrm{L}]K_{Ox}K_L}{(1 + K_{Ox}[\mathrm{Ox}] + K_L[\mathrm{L}])^2}. \quad (8)$$

Here, $k = k'S_0^2$, where k is the rate constant of the surface reaction, and S_0 is the number of active centers per unit surface area.

Apparent equilibrium constants, enthalpies, and entropies of adsorption of $CpFe(CO)_2Cl$, DMSO, and DMF on the copper surface; rate constants and activation energies of the reactions

T, K	K_{Ox}	K_L	$-\Delta H^{Ox}_{ads}$, kJ mol^{-1}	$-\Delta S^{Ox}_{ads}$, J mol^{-1} K^{-1}	$-\Delta H^{L}_{ads}$, kJ mol^{-1}	$-\Delta S^{L}_{ads}$, J mol^{-1} K^{-1}	$k \times 10^4$, g cm^{-2} min^{-1}	E_a, kJ mol^{-1}
				DMSO				
323	8.2	0.10	25 ± 4	61 ± 9	20 ± 4	92 ± 8	3.0	51 ± 1
333	6.7	0.07					5.4	
343	4.7	0.06					9.2	
				DMF				
323	8.4	0.55	28 ± 5	70 ± 11	39 ± 4	130 ± 12	8.0	51 ± 4
333	6.8	0.38					13.1	
343	4.5	0.23					24.0	

The experimental data processed in the coordinates $(C_{Ox}/V)^{1/2} = f(C_{Ox})$ at C_L = const and $(C_L/V)^{1/2} = f(C_L)$ at C_{Ox} = const at various temperatures allowed calculation of the apparent equilibrium constants of adsorption of the oxidant and ligand on the metal surface, of the enthalpy and entropy of these processes, and of the apparent rate constants and activation energies (see table).

EXPERIMENTAL

The IR spectra were recorded on an IKS-29 spectrophotometer.

Copper wire [GOST (State Standard) 7262–54] 0.24 mm in diameter, containing 99.99% main substance, was kept for 24 h in DMF. Then the wire was cleaned to remove the swollen insulating film, immersed in concentrated HNO_3 immediately before the experiment, washed successively with water and acetone, and dried at reduced pressure. Dicarbonylcyclopentadienyliron chloride was prepared according to [10]. The compound was 99.6% pure according to analysis for chlorine and iron [5]; it decomposed at 88.9°C, in agreement with published data [10]. The copper(II) content in the reaction mixture was determined by the procedure described in [5]. Carbon monoxide was determined chromatographically (Tsvet-106 chromatograph, thermal conductivity detector, 1000 × 5-mm glass column, sorbent NaX 4 Å, column temperature 30°C, detector temperature 50°C, carrier gas helium, flow rate 40 ml min^{-1}). The solvents were purified and dried by common procedures [11] and degassed before use by repeated freeze–pump–thaw cycles. Syntheses of organometallic compounds and all manipulations with them were performed at reduced pressure or in an atmosphere of dry oxygen-free argon. Kinetic measurements were performed by the resistometric method [12] modified to exclude the access of atmospheric oxygen and moisture to the reaction mixtures.

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