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Oxidation of Zinc with Dicarbonylcyclopentadienyliron Chloride in Polar Solvents

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Abstract—The kinetic and activation parameters of zinc oxidation with dicarbonylcyclopentadienyliron chloride in dimethylformamide were found. The apparent equilibrium constants, enthalpy, and entropy of the adsorption of the reagents on the metal surface were determined. A reaction scheme was suggested.

The synthesis of an organometallic compound with a Mg–Fe bond by the oxidation of magnesium with dicarbonylcyclopentadienyliron chloride **I** was reported in [1]. In this study we examined the kinetics and products of the reaction of **I** with zinc. The plots of the reaction rate vs. concentrations of **I** and dimethylformamide (DMF), used as a polar solvent, have maxima (Figs. 1, 2). This means that, according to [2], the process can be described by Langmuir–Hinshelwood's scheme for the case when the reagents are adsorbed on similar active sites of the metal surface [schemes (1)–(3)].

$$\mathrm{Ox} + \mathrm{S} \overset{K_{\mathrm{Ox}}^{\mathrm{ads}}}{\rightleftarrows} \mathrm{Ox(S)}, \quad (1)$$

$$\mathrm{L} + \mathrm{S} \overset{K_{\mathrm{L}}^{\mathrm{ads}}}{\rightleftarrows} \mathrm{L(S)}, \quad (2)$$

$$\mathrm{Ox(S)} + \mathrm{L(S)} \xrightarrow{k'} \text{Reaction products}. \quad (3)$$

The reaction rate is expressed by Eq. (4).

$$v = \frac{k' K_{\mathrm{Ox}}^{\mathrm{ads}} c_{\mathrm{Ox}} K_{\mathrm{L}}^{\mathrm{ads}} c_{\mathrm{L}}}{(1 + K_{\mathrm{Ox}}^{\mathrm{ads}} c_{\mathrm{Ox}}) K_{\mathrm{L}}^{\mathrm{ads}} c_{\mathrm{L}}}. \quad (4)$$

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

The treatment of the experimental data obtained in the coordinates $(c_{\mathrm{Ox}}/v)^{1/2} = f(c_{\mathrm{Ox}})$ at c_{L} = const and $(c_{\mathrm{L}}/v)^{1/2} = f(c_{\mathrm{L}})$ at c_{Ox} = const allowed us to calculate the effective equilibrium constants of adsorption of the oxidant and ligand and the rate constant. The enthalpy, entropy, and activation energy of the process (see table) were determined from the temperature dependences of these quantities. The value of the activation energy indicates that the reaction was kinetically controlled [3].

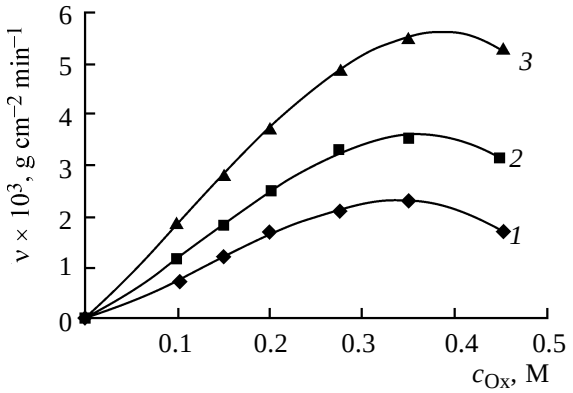

Fig. 1. Rate v of zinc oxidation with dicarbonylcyclopentadienyliron chloride in a DMF–toluene mixture as a function of oxidant concentration c_{Ox}. Temperature, K: (*1*) 278, (*2*) 288, and (*3*) 298 K (c_{DMF}^0 10 M).

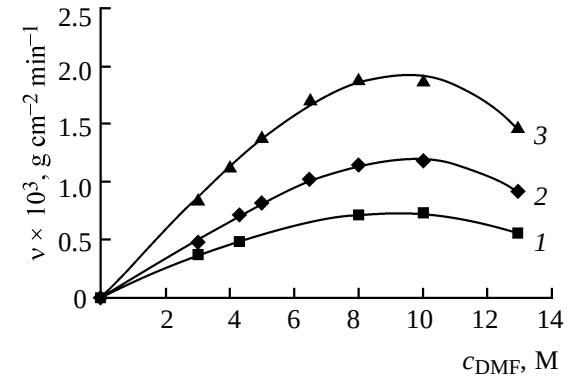

Fig. 2. Rate of the reaction of dicarbonylcyclopentadienyliron chloride with zinc as a function of DMF concentration. Temperature, K: (*1*) 278, (*2*) 288, and (*3*) 298 (c_{Ox}^0 0.1 M, inert solvent toluene).

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Oxidation of zinc with dicarbonylcyclopentadienyliron chloride in dimethylformamide

T, K	K_{Ox}^{ads}	$-\Delta H_{Ox}^{ads}$, kJ mol^{-1}	$-\Delta S_{Ox}^{ads}$, J mol^{-1} K^{-1}	K_{L}^{ads}	$-\Delta H_{L}^{ads}$, kJ mol^{-1}	$-\Delta S_{L}^{ads}$, J mol^{-1} K^{-1}	$k \times 10^2$, g cm^{-2} min^{-1}	E_a, kJ mol^{-1}
278	3.89			0.19			1.35	
288	2.32	32 ± 2	103 ± 4	0.13	21 ± 2	91 ± 5	2.91	54 ± 1
298	1.56			0.10			4.94	

On completion of the reaction of **I** (c_0 0.2 M in DMF) with zinc taken in a fivefold excess, the initially red reaction mixture became brown. The consumption of Zn was 0.51 mol per mole of reacted **I**. After separation of unchanged zinc and removal of the solvent at a reduced pressure, a light green oily liquid remained in the vessel. We failed to isolate individual reaction products from it. Therefore, we hydrolyzed the liquid phase after the reaction completion by oxygen-free water. According to [4], dicarbonylcyclopentadienyliron hydride forming upon the hydrolysis of compounds with an M–Fe bond (M is a Group II metal) is unstable and converts to bis(dicarbonylcyclopentadienyliron). The solvent was removed from the system, and the residue was recrystallized from chloroform–heptane. The resulting red-violet compound $[Cp(CO)_2Fe]_2$ (**II**) was identified by the analysis for iron (31.68%; calculated: 31.70%), decomposition point (195°C), and IR spectrum [ν_{CO} ($CHCl_3$), cm^{-1}: 1775, 1955, 1995]. Published data [5]: decomposition point 195°C; ν_{CO}, cm^{-1}: 1773, 1955, 1995.

When zinc is oxidized in THF and DMF and cadmium, in DMF with $Cp(CO)_3MCl$ (M = Mo, W [6]), oligomeric derivatives $[Cp(CO)_3MM'Cl]_x$ (M' = Zn, Cd) are formed as the major products.

Compound **II** can be formed both upon the hydrolysis of the initial product of $Cp(CO)_2FeZnCl$ oxidation [schemes (5) and (6)] and by its reaction with a molecule of the starting oxidant [scheme (7)].

$$Cp(CO)_2FeZnCl + H_2O \rightarrow Cp(CO)_2FeH + Zn(OH)Cl, \quad (5)$$

$$2Cp(CO)_2FeH \longrightarrow [Cp(CO)_2Fe]_2 + H_2, \quad (6)$$

$$Cp(CO)_2FeZnCl + Cp(CO)_2FeCl \longrightarrow [Cp(CO)_2Fe]_2 + ZnCl_2. \quad (7)$$

To elucidate the actual pathway of formation of **II**, we analyzed the products of zinc oxidation in THF (c_0 0.2 M, 20°C). After the reaction completion, the mixture was separated from excess metal, and the solvent was distilled off. The residue was treated several times with hot chloroform. On the addition of heptane to the extract and cooling of the solution, we isolated violet-red crystals. Their iron content, decomposition point, and IR spectrum corresponded to those of **II**. The yield of the product was 0.38 mol per mole of **I**.

It follows from the foregoing that the initial step of zinc oxidation with **I** is reaction (8).

$$Zn + Cp(CO)_2FeCl \longrightarrow Cp(CO)_2FeZnCl. \quad (8)$$

The molecule of the Grignard-like reagent formed passes into the solution, where it reacts with a molecule of the starting oxidant [Eq. (7)]. Chloride in the reaction products was determined without noticeable loss.

EXPERIMENTAL

Zinc (Technical Specifications TU 6-09-5294–86) as turnings and a wire (0.5 mm in diameter) was used without additional surface treatment. Dicarbonylcyclopentadienyliron chloride was synthesized as described in [6]. According to the analysis for chlorine and iron [7], the resulting product contained no less than 99% main substance; decomposition point 89°C. Organic solvents were purified by standard procedures [8]. All operations with organometallic compounds and their solutions were carried out under reduced pressure or in an argon atmosphere. The kinetic measurements were carried out by a resistometric method modified for the work with readily oxidizable and hydrolyzable compounds [9]. The IR spectra were recorded on an IKS-29 instrument.

REFERENCES

1. Piskunov, A.V., Maslennikov, S.V., Spirina, I.V., Maslennikov, V.P., and Artemov, A.N., *Zh. Obshch. Khim.*, 2002, vol. 72, no. 10, p. 1585.
2. Bremer, H. and Wendlandt, K.-P., *Heterogene Katalyse*, Berlin: Akademie, 1978.
3. Benson, S.W., *The Foundations of Chemical Kinetics*, New York: McGraw-Hill, 1960.
4. Nikitina, T.V., *Methody elementoorganicheskoi khimii. Metalloorganicheskie soedineniya zheleza* (Methods of Organometallic Chemistry. Organometallic Compounds

of Iron), Moscow: Nauka, 1985.

5. *Handbuch der präparativen anorganischen Chemie*, Brauer, G., Ed., Stuttgart: Enke, 1986. Translated under the title *Rukovodstvo po neorganicheskomu sintezu*, Moscow: Khimiya, 1989, vol. 6, pp. 1983, 2063.
6. Piskunov, A.V., Maslennikov, S.V., Spirina I.V., Maslennikov, V.P., and Artemov, A.N., *Zh. Obshch. Khim.*, 2001, vol. 71, no. 5, p. 714.
7. Charlot, G., *Les methodes de la chimie analytique. Analyse quantitative minerale*, Paris: Masson, 1965, 4th ed.
8. Gordon, A.J. and Ford, R.A., *The Chemist's Companion. A Handbook of Practical Data, Techniques, and References*, New York: Wiley–Interscience, 1972.
9. Zhukov, S.A., Lavrent'ev, I.P., and Nifontova, T.A., *React. Kinet. Catal. Lett.*, 1974, no. 4, p. 512.