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Oxidation of Zinc and Cadmium with Tricarbonylcyclopentadienylmolybdenum Chloride and Tricarbonylcyclopentadienyltungsten Chloride

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Abstract—The rate of the reaction of zinc and cadmium with tricarbonylcyclopentadienylmolybdenum chloride and tricarbonylcyclopentadienyltungsten chloride and the yield of the final products of these reactions were studied as influenced by the solvent nature. Kinetic features of oxidation of zinc and cadmium with tricarbonylcyclopentadienylmolybdenum chloride in the presence of dimethylformamide were determined. The thermodynamic parameters of adsorption of the oxidizing agent and the ligand on the metal surface were determined.

Previously [1] we reported synthesis of $Cp(CO)_3MMgCl$ and $[Cp(CO)_3M]_2Mg$ (M = Mo, W; $Cp = \eta^5\text{-}C_5H_5$) by reaction of tricarbonylcyclopentadienyl chlorides of these metals with magnesium in tetrahydrofuran (THF). In this work we prepared compounds with M–M' bond (M = Mo, W; M' = Zn, Cd) by oxidation of zinc and cadmium metals with $Cp(CO)_3MoCl$ (**I**) and $Cp(CO)_3WCl$ (**II**).

Since kinetic features of reaction of magnesium with **I** and **II** are similar [1], we studied only the kinetics of oxidation of zinc and cadmium with compound **I**. As coordinating solvent we used dimethylformamide (DMF), since all the tested metals (Mg, Zn, and Cd) are oxidized with **I** and **II** only in this solvent.

The dependences of the oxidation rate of both zinc and cadmium on the concentrations of **I** and DMF pass through a maximum. Hence, when the reagents are adsorbed on the similar reaction centers of the metal surface, the process can be described by the Langmuir–Hinshelwood scheme [2]. Magnesium oxidation with compound **I** (Ox) in DMF (L) can be described similarly [reactions (1)–(3)] [1]. The reaction rate is described by Eq. (4).

$$\mathrm{Ox} + \mathrm{S}_0 \overset{K_{\mathrm{Ox}}}{\rightleftarrows} \mathrm{OxS}, \tag{1}$$

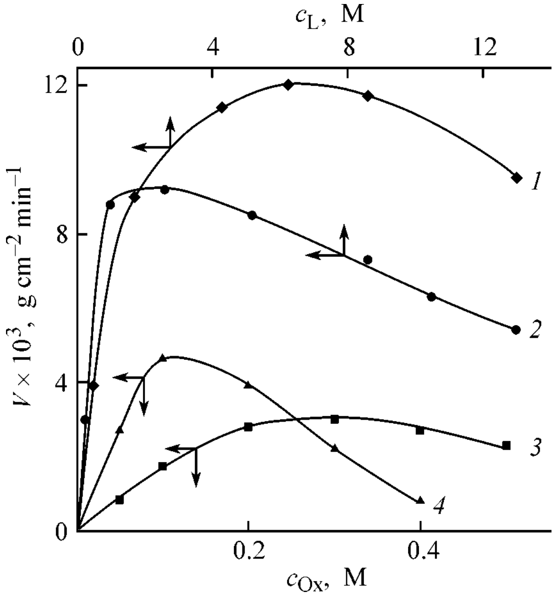
$$\mathrm{L} + \mathrm{S}_0 \overset{K_{\mathrm{L}}}{\rightleftarrows} \mathrm{LS}, \tag{2}$$

$$\mathrm{OxS} + \mathrm{LS} \overset{k}{\rightleftarrows} \mathrm{Products}, \tag{3}$$

$$V = k' \frac{[\mathrm{Ox}][\mathrm{L}]K_{\mathrm{Ox}}K_{\mathrm{L}}}{(1 + K_{\mathrm{Ox}}[\mathrm{Ox}] + K_{\mathrm{L}}[\mathrm{L}])^2}, \tag{4}$$

where $k' = k[S_0]^2$, k is the rate constant, $[S_0]$ is the number of active centers on the unit surface area, and K_{Ox} and K_L are the equilibrium constants of adsorption of the oxidizing agent and the ligand, respectively.

The equilibrium constants of adsorption of the oxidizing agent and the ligand and the apparent rate constants of the reactions were determined by treatment of the experimental data in the $(c_{Ox}/V)^{1/2} = f(c_{Ox})$ coordinates at c_L = const and in the $(c_L/V)^{1/2} = f(c_L)$ coordinates at c_{Ox} = const with subsequent solution of



Rates of oxidation of (*2, 3*) zinc and (*1, 4*) cadmium with $Cp(CO)_3MoCl$ (Ox) in a DMF (L)–benzene mixture at 293 K. (*1*) c_{Ox} = 0.2, (*2*) c_{Ox} = 0.3, (*3*) c_L = 0.5, and (*4*) c_L = 0.25 M.

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Table 1. Oxidation of zinc and cadmium with $Cp(CO)_3MoCl$ (**I**). Equilibrium constants, enthalpy and entropy of adsorption of **I** (Ox) and DMF (L) on the zinc and cadmium surface, apparent rate constants, and activation energies of the reaction

Me	T, K	K_{Ox}	K_L	$-H^{Ox}_{ads}$, kJ mol^{-1}	$-S^{Ox}_{ads}$, J mol^{-1} deg^{-1}	$-H^{L}_{ads}$, kJ mol^{-1}	$-S^{L}_{ads}$, J mol^{-1} deg^{-1}	$k \times 10^2$, g cm^{-2} min^{-1}	E_a, kJ mol^{-1}
Zn	283	5.3	1.17	29 ± 4	88 ± 5	21 ± 1	71 ± 4	4.0	43 ± 4
	293	4.2	0.85					7.1	
	303	2.3	0.65					14	
Cd	288	26.8	0.75	42 ± 1	121 ± 4	22 ± 2	79 ± 5	2.4	79 ± 5
	293	19.6	0.66					4.6	
	298	14.4	0.55					7.7	

Table 2. Rates of oxidation of zinc and cadmium with **I** and **II** in different solvents at 293 K and the yields of products of this reaction (c_{Ox} = 0.2 M)

Solvent	$V \times 10^3$, g cm^{-2} min^{-1}				Yield of $Cp(CO)_3MM'Cl$, mol per mole of $Cp(CO)_3MCl$			
	I–Zn	**II**–Zn	**I**–Cd	**II**–Cd	**I**–Zn	**II**–Zn	**I**–Cd	**II**–Cd
Acetonitrile	14.5	12.0	0.1	–	0.54	0.50	–	–
Ethyl acetate	3.7	3.8	–	–	–	–	–	–
THF	2.5	2.6	–	–	0.97	0.71	–	–
Diglyme	2.9	2.0	1.4	–	0.41	0.63	–	–
DMF	5.4	4.1	9.5	7.6	0.96	0.95	0.85	0.80
DMSO	3.9	3.4	7.0	6.0	0.94	0.82	0.71	0.72
Pyridine	0.1	–	6.2	5.0	–	–	0.72	0.71
Hexamethylphosphoramide	0.5	0.4	0.4	0.5	–	–	–	–

the resulting system of the equations. From the temperature dependences of these parameters the enthalpies and entropies of adsorption of the reagents on the zinc and cadmium surface and the apparent activation energies were calculated (Table 1). The values of the apparent activation energies indicate that the reaction is kinetically controlled [3].

As found previously [1], magnesium reacts with **I** and **II** only in THF and DMF. However, when the reaction was performed in DMF, no products with the Mo–Mg or W–Mg bonds were found because of reaction of these compounds with the solvent [4]. The reaction in THF yields $Cp(CO)_3MMgCl$ and $[Cp(CO)_3M]_2Mg$ (M = Mo, W) [1]. Formation of magnesium bis-organoelement derivatives is due to equilibrium (5).

$$2Cp(CO)_3MMgCl \rightleftarrows [Cp(CO)_3M]_2Mg + MgCl_2, \quad (5)$$

$$M = Mo, W.$$

Zinc and cadmium, unlike magnesium, are oxidized with **I** and **II** in other solvents to form $Cp(CO)_3MM'Cl$ (M = Mo, W; M' = Zn, Cd) (Table 2). The zinc derivatives are formed in THF, DMF, acetonitrile, diglyme, and dimethyl sulfoxide (DMSO); and the cadmium derivatives, in DMF, DMSO, and pyridine. The absence of $[Cp(CO)_3M]_2M'$ (M = Mo, W; M' = Zn, Cd) in the reaction products is due to the fact that equilibrium (5) in these systems is completely shifted to the left [5, 6].

Yellow crystals of $Cp(CO)_3MZnCl \cdot 2,2'\text{-bipy}$ [mp 285°C (dec) (M = Mo) and 305°C (dec) (M = W)] were quantitatively precipitated by addition of a toluene solution of bipyridyne (2,2'-bipy) to solutions formed in the reaction of zinc with **I** or **II**. These data agree with the results of work [7]. The mercury derivatives $Cp(CO)_3MHgCl$ were obtained in a quantitative yield by treatment with mercury(II) chloride of the mixtures formed after completion of the reaction between complexes **I** or **II** and zinc. The organobimetallic compound was isolated from products of reaction of **I** and **II** with zinc in THF. White polymers $[Cp(CO)_3MZnCl]_x$ [mp 240°C (dec) (M = Mo) and 285°C (dec) (M = W)] were isolated after removal of the solvent under reduced pressure [7].

The final product of reaction between **I** and zinc in diethyl ether and ethyl acetate is the dimer $[Cp(CO)_3Mo]_2$ (**III**). The yield of **III** per mole of the initial oxidizing agent is 0.4 and 0.44 mol, respectively. Reaction of **I** with cadmium in diglyme also yields dimer **III** in amounts of 0.07 mol per mole of **I**. This compound is formed by reaction of **I** with $Cp(CO)_3MoZnCl$ formed in the first steps.

$$Cp(CO)_3MoCl + M \rightarrow Cp(CO)_3MoMCl,$$

$$Cp(CO)_3MoMCl + Cp(CO)_3MoCl$$

$$\rightleftarrows [Cp(CO)_3Mo]_2 + MCl_2,$$

$$M = Zn, Cd.$$

Similar scheme was proposed [8, 9] for reaction of organoelement halides R_3ECl (E = Si, Ge, Sn) with alkali metals and magnesium in THF to form R_3EER_3.

EXPERIMENTAL

Zinc [TU (Technical Specifications) MKhP 112–40] and cadmium [TU MKhP 35–55] in the form of cuttings and wire (0.5 mm in diameter) were used without additional surface treatment. Complexes **I** and **II** were prepared by the procedure in [10, 11], respectively. As determined by the elemental analysis for chlorine and molybdenum (or tungsten) [12], the content of the main compound in the samples was no less than 99%. The melting points of the resulting compounds agree with the published data [10, 11]. Organic solvent were purified and dried by the procedure in [13]. All manipulations with organobimetallic compounds and their solutions were performed under reduced pressure or under argon. The kinetic experiments were performed by the procedure in [14], modified for readily oxidizing and readily hydrolyzing compounds.

The yield of $Cp(CO)_3MM'Cl$ (M = Mo, W; M' = Zn, Cd) in oxidation of zinc and cadmium with **I** and **II** was estimated gravimetrically by the weight of $Cp(CO)_3MHgCl$ formed after treatment of the reaction mixture with mercury(II) chloride. $Cp(CO)_3MCl$ (15 mmol) was mixed with a fourfold excess of metal cuttings in 5 ml of the solvent. In 3 days the excess metal was filtered off, and $HgCl_2$ (15 mmol) was added to the filtrate. The solvent was removed in a vacuum, $Cp(CO)_3MHgCl$ was extracted with acetone and recrystallized from ethanol.

The mercury derivatives were characterized by melting points [15] and elemental analysis. A weighed portion of the sample was mineralized by the procedure in [16] and the inorganic residue was analyzed for molybdenum (or tungsten), mercury, and chlorine [12]. **$Cp(CO)_3MoHgCl$.** Found, %: Cl 7.2; Hg 40.8; Mo 19.1. $C_8H_5ClHgMoO_3$. Calculated, %: Cl 7.4; Hg 41.7; Mo 19.5. **$Cp(CO)_3WHgCl$.** Found, %: Cl 6.0; Hg 34.5; W 31.3. $C_8H_5ClHgO_3W$. Calculated, %: Cl 6.2; Hg 35.2; W 32.3.

The dimer $[Cp(CO)_3Mo]_2$ (**III**) was characterized by the melting point and IR and UV spectroscopy [17].

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