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Reactions of Tin and Lead with Tricarbonylcyclopentadienylmolybdenum(II) and Tricarbonylcyclopentadienyltungsten(II) Chlorides

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Abstract—Tin was oxidized with tricarbonylcyclopentadienylmolybdenum and tricarbonylcyclopentadienyltungsten chlorides to obtain polynuclear organometallic compounds $[\eta^5\text{-}C_5H_5M(CO)_3]_2SnCl_2$ (M = Mo, W). The reactions of the above-mentioned oxidants with lead gave lead chloride and $[\eta^5\text{-}C_5H_5M(CO)_3]_2$ dimers. Formal-kinetic regularities of tin oxidation with tricarbonylcyclopentadienylmolybdenum chloride in *N,N*-dimethylformamide were found. Thermodynamic parameters of adsorption of the reagent on the metal surface were determined.

Tricarbonylcyclopentadienylmolybdenum (**I**) and tricarbonylcyclopentadienyltungsten (**II**) chlorides are shown to be promising reagents in the synthesis of polyorganometallic compounds by direct oxidation of Group II metals [1–3].

The aim of this work was to find out the possibility and special features of the synthesis of polynuclear organic compounds of nontransition Group IV metals by their oxidation with compounds **I** and **II** in donor solvents.

Metallic germanium fails to react with compounds **I** and **II** for 500 h in any solvent, whereas tin reacts with these compounds in tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and pyridine (Py) media even at room temperature. Therewith, absorption bands typical of the starting molybdenum and tungsten organohalides {ν_{CO} 2055, 1983, and 1960 cm^{-1} (**I**) [4] and ν_{CO} 2053, 1968, and 1947 cm^{-1} (**II**) [5]} disappear from the IR spectra of the reaction mixtures. Simultaneously, the following absorption bands appear: ν_{CO} 2029, 2006, 1958, 1940, and 1916 cm^{-1} (reaction of tin with **I**) ν_{CO} 2023, 2002, 1948, 1931, and 1905 cm^{-1} (reaction of tin with **II**). According to [6, 7], these data point to formation of $[CpM(CO)_3]_2SnCl_2$ compounds [M = Mo (**III**), W (**IV**)]. The metal weight loss corresponds to the reaction of 0.5 mol of tin per 1 mol of the starting oxidant. The above observables point to reaction (1).

$$2C_5H_5M(CO)_3Cl + Sn \longrightarrow [C_5H_5M(CO)_3]_2SnCl_2, \quad (1)$$

$$M = Mo,\ W.$$

The highest yield of the target product is attainable in a DMSO medium: ~0.47 mol of a “crude” product per 1 mol of the starting molybdenum or tungsten organohalide. After double recrystallization from a 2 : 1 heptane–benzene mixture we obtained compounds **III** and **IV** as golden yellow crystals. Their melting points, 200 and 225°C, respectively, were consistent with those reported in [6]. The reaction in DMF gave 0.41 mol of triorganometallic compound per 1 mol of the starting oxidant. We emphasize that this reaction favorably compares with the generally accepted method of synthesis of compounds **III** and **IV**, that involves the thermo- or photoinduced reaction of $[CpM(CO)_3]_2$ dimers [M = Mo (**V**), W (**VI**)] with tin(II) chloride, yielding $CpM(CO)_3SnCl_3$ derivatives along with the target product [8, 9].

Tetrahydrofuran and pyridine proved to be less suitable for preparing compounds **III** and **IV** by reaction (1). The yields of the target products in these solvents are 0.28 and 0.12 mol per 1 mol of the starting oxidant, respectively. The low yield in THF results from the low rate of the process, whereas in pyridine a side reaction seems to occur.

Lead, too, readily reacts with compounds **I** and **II** in DMF and DMSO. However, these reactions occur by a route different from reaction (1), giving dimers **V** and **VI** and lead(II) chloride in quantitative yields. Probably, the dilead derivative formed in the first stage reacts with the starting oxidant.

$$C_5H_5M(CO)_3Cl + Pb \longrightarrow [C_5H_5M(CO)_3]PbCl, \quad (2)$$

$$[C_5H_5M(CO)_3]PbCl + C_5H_5M(CO)_3Cl \longrightarrow [C_5H_5M(CO)_3]_2 + PbCl_2. \quad (3)$$

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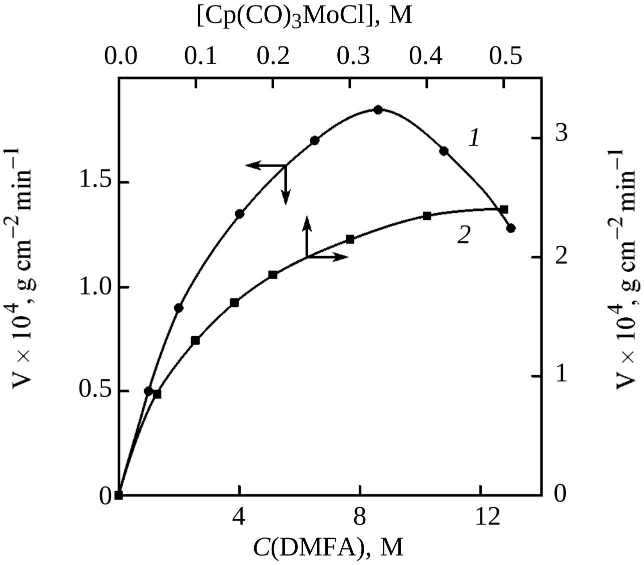

Rate of tin oxidation in the $CpMo(CO)_3Cl$–DMF–*p*-xylene system on reagent concentrations at 323 K. *C*, M: (*1*) $CpMo(CO)_3Cl$ 0.2 and (*2*) DMF 8.6.

Compounds **V** and **VI** were characterized by their melting points and IR and UV spectra. The observed parameters are consistent with those reported in [10].

The dependence of the rate of tin oxidation with compound **I** in DMF on oxidant concentration fits Langmuir's isotherm, and the $V = f(C_{DMF})$ plot passes through a maximum (see figure). The shape of the kinetic curves points to the fact that the oxidation reaction is described by the Langmuir–Hinshelwood scheme with reagent adsorption on similar active surface centers [11].

$$\mathrm{Ox} + \mathrm{S}_0 \overset{K_{\mathrm{Ox}}}{\rightleftarrows} \mathrm{OxS}, \tag{4}$$

$$\mathrm{L} + \mathrm{S}_0 \overset{K_{\mathrm{L}}}{\rightleftarrows} \mathrm{LS}. \tag{5}$$

$$\mathrm{OxS} + \mathrm{LS} \xrightarrow{k} \text{Products}. \tag{6}$$

Here K_{Ox} and K_L are the equilibrium constants of oxidant and ligand adsorption, respectively, and k is the rate constant of surface reaction.

Similar mechanisms have been proposed for the reactions of compound **I** in DMF with magnesium [1] and zinc and cadmium [2].

The rate of the process will be expressed by Eq. (7):

$$V = k' \frac{C_{\mathrm{Ox}} C_{\mathrm{L}} K_{\mathrm{Ox}} K_{\mathrm{L}}}{(1 + K_{\mathrm{Ox}} C_{\mathrm{Ox}} + K_{\mathrm{L}} C_{\mathrm{L}})^2}. \tag{7}$$

Here $k' = kS_0^2$ and S_0 is the number of active centers per unit surface area.

Processing the experimental data 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 allowed us to calculate the apparent rate constants of the reaction and the equilibrium constants of oxidant and ligand adsorption on metal surface. From the temperature dependences of these values we determined the apparent activation energy and the enthalpy and entropy of reagent adsorption on the surface of zinc and cadmium.

T, K	k, g cm^{-2} min^{-1}	K_{Ox}^{ads}	K_{L}^{ads}
323	8.2×10^{-6}	9.4	0.34
333	1.9×10^{-5}	6.5	0.25
343	4.1×10^{-5}	3.6	0.19

$$\Delta H_{\mathrm{Ox}}^{\mathrm{ads}}\ -(30 \pm 1)\ \text{kJ/mol};\ \Delta S_{\mathrm{Ox}}^{\mathrm{ads}}\ -(74 \pm 2)\ \text{J mol}^{-1}\,\text{K}^{-1},$$

$$\Delta H_{\mathrm{L}}^{\mathrm{ads}}\ -(26 \pm 1)\ \text{kJ/mol};\ \Delta S_{\mathrm{L}}^{\mathrm{ads}}\ -(92 \pm 3)\ \text{J mol}^{-1}\,\text{K}^{-1},$$

$$E_{\mathrm{a}}\ 74 \pm 1\ \text{kJ/mol}.$$

The value of the apparent activation energy points to a reaction occurring in the kinetic mode [12].

The dependence of reaction rate on oxidant concentration does not obey a second-order kinetic equation, which may imply that the reaction occurs by scheme (1). Probably, the initially formed tin(II) derivative passess into bulk solution, where it reacts with the starting oxidant.

$$C_5H_5M(CO)_3Cl + Sn \longrightarrow [C_5H_5M(CO)_3]SnCl, \tag{8}$$

$$[C_5H_5M(CO)_3]SnCl + C_5H_5M(CO)_3Cl \longrightarrow [C_5H_5M(CO)_3]_2SnCl_2. \tag{9}$$

As shown in [2], the dependence of the rate of zinc and cadmium oxidation on the donor number of the solvent used [13] has an extremum. The rate maximum was observed in DMF. With tin, this maximum falls on pyridine (C_{Ox} 0.2 M, T 323 K).

Solvent	Ethyl acetate	THF	DMF	DMSO	Py	HMPA
DN($SbCl_5$), kJ/mol	71.8	83.7	111.3	125.9	139.6	162.5
$V \times 10^4$, g cm^{-2} min^{-1}	0.5	0.7	1.8	4.8	5.4	0.3

The extremal shape of the dependence of the rate of tin solution is associated with selective ligand adsorption on the metal surface. Some aspects of this problem have been discussed in [14].

EXPERIMENTAL

The IR spectra of the reaction mixtures were recorded on an IKS-29 spectrometer in CaF_2 cells. The UV spectra were recorded on an SF-46 spectrophotometer in an evacuated quartz cell.

The following metals were used: Ge RE TU 605-59, Sn TU 6-09-2704-78, and Pb TU 6-09-4030-67.

Compounds **I** and **II** were prepared by the procedures described in [4, 5]. The purity of the reagents was controlled by the contents of chlorine and metals [15, 16] and by the melting points [4, 5]. The purities of the synthesized compounds were no less than 99%.

The rates of the reactions between tin and compound **I** in various solvents were followed by the resistometric method [17] modified for working with easily oxidized and easily hydrolyzed compounds.

Organic solvents were purified and dried according to [18]. Before use all substances were degassed by repeated freezing–pumping–thowing.

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