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Oxidation of Magnesium, Indium, and Thallium with Molybdenum and Cobalt Binuclear Carbonyl Complexes in Polar Solvents

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Abstract—Oxidation of magnesium and thallium with bis(η^5-cyclopentadienyltricarbonylmolybdenum) in dimethyl sulfoxide and of indium with octacarbonyldicobalt in tetrahydrofuran was studied. The formal-kinetics relationships of the processes were revealed, and the intermediate and final products were identified. The apparent equilibrium constants, enthalpies and entropies of adsorption of reactants on the metal surface, and rate constants and activation energies of the reactions were determined. The reaction scheme was suggested.

Redox insertion into the M–M bond in binuclear complexes (M is a main-group or transition metal) was studied in [1–3]. Thermal [1] or photochemical [4] activation weakens the M–M bond in compounds $[Cp(CO)_nM]_2$ and promotes its dissociation with the formation of two 17-electron radicals [5]; this reaction is successfully used in the synthesis of polynuclear derivatives. According to [6], the rate of the reaction of $[Cp(CO)_3Cr]_2$ with thallium in THF at 25°C is 250 times higher than the rate of thallium oxidation with $[Cp(CO)_3Mo]_2$ under similar conditions. This relationship is consistent with the enthalpies of dissociation of the M–M bond in bis(η^5-cyclopentadienyltricarbonylmetals) [7]:

Compound	$[Cp(CO)_3W]_2$ **I**	$[Cp(CO)_3Mo]_2$ **II**	$[Cp(CO)_3Cr]_2$ **III**
ΔH_{M-M}, kJ mol^{-1}	233.7	139.5	66.0

Furthermore, in accordance with [5], the capability of metal-centered radicals generated by dissociation of binuclear complexes to abstract a halogen atom from halohydrocarbons decreases in the order η^5-$Cp(CO)_3W$ > η^5-$Cp(CO)_3Mo$ > η^5-$Cp(CO)_3Cr$ > $Co(CO)_4$. The bond energy in the corresponding dimer should vary in the opposite direction.

Thus, certain success has been gained in studying the reactions under consideration and in choosing appropriate conditions to obtain the highest product yield. At the same time, some aspects of these reactions are still poorly understood. The kinetic relationships of the processes and the thermodynamic parameters of adsorption of the reactants on the metal surface are unknown. Moreover, there are no substantiated concepts concerning the reaction mechanism. It is also important to find how the reaction rate depends on the donor properties of the solvent used.

The experimental results of this study show that the dependence of the rate of metal insertion into the M–M bond of a binuclear complex on the donor power of the solvent passes through a maximum, as in the case of metal oxidation with other oxidants [8]. The oxidation of magnesium and thallium is the fastest in DMSO. For the oxidation of indium, we used a solution of octacarbonyldicobalt **IV** in THF, since specifically in THF the dependence of the relative reaction rate on the solvent donor number $DN(SbCl_5)$ [9] has a maximum.

The reaction of Mg with **II** in DMSO (C_0 0.125 M) was performed at a reactant ratio of 10 : 1 and 60°C; the mixture was stirred with a magnetic stirrer. After the reaction completion, the liquid phase was separated from the unchanged metal, and the major fraction of the solvent was removed under reduced pressure. Addition of preliminarily degassed THF to the residue resulted in the formation of a light-colored precipitate. The Mg : Mo ratio in the liquid phase and precipitate was 1 : 2 and 0.99 : 2, respectively. The decomposition point of the precipitate was 160°C. According to [10], the decomposition point of $[Cp(CO)_3Mo]_2Mg$ is 160°C. The product yield was 96% based on the converted binuclear complex.

In the reaction of In with **IV** in THF (C_0 0.154 M) at the reactant molar ratio of 2 : 1, under stirring with

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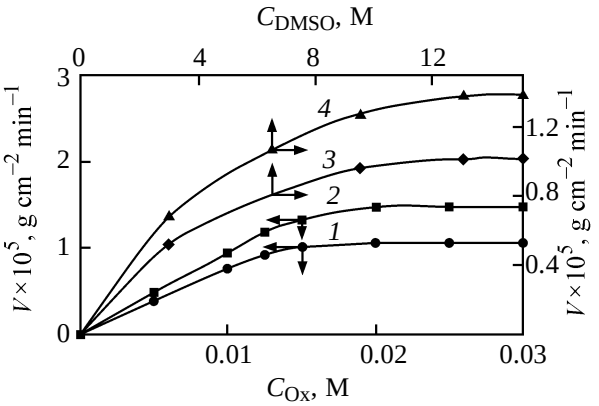

Fig. 1. Rate of magnesium oxidation with $[Cp(CO)_3Mo]_2$ in the DMSO–*p*-xylene mixture as a function of the concentrations of the (*1*, *2*) oxidant (C^0_{DMSO} 14 M) and (*3*, *4*) polar solvent (C^0_{ox} 0.015 M). *T*, K: (*1*, *3*) 353 and (*2*, *4*) 363.

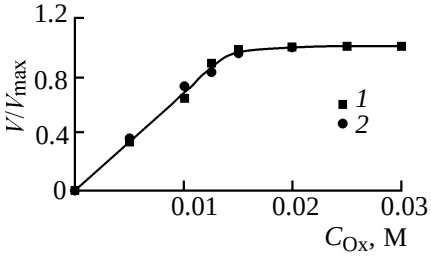

Fig. 2. Relative rate V/V_{max} of the reaction of $[Cp(CO)_3Mo]_2$ with Mg in the DMSO–*p*-xylene mixture as a function of the oxidant concentration (353 K). C^0_L, M: (*1*) 8 and (*2*) 14.

a magnetic stirrer, the initially brown solution became red. The In : Co concentration ratio in the liquid phase after the reaction completion was 1 : 3.04. The liquid was separated from the unchanged metal, and the solvent was removed. This was accompanied by precipitation of a red substance. The In : Co molar ratio in this product after recrystallization was 1 : 2.92, and its melting point in Ar was 94°C. According to [11], the melting point of $In[Co(CO)_4]_3$ is 94°C. The product yield based on the starting oxidant was 94%.

In the oxidation of Tl with **II** in DMSO (C_0 0.10 M, reactant molar ratio 10 : 1) at 60°C under stirring with a magnetic stirrer, a univalent thallium compound, $Cp(CO)_3MoTl$, was detected in the course of the reaction by TLC. After the reaction completion, the liquid phase, in which the Mo : Tl concentration ratio was 3.01 : 1, was separated from the unchanged metal. The major fraction of the solvent was removed under reduced pressure, and the residue was diluted with petroleum ether. The red precipitate that formed was dried at 5×10^{-2} mm Hg, and its IR spectrum (solution in $CHCl_3$) was recorded. The observed carbonyl bands (1971, 1953, 1920, 1903, 1884, and 1863 cm^{-1}) are virtually the same as those reported in [6] (1970, 1953, 1918, 1910, 1885, and 1863 cm^{-1}). The Mo : Tl molar ratio in the product was 3.11 : 1. The yield of $[Cp(CO)_3Mo]_3Tl$ was 95.6% based on the starting content of the oxidant in the reaction mixture.

The plots of the magnesium oxidation rate vs. concentrations of bis(η^5-cyclopentadienyltricarbonylmolybdenum) and DMSO are flattening-out curves (Fig. 1). To reveal the character of reactant adsorption on the metal surface, we examined the dependences $V/V_{max} = f(C_{Ox})$, where V and V_{max} are the rate and maximal rate of magnesium oxidation at various concentrations of the ligand, respectively (Fig. 2). The experimental data show that the reaction can be described by the Langmuir–Hinshelwood scheme [12] involving adsorption of the reactants on active surface centers of different nature [Eqs. (1)–(3)]:

$$Ox + S_1 \overset{K^{ads}_{Ox}}{\rightleftharpoons} Ox(S_1), \quad (1)$$

$$L + S_2 \overset{K^{ads}_{L}}{\rightleftharpoons} L(S_2), \quad (2)$$

$$Ox(S_1) + L(S_2) \xrightarrow{k'} \text{Products}. \quad (3)$$

Here Ox is the oxidant; L, ligand; S_1 and S_2, active centers of the metal surface; K_{Ox}^{ads} and K_L^{ads}, equilibrium constants of adsorption of the oxidant and ligand, respectively; $k' = kS_{01}S_{02}$, where k is the rate constant of the surface reaction, and S_{01} and S_{02} are the numbers of active centers of kinds 1 and 2 per 1 cm^2 of the surface. The reaction rate is given by

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

Linearization of the kinetic curves in the $1/V$–$1/C$ coordinates at constant concentrations of the oxidant and ligand allows us to calculate the equilibrium constants of adsorption of the reactants and the rate constant of the process. From the temperature dependences of these quantities, we obtained the apparent activation energy and the enthalpy and entropy of adsorption of the oxidizing mixture components on the metal surface (see table).

The shape of the kinetic curves characterizing the dependence of the rate of Tl oxidation with **II** on the oxidant and DMSO concentrations (Fig. 3) shows that the reaction can be described by the Langmuir–Hinshelwood scheme [12] for the case when the reactants are adsorbed on active centers of the same kind on the metal surface [Eqs. (5)–(7)].

Apparent equilibrium constants and enthalpies and entropies of adsorption of bis(η^5-cyclopentadienyltricarbonylmolybdenum) and dimethyl sulfoxide on the magnesium and thallium surfaces. Rate constants and activation energies of oxidation of the metals

T, K	K_{Ox}^{ads}	K_L^{ads}	$-\Delta H_{Ox}^{ads}$, 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}	$k\times 10^5$, g cm^{-2} min^{-1}	E, kJ mol^{-1}
				Mg				
353	39.9	0.18					3.7	
363	28.3	0.16	38.2	9.3	11.3	5.6	6.4	62.9
368	23.3	0.15					9.0	
				Tl				
343	155.4	0.070	28.4				37.0	
353	104.0	0.054		76.0	18.4	41.2	69.0	69.7
363	89.9	0.042					14.2	

$$Ox + S \overset{K_{Ox}^{ads}}{\rightleftharpoons} Ox(S), \quad (5)$$

$$L + S \overset{K_L^{ads}}{\rightleftharpoons} L(S), \quad (6)$$

$$Ox(S) + L(S) \xrightarrow{k'} Products. \quad (7)$$

The expression for the reaction rate is as follows:

$$V = \frac{k' K_{Ox}^{ads} C_{Ox} K_L^{ads} C_L}{(1 + K_{Ox}^{ads} C_{Ox} + 1 + K_L^{ads} C_L)^2}. \quad (8)$$

In this case, $k' = kS_0^2$. Treatment of 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, followed by solution of the equations obtained, allows calculation of the adsorption and kinetic parameters of the process (see table).

Figure 4 shows the dependence of the rate of indium oxidation with octacarbonyldicobalt in THF on the oxidant concentration. The apparent activation energy of the process in the range 288–303 K is 50 kJ mol^{-1}. Unfortunately, we failed to obtain the dependence of the reaction rate on the ligand concentration. With toluene, *p*-xylene, and heptane used as inert solvents, the reaction stopped at very low conversions. The metal got coated with a yellow deposit. Apparently, the products of indium oxidation with octacarbonyldicobalt are poorly soluble in these media.

It should be noted that oxidation of magnesium, thallium, and indium in polar media is kinetically controlled. This is indicated by the apparent activation energies of the reactions [13]. With all the metals tested, the reaction rates before the inflection point are proportional to the oxidant concentration. Hence, in the rate-determining reaction step the metal atom reacts with one molecule of the binuclear complex adsorbed on the surface. In this case, the mechanism

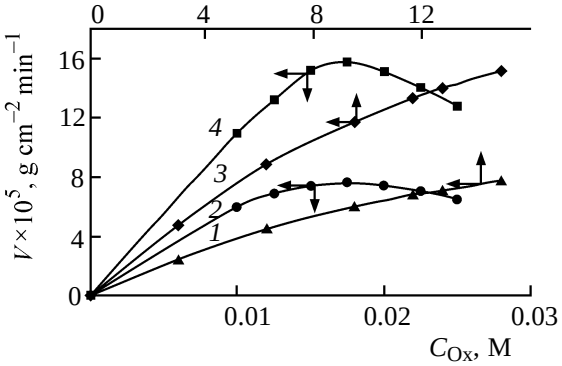

Fig. 3. Rate of thallium oxidation with $[Cp(CO)_3Mo]_2$ in the DMSO–*p*-xylene mixture as a function of the concentrations of the (*2*, *4*) oxidant (C^0_{DMSO} 14 M) and (*1*, *3*) polar solvent (C^0_{ox} 0.015 M). *T*, K: (*1*, *2*) 353 and (*3*, *4*) 363.

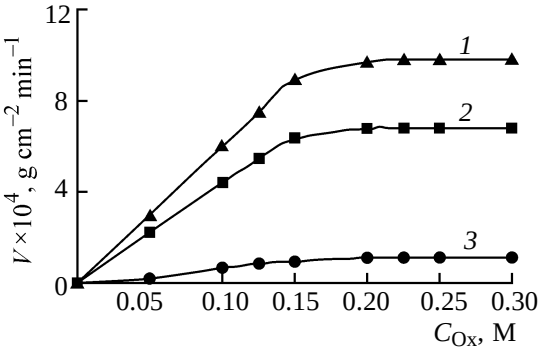

Fig. 4. Rate of the reaction of indium with octacarbonyldicobalt in THF as a function of the oxidant concentration. *T*, K: (*1*) 303, (*2*) 298, and (*3*) 288.

of magnesium oxidation can be described by the scheme suggested by Walborsky [14] for formation of the Grignard reagent and involving one-electron transfer from the metal surface to the oxidant.

The detection of the univalent thallium derivative $Tl[Mo(CO)_3Cp]$ in the course of thallium oxidation with bis(η^5-cyclopentadienyltricarbonylmolybdenum) suggests that adsorption of the oxidant on the metal involves significant deformation of the Mo–Mo bond, ultimately resulting in its dissociation. The radicals generated in the process react with the surface metal atoms. The univalent thallium derivative passes into the solution, where it reacts with the oxidant molecule to form the final product:

$$[Cp(CO)_3Mo]Tl + [Cp(CO)_3Mo]_2 \rightarrow [Cp(CO)_3Mo]_3Tl. \quad (9)$$

Weakening of the Mo–Mo bond in $[Cp(CO)_3Mo]_2$ upon adsorption is suggested by small (in the absolute value) ΔH_{Ox}^{ads} (see table), compared to the enthalpy of dissociation of this bond (139.5 kJ mol^{-1} [7]). According to [15], the higher the energy of the dissociating bond in the oxidant molecule, the higher (in the absolute value) the apparent enthalpy of adsorption of this compound.

In oxidation of indium with octacarbonyldicobalt, initially one electron is transferred to the oxidant molecule adsorbed on the metal surface. As we failed to detect the univalent indium derivative $In[Co(CO)_4]$ in the reaction mixture in the course of oxidation, we believe that the final product is formed at a high rate by reaction (10):

$$InCo(CO)_4 + Co_2(CO)_8 \longrightarrow In[Co(CO)_4]_3. \quad (10)$$

It is unclear, however, whether this reaction occurs with the oxidant molecule adsorbed on the metal surface, or the univalent indium derivative has time to pass into the solution where it is rapidly oxidized.

EXPERIMENTAL

Magnesium [GOST (State Standard) 804–56, 99.92%), indium (INO, GOST 10297–75, 99.998%), and thallium [VK, SNKhTU (Technical Specifications) 1–58; 99.98%) in the form of wire (0.5 mm in diameter) and turnings were used without additional treatment. Dimethyl sulfoxide, *p*-xylene, toluene, heptane, and tetrahydrofuran, if required, were purified and dried by standard procedures [16]. The content of Mg, In, Tl, and Co in the starting chemicals and reaction products was determined by standard procedures [17]. The procedure for determining molybdenum is given in [18]. The syntheses of the organometallic compounds and all manipulations with them were performed under dried and deoxygenated argon or under reduced pressure. Liquid mixtures were degassed by repeated freeze–pump–thaw cycles. Octacarbonyldicobalt was kindly submitted by Prof. F. Uhlig (Dortmund University, Germany). According to the results of spectrophotometric analysis using the extinction coefficients of **IV** at analytical wavelengths [19], the main substance content in this sample was 98.7%. Compound **II** was prepared according to [20]. Its decomposition point was 217°C (published data [21]: decomposition point 216°C). According to the results of analysis for molybdenum, the main substance content in this sample was no less than 99.5%. The IR spectra of **II** were recorded on an IKS-29 spectrometer in KBr cells. Samples were prepared as chloroform solutions under argon.

The composition of the reaction mixture in the course of thallium oxidation with $[Cp(CO)_3Mo]_2$ was determined by TLC on Al_2O_3 supported on Al foil, with acetone–petroleum ether (1 : 2 by volume) as eluent. The retention factors R_f of the products of thallium oxidation with $[Cp(CO)_3Mo]_2$ in DMSO (C_0 0.1 M, 333 K, 5 h) as pure compounds and components of the reaction mixture are given below.

	R_f of pure compound	R_f in the mixture
$[Cp(CO)_3Mo]Tl$	0.32	0.32
$[Cp(CO)_3Mo]_2$	0.65	0.64
$[Cp(CO)_3Mo]_3Tl$	0.46	0.46

The kinetic measurements were performed by the resistometric procedure [22] adapted for readily oxidizable and hydrolyzable compounds.

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