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Oxidation of Magnesium with Diphenylbismuth and Diphenylantimony Chlorides in Polar Solvents

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Abstract—The intermediate and final products of the reactions of magnesium with diphenylantimony and diphenylbismuth chlorides were identified, and the formal kinetic relationships of the process were elucidated. The apparent equilibrium constants, enthalpies, and entropies of adsorption of the reagents on the metal surface, and also the rate constants and activation energies of the reactions in dimethylformamide–*p*-xylene mixture were determined. Probable schemes of magnesium oxidation with the organobismuth and organoantimony chlorides were considered.

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Organometallic halides are used as effective oxidants in syntheses of heterometallic compounds [1]. Organoantimony and organobismuth halides oxidize magnesium under relatively mild conditions in polar solvents [2, 3]. Herbstman [2] suggested that oxidation of magnesium turnings with $(n\text{-}C_4H_9)_2SbBr$ in THF involves formation of $[(n\text{-}C_4H_9)_2Sb]_2Mg$. The final reaction products are $(n\text{-}C_4H_9)_3Sb$, $(n\text{-}C_4H_9Sb)_n$, Sb, originating from transformations of the unstable intermediate $[(n\text{-}C_4H_9)_2Sb]_2$, and also $MgBr_2$ [4, 5]. According to [3], reduction of Ph_2SbBr with Mg initially yields, as in [2], a Grignard-like reagent. Thus, the scheme of the reaction of Mg with diphenylantimony chloride **I** can be represented as follows:

$$Ph_2SbCl + Mg \longrightarrow Ph_2SbMgCl, \quad (1)$$

$$2Ph_2SbMgCl \rightleftarrows (Ph_2Sb)_2Mg + MgCl_2, \quad (2)$$

$$Ph_2SbMgCl + Ph_2SbCl \longrightarrow Ph_2Sb\text{–}SbPh_2 + MgCl_2, \quad (3)$$

$$Ph_2Sb\text{–}SbPh_2 \longrightarrow Ph_3Sb + (PhSb)_n + Sb. \quad (4)$$

As antimony and bismuth are elements of the same subgroup, there are good grounds to anticipate that oxidation of magnesium with diphenylbismuth chloride **II** will follow a similar pattern. To determine the composition and yield of products formed in the reaction of Mg with **II**, a 0.05 M solution of **II** in THF was added at 293 K to a tenfold excess of Mg. In the process, a black precipitate formed and a metallic mirror deposited on the reactor walls. After separation of the liquid phase and unchanged metal, the residue was repeatedly washed with THF and dried at reduced pressure. Treatment of the precipitate with 4 ml of acetic acid is accompanied by transfer of soluble Bi compounds into solution. Analysis of this solution for Bi ions [6] revealed the presence of 0.205 mol of Bi^{3+} per mole of **II**. The metallic mirror did not dissolve in acetic acid, and it was dissolved in 20% HNO_3; the resulting solution contained 0.237 mol of Bi^{3+} per mole of **II**. The liquid phase was evaporated, and the residue (a mixture of a greenish oil and a white crystalline substance) was treated with 5 ml of toluene. The crystals insoluble in toluene were identified by chemical analysis as $MgCl_2$ (yield 0.47 mol per mole of **II**). The toluene solution was treated with warm (40°C) concentrated HCl; in so doing, Ph_3Bi, if present in solution, should transform by the reaction [5]

$$Ph_3Bi + 3HCl \longrightarrow 3PhH + BiCl_3. \quad (5)$$

In the organic layer, we determined chromatographically benzene and diphenyl; their yields were, respectively, 1.51 and 0.1 mol per mole of **II**. The content of the Bi^{3+} ions in the aqueous phase was equivalent to 0.5 mol of $BiCl_3$ per mole of **II** [6]. In a parallel experiment, the organic layer after acid hydrolysis was evaporated; the crystalline residue had mp 70.4°C, which corresponded to diphenyl (mp 70.5°C [7]). According to [4, 5], $(Ph_2Bi)_2$ disproportionated to form Ph_3Bi, $(PhBi)_n$, Bi, and Ph_2. Thus, the scheme of the reaction of **II** with Mg can be represented as follows:

$$Ph_2BiCl + Mg \longrightarrow Ph_2BiMgCl, \quad (6)$$

$$Ph_2BiMgCl + Ph_2BiCl \longrightarrow Ph_2Bi\text{–}BiPh_2 + MgCl_2, \quad (7)$$

$$Ph_2Bi\text{–}BiPh_2 \longrightarrow Ph_3Bi + (PhBi)_n + Bi + Ph_2. \quad (8)$$

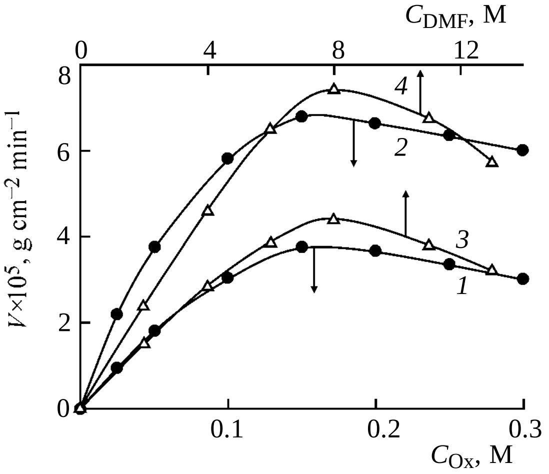

Fig. 1. Rate of magnesium oxidation with diphenylantimony chloride in DMF–*p*-xylene as a function of the concentration of the (*1, 2*) oxidant (C^0_{DMF} 13 M) and (*3, 4*) ligand (C^0_{Ox} 0.1 M). *T*, K: (*1, 3*) 323 and (*2, 4*) 343.

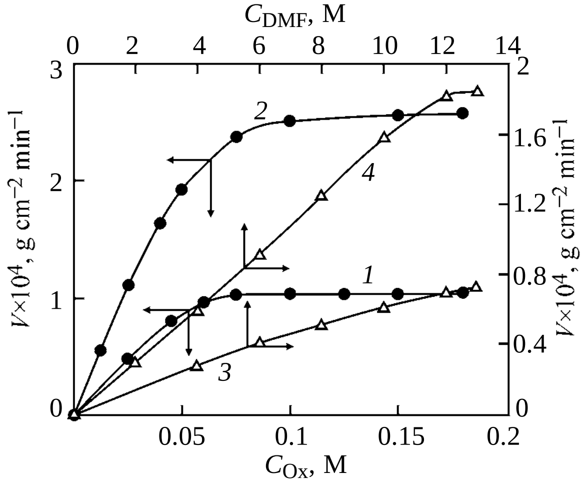

Fig. 2. Rate of magnesium oxidation with diphenylbismuth chloride in DMF–*p*-xylene as a function of the concentration of the (*1, 2*) oxidant (C^0_{DMF} 13 M) and (*3, 4*) ligand (C^0_{Ox} 0.05 M). *T*, K: (*1, 3*) 283 and (*2, 4*) 303.

It is interesting to compare the reaction products formed in the systems Mg–**II** and Mg–$[Cp(CO)_3Mo]_2\cdot BiCl$ [8, 9]. In the latter case, the reaction system does not contain $[Cp(CO)_3MoBi]_n$ and $[Cp(CO)_3Mo]_2$. It should be noted that bis(η^5-cyclopentadienyltricarbonylmolybdenum) is relatively stable (decomposition point 216°C [10]). According to [11], it reacts with Mg, but the reaction occurs at a measurable rate at temperatures higher than those in [8] by 60–70°C. Hence, in organobismuth compounds in which the central atom is bonded to metal-containing substituents, the pathway similar to the transformation of tetraphenyldibismuthine into diphenyl and polymer $(PhBi)_n$ is not realized. Apparently, in this case the intermediate dimer $\{[Cp(CO)_3Mo]_2Bi\}_2$ decomposes into $[Cp(CO)_3Mo]_3Bi$ and unstable intermediate $[Cp(CO)_3MoBi]$, which subsequently disproportionates into $[Cp(CO)_3Mo]_3Bi$ and Bi.

The dependence of the rate of magnesium oxidation with **I** and **II** on the donor power of the solvent passes through a maximum with dimethyl sulfoxide. However, as previous experiments on oxidation of Mg with other compounds were performed in dimethylformamide [12], in this study we also used DMF as polar solvent.

The kinetic curves of magnesium oxidation with **I** in DMF–*p*-xylene (Fig. 1) show that the process can be described by the Langmuir–Hinshelwood scheme with adsorption of the reagent and ligand (polar solvent) on similar active centers of the metal surface [13]. With **II**, the reaction kinetics (Fig. 2) does not allow unambiguous conclusion on the scheme of magnesium oxidation in DMF–*p*-xylene. However, examination of the influence exerted by the oxidant concentration at various ligand concentrations on the relative reaction rate V/V_{max} (V, reaction rate under given conditions; V_{max}, maximal reaction rate; Fig. 3) shows that in this case, too, the reagent and ligand are adsorbed on similar reaction centers. Thus, the reaction scheme can be represented by Eqs. (9)–(11):

$$\mathrm{Ox} + \mathrm{S} \xrightleftharpoons{K_{Ox}^{ads}} \mathrm{Ox(S)}, \quad (9)$$

$$\mathrm{L} + \mathrm{S} \xrightleftharpoons{K_{L}^{ads}} \mathrm{L(S)}, \quad (10)$$

$$\mathrm{Ox(S)} + \mathrm{L(S)} \xrightarrow{k} \mathrm{Products}, \quad (11)$$

where K_{Ox}^{ads} and K_{L}^{ads} are the equilibrium constants of adsorption of the oxidant and ligand, respectively.

In this case, the reaction rate is described by Eq. (12):

$$V = \frac{kK_{Ox}^{ads}C_{Ox}K_{L}^{ads}C_{L}}{(1 + K_{Ox}^{ads}C_{Ox} + K_{L}^{ads}C_{L})}, \quad (12)$$

where C_{Ox} is the oxidant concentration; C_L, ligand concentration; $k = k'S_0^2$ (k', rate constant; S_0, number of adsorption-active centers per unit surface area of the metal).

Linearization of Eq. (12) in the coordinates $(C_{Ox}/V)^{1/2}$–C_{Ox} at C_L = const and $(C_L/V)^{1/2}$–C_L at C_{Ox} = const and combined solution of the resulting

Apparent equilibrium constants, enthalpies, and entropies of adsorption; rate constants and activation energies of magnesium oxidation with diphenylantimony and diphenylbismuth chlorides in DMF–*p*-xylene[a]

T, K	$K_{\mathrm{Ox}}^{\mathrm{ads}}$	$L_{\mathrm{L}}^{\mathrm{ads}} \times 10^2$	$K \times 10^3$, g cm^{-2} min^{-1}
		Ph_2SbCl	
323	26.4	32	2.0
333	23.0	28	2.9
343	20.8	23	3.9
		Ph_2BiCl	
283	5.1	0.46	85
293	5.0	0.30	206
303	4.9	0.18	499

[a] Ph_2SbCl: $\Delta H_{\mathrm{Ox}}^{\mathrm{ads}}$ 11.0 ± 0.8 kJ mol^{-1}, $\Delta S_{\mathrm{Ox}}^{\mathrm{ads}}$ 7.0 ± 1.2 J mol^{-1} K^{-1}, $\Delta H_{\mathrm{L}}^{\mathrm{ads}}$ 15.2 ± 1.9 kJ mol^{-1}, $\Delta S_{\mathrm{L}}^{\mathrm{ads}}$ 57.0 ± 0.7 J mol^{-1} K^{-1}, E 30.0 ± 1.0 kJ mol^{-1}; Ph_2BiCl: $-\Delta H_{\mathrm{L}}^{\mathrm{ads}}$ 1.4 ± 0.1 kJ mol^{-1}, $-\Delta S_{\mathrm{Ox}}^{\mathrm{ads}}$ 8.5 ± 1.0 J mol^{-1} K^{-1}, $-\Delta H_{\mathrm{L}}^{\mathrm{ads}}$ 33.4 ± 2.4 kJ mol^{-1}, $-S_{\mathrm{L}}^{\mathrm{ads}}$ 62.5 ± 1.0 J mol^{-1} K^{-1}, E 63.2 ± 1.4 kJ mol^{-1}.

equations allow calculation of the apparent equilibrium constants of adsorption of the reagent and ligand and of the reaction rate constant. From the temperature dependences of these quantities, we calculated the apparent enthalpies and entropies of adsorption of the oxidant and ligand and the activation energy of the corresponding reactions (see table).

It should be noted that the enthalpy of adsorption of **II** on the Mg surface is lower by almost an order of magnitude than that of **I**. This may be due to a larger energy required to deform of the Bi–Cl bond compared to the Sb–Cl bond. Similar relationships were observed previously, in particular, with organic halides used as oxidants [14].

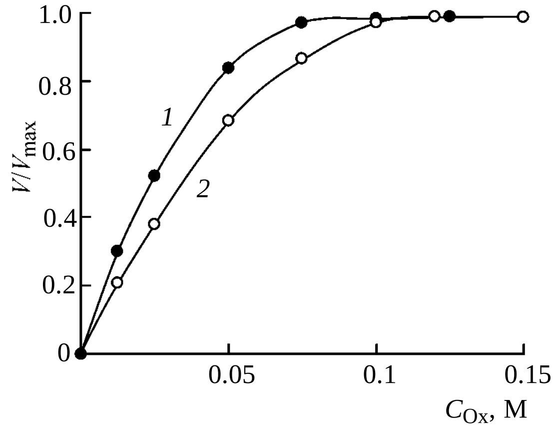

Fig. 3. Relative rate of magnesium oxidation with diphenylbismuth chloride as a function of the oxidant concentration in DMF–*p*-xylene at 293 K. C_{DMF}, M: (*1*) 13 and (*2*) 8.

EXPERIMENTAL

Magnesium wire [GOST (State Standard) 804–56, 99.92%) 0.5 mm in diameter and magnesium turnings were used without additional treatment. Organic solvents, if necessary, were purified and dried by standard procedures [15]. The content of Mg, Sb, Bi, and Cl in the starting substances and reaction products was determined according to [6]. Liquid mixtures were degassed by repeated freeze–pump–thaw cycles. Diphenylantimony and diphenylbismuth chlorides were synthesized by procedures suggested in [5]. According to the content of Cl and Sb [6], the Ph_2SbCl sample contained 99.6% main substance, mp 68.7°C (published data: mp 68–69°C [5]). Ph_2BiCl used in the experiments was 99.6% pure according to the analysis for Cl and Bi [6]; mp 184.8°C (published data: mp 184–185°C [5]).

Diphenyl and benzene were determined chromatographically with a Tsvet-105 device. Analysis conditions: 2.5 × 3000-mm glass column, 10% Reoplex-400 on Cellite 545; thermal conductivity detector, **I** 180 mA; carrier gas He, flow rate 60 ml min^{-1}; temperature of the injector, detector, and oven 180°C; retention time: benzene 35 s and diphenyl 7 min 15 s.

The reaction kinetics was monitored by the resistometric method [16] modified for experiments with readily hydrolyzable and oxidizable substances.

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