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# Oxidation of Magnesium with Benzoyl Chloride in a Mixture of Tetrahydrofuran and Benzene

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**Abstract**—The kinetic features of magnesium oxidation with benzoyl chloride in a mixture of tetrahydrofuran and benzene were studied. A reaction mechanism was suggested, involving attack of the oxidant molecule adsorbed on the metal surface by a similar molecule from the bulk of the solution.

Among organic compounds capable of oxidizing metals, a particular place is occupied by acyl halides. On the one hand, significant polarization of the carbon–halogen makes these compounds reactive in organic and organometallic syntheses. However, acyl halides can also react with polar substances that are usually used as solvents in organometallic syntheses [1, 2]. Such processes are catalyzed by Lewis acids [3]. It was also shown in [3] that at common temperatures benzoyl chloride does not react with zinc in benzene, carbon disulfide, carbon tetrachloride, and petroleum ether. According to [4], aliphatic acyl bromides react with beryllium in diethyl ether and dioxane slowly, whereas in anhydrous ethyl acetate the reaction is very vigorous. In aromatic hydrocarbons, beryllium bromide formed in the process catalyzes the reaction of acyl bromides with the solvent molecules, yielding the corresponding ketones. Thus, when studying the reactivity of acyl halides toward metals, the possible reactions of the oxidant with the solvent and with primary reaction products should be taken into account [5].

In this work, we chose tetrahydrofuran (THF) as solvent, in view of the following facts. First, according to the published data [6] on the dependence of the magnesium oxidation rate *V* on the donor number or ionization potential of the solvent (dioxane, methyl acetate, ethyl acetate, diethyl ether, tetrahydrofuran, and diglyme were tested), in THF, other conditions being the same (benzoyl chloride concentration $c^0_{\mathrm{BC}}$ 0.5 M, 298 K), the rate of the reaction with benzoyl chloride is the highest. Second, the rate of magnesium oxidation with benzoyl chloride is much higher than the rate of reaction of benzoyl chloride with THF. Third, δ-chlorobutyl benzoate formed by the latter reaction was inert toward magnesium under the reaction conditions (Fig. 1).

In Fig. 1 the rate of magnesium concentration at various temperatures is plotted vs. the initial concentration of benzoyl chloride. The apparent activation energy calculated from the experimental data is 16 ± 1 kcal mol$^{-1}$. From the slope of the straight line in the coordinates $\log V$–$\log c^0_{\mathrm{BC}}$, we calculated the reaction order with respect to the oxidant, which amounted to 2. These results suggest that oxidation of magnesium with benzoyl chloride is described by the Ealy–

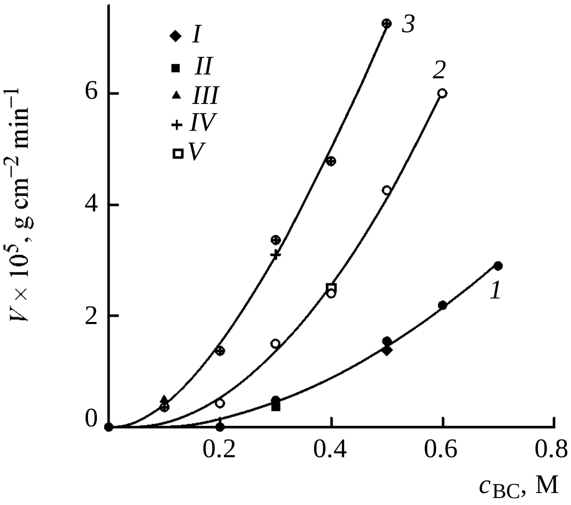

**Fig. 1.** Rate of magnesium oxidation with benzoyl chloride as a function of the benzoyl chloride concentration in THF–benzene ($c_{\mathrm{THF}}$ 8.0 M). Temperature, K: (*1*) 298, (*2*) 303, and (*3*) 313. Other compounds added to the initial solution of benzoyl chloride: (*I*) 0.0022 M $MgCl_2$, (*II*) 0.005 M $MgCl_2$, (*III*) 0.1 M δ-chlorobutyl benzoate, and (*IV*) 0.3 M δ-chlorobutyl benzoate. (*V*) The initial reaction mixture contains the products of reaction of benzoyl chloride with magnesium in the same concentration as formed in the liquid phase after complete consumption of the oxidant ($c^0$ 0.3 M) and removal of magnesium chloride.

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Rideal mechanism involving attack of the oxidant molecule adsorbed on the metal surface by a similar molecule from the bulk of solution [7]. In Fig. 2 the rate of magnesium oxidation is plotted vs. THF concentration in the reaction mixture. In the coordinates of the Kirkwood equation [8] $\log V$–$(\varepsilon - 1)/(2\varepsilon + 1)$, where $\varepsilon$ is the dielectric permittivity of the liquid phase, the plot is linearized (Fig. 2b). This means that the event determining the reaction rate involves the polarized benzoyl chloride molecule whose reactivity increases as the THF content and hence the dielectric permittivity of the liquid phase are increased.

Thus, the pattern of the reaction of benzoyl chloride with magnesium can be represented as follows:

$$C_6H_5C(O)Cl + C_6H_5C(O)Cl$$
$$\xrightarrow[///Mg///]{} C_6H_5\text{–}C(O)C(O)\text{–}C_6H_5.$$

This scheme is consistent with the detection of hexamethylbenzil as the reaction product of magnesium and 2,4,6-trimethylbenzoyl chloride [9]. The data obtained in [4, 5] on oxidation of beryllium with aliphatic acyl chlorides are also nicely consistent with this scheme. According to [4, 5], the primary reaction product is acylmagnesium halide RC(O)MgX, as suggested by the formation of the aldehyde on saponification of the reaction mixture. Acylmagnesium halide further reacts with acyl chloride to form the corresponding diketone. A similar mechanism was suggested in [10, 11] for oxidation of lanthanides with benzoyl chloride in THF.

The reaction of magnesium with a benzoyl chloride solution ($c^0_{BC}$ 0.5 M, 298 K; metal-to-oxidant ratio 3 : 1), performed to ≤20% conversion, gave the following products (per mole of converted benzoyl chloride): 0.1 mol of $C_6H_5C(O)C(O)C_6H_5$, 0.48 mol of $MgCl_2$, and 0.03 mol of $C_6H_5C(O)(CH_2)_4Cl$ formed by the reaction of THF with the oxidant. After removal of volatiles (including unchanged benzoyl chloride) at $5 \times 10^{-2}$ mm and 298 K and treatment of the residue with water to remove $MgCl_2$, a yellow resinous substance was obtained. Its IR spectrum contained strong absorption bands at 1590 and 1620 $cm^{-1}$ assignable to the C=C bond conjugated with the benzene ring [12]. Similar compounds were formed in the reactions of sodium with aliphatic acyl chlorides in ether [13].

It should be noted that in the initial stages the reaction products do not affect noticeably the reaction rate. For example, the rate of magnesium oxidation did not change when concentration of β-chlorobutyl benzoate in the initial mixture had been increased from 0.1 to 0.3 M (Fig. 1). No changes were observed, either, on adding $MgCl_2$ in an amount equal to the amount that is formed by the end of the kinetic experiment, and on adding a solution of the reaction products (after complete consumption of benzoyl chloride and removal of magnesium chloride; Fig. 1).

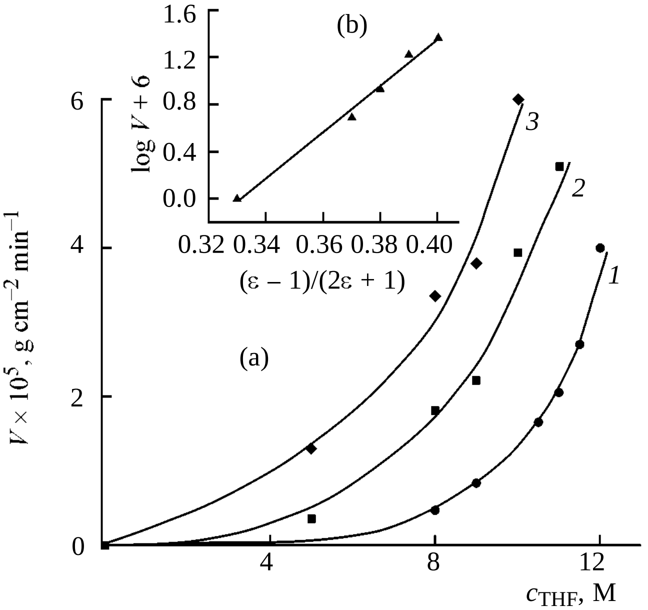

**Fig. 2.** (a) Rate of magnesium oxidation with benzoyl chloride ($c^0$ 0.3 M) in THF–benzene at (*1*) 298, (*2*) 303, and (*3*) 313 K as a function of THF concentration; (b) logarithm of the oxidation rate at 293 K vs. the Kirkwood function of the solvent.

## EXPERIMENTAL

Magnesium wire (0.5 mm in diameter) and magnesium turnings [MCh-1, GOST (State Standard) 804–86, 99.9% main substance] were used without additional surface treatment. Organic solvents were purified and dried by standard procedures [14]. Liquid mixtures were degassed by repeated freeze–pump–thaw cycles. The initial solutions were prepared and the reaction product analyzed with protection from ambient air.

Analytically pure grade benzoyl chloride was used without additional purification. Anhydrous magnesium chloride was prepared as described in [15] and analyzed according to [16]; the main substance content in the product was 99.8%. δ-Chlorobutyl benzoate was prepared according to [17]; $n_D^{20}$ 1.5183 (published data [17]: $n_D^{20}$ 1.5186).

The dielectric permittivities of THF–benzene mixtures were calculated by the equation suggested in [18]. The reaction kinetics was monitored resistometrically [19]; the procedure was modified to exclude contact of reactants with ambient air.

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