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COORDINATION COMPOUNDS

Solid-Phase Synthesis of Cobalt β-Diketonates upon Mechanical Activation

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Abstract—It was shown that the solid-phase interaction of cobalt(II) chloride with alkali metal β -diketonates in the course of mechanical treatment in a vibratory ball mill leads to the formation of the corresponding cobalt β -diketonates and, in some cases, of the MCo(β -diketonate)₃ anion complexes. The effects of the mechanical treatment conditions and the nature of the reagents on the process and the yield of the products were studied. The yield of cobalt β -diketonates reaches 85–90% under optimal conditions. It was found that, after a preliminary activation of the reaction mixture, the synthesis of cobalt β -diketonates can be carried out in the self-heated self-propagating mode.

Mechanochemical methods find expanding applications in various fields of chemistry [1]. In our previous investigations of the solid-phase interaction of chromium (III) chloride with alkali metal β -diketonates, we found that a limited mechanical treatment of a mixture of solid reagents led to its activation, making the reagents able to exothermally react upon mechanical or thermal initiation to form the appropriate chromium (III) β -diketonates. Subsequent conversion of mechanically activated mixtures into the products can be carried out as an explosive mechanochemical synthesis, a thermal explosion, or a self-propagating reaction depending on the initiation method [2-4]. Such systems are interesting for the ability of their components to undergo self-heated interaction as a result of mechanical treatment and processes in these systems occurring at relatively low temperatures as opposed to classic self-propagating high-temperature synthesis [5]. In this work, with the aim of studying the effect of mechanical treatment on the transition metal chlorideorganic anion salt systems in more detail, and to search for new examples of mechanical activation-stimulated reactions of self-propagating synthesis of complex compounds, we studied the solid-phase interaction of cobalt(II) chloride with alkali metal B-diketonates upon mechanical treatment of the reaction mixtures in a vibratory ball mill [6].

EXPERIMENTAL

The anhydrous alkali metal β -diketonates (NaAcac, KDPM) were obtained according to the procedures reported in [3, 7]. Cobalt (II) chloride of high purity grade was heated in vacuo (by gradually elevating the temperature to 150°C) to remove water traces. Preparations of mixtures for synthesis and of samples for phys-

icochemical study, mechanical treatment, and isolation of products were carried out in an inert atmosphere.

X-ray diffraction analysis of the samples was performed on a DRON–2 diffractometer (CuK_{α} radiation). IR spectra of the starting reagents, reaction mixtures, and products were recorded on a UR-20 spectrophotometer in the range of 400–4000 cm⁻¹. The samples were mineral-oil mulls (a capillary layer between KBr plates).

Thermal investigations were carried out on a Q-1000 MOM derivatograph in the temperature range of 20–500°C (the heating rate was 10 K/min, and the sample size approximated 100 mg). The integral intensities of the DTA peak were derived from the area of the appropriate peak normalized to the sample weight.

The melting points were determined with a Boetius heating stage. Near the melting point, the samples in the capillaries were heated at a rate of 4 K/min.

Mechanical treatment was performed in stainless steel reactors of ~80 cm³ volume with the use of a vibratory mill [8] manufactured at the Institute of New Chemical Problems. The operation frequency was 12 Hz, and the amplitude was 11 mm. Steel balls of 12.3 mm in diameter were used as an activating packing.

To carry out a mechanical activation, the reactor was filled with weighed portions of the cobalt chloride, alkali metal β -diketonate, and activating packing. The reactor was sealed, placed on the vibratory mill, and vibrated for the set period of time. After the process was over, the reactor was opened, and the reaction mixture was separated for use in the physicochemical studies and isolation of the target products.

To carry out the reaction in the mode of self-propagating synthesis, a mechanically activated mixture of

Activa- tion time, min	Combus- tion rate, mm/s	Ignition tem- perature (out- side), °C	The peak temperature of the exotherm (on the DTA curve), °C	The onset temper- ature of the self- heated process, °C	Highest tempera- ture in the combus- tion zone, °C	Self-heating, °C	The tempera- ture elevation duration, s
15	1.14	120	95	52	133	81	14
30	1.51	83	83	40	120	80	4
60	0.90	78	70	34	108	74	3

The parameters of the self-heated interaction between the components of the $CoCl_2$ -potassium dipivaloylmethoxide mixture as a function of the time of preliminary mechanical activation

~1 g weight was placed in a quartz tube 7.1 mm in diameter and ~14 mm in height and slightly compacted. The reaction was initiated by heating the bottom end of the tube on a heating table at a rate of ~30 K/min from room temperature until the reaction front commenced movement. The propagation of the reaction front was observed by the change in the mixture color. The linear rate of the reaction propagation was derived from the duration of the process and the rod height. The temperature in the reaction zone was measured using a Chromel-Alumel thermocouple (the wire diameter was 0.15 mm) pressed into the upper layer of the mixture to a depth of ~2 mm. The temperature profile of a reaction wave was recorded with a KSPP-4 recording potentiometer. The accuracy of the temperature measurements was $\pm 2^{\circ}$ C.

The ignition temperature of the mixtures was determined by measuring the temperature of the heating stage at the instant when the color of the mixture at the bottom face changed and was found graphically as the inflection point on the temperature profile of the reaction wave. The values obtained are close to one another and comparable with the peak temperatures of the exotherms in the DTA curves.

The cobalt β -diketonates were isolated either by sublimation or by extraction. For sublimation, a weighed portion of the reaction mixture was placed in a sublimator and heated in vacuo (the outer heater temperature was 160–170°C; the pressure was approximately 0.1 mm Hg). For extraction, benzene was used as a solvent. The yield was determined in relation to the weighed portion of the reaction mixture taken. The products were identified by chemical analyses and physicochemical methods. Chemical analyses were performed at the chemical-analytical laboratory of the Institute of New Chemical Problems.

Preparation of cobalt(II) acetylacetonate, $Co(Acac)_2$. A mixture of 0.2416 g (1.86 mmol) CoCl₂ and 0.522 g (4.28 mmol) sodium acetylacetonate in the presence of the activating packing (150 g) was subjected to mechanical treatment for 30 min, after which a 0.1612-g portion of the reaction mixture was used to isolate the product by sublimation. Cobalt acetylacetonate was obtained in purple-colored crystals. The yield was 0.0745 g (70.5%). The DTA curve of the product features an endotherm (due to phase transition) with a maximum at 170–175°C. The literature value: 175°C [9].

For Co(Acac)₂ anal. calcd. (%): Co, 22.9. Found (%): Co, 22.8.

Preparation of cobalt(II) dipivaloylmethanate, Co(DPM)₂ (DPM = dipivaloylmethane anion). A mixture of 0.1274 g (0.98 mmol) CoCl₂ and 0.502 g (2.25 mmol) potassium dipivaloylmethanate was subjected to mechanical treatment in the presence of the activating packing (150 g) for 90 min, after which a 0.246-g portion of the reaction mixture was used to isolate the product by sublimation. Purple crystals of Co(DPM)₂ were obtained in a yield of 0.144 g (88.2%). $T_{\rm m} = 141-142^{\circ}$ C. The literature value: $T_{\rm m} = 141-143^{\circ}$ C [10].

For Co(DPM)₂ anal. calcd. (%): Co, 13.85. Found (%): Co, 13.8.

RESULTS AND DISCUSSION

In our previous studies of the effect of mechanical action on mixtures of solid cobalt (II) chloride and solid sodium acetylacetonate, we have shown the feasibility of obtaining cobalt acetylacetonate by this method; $Co(Acac)_2$ was obtained in a 36% yield by heating the activated mixture in vacuo [6]. Our new study of the product yield as a function of the duration of mechanical treatment showed that the maximal yield of ~75% is achieved in ~20 min (Fig. 1, curve *a*). The mixture, after being mechanically activated for a long time, changes from bluish to violet and then to pinkish, which is accompanied by a decrease in the yield of $Co(Acac)_2$.

A comprehensive thermal study of reaction mixtures showed that mechanical treatment of a mixture of sodium acetylacetonate and $CoCl_2$ leads to the appearance of a new exotherm in the DTA curves in the range of 60–180°C (Fig. 2). The value of this peak increases with an increase in the activation time to 5–6 min, after which its intensity decreases (Fig. 1, curve *b*). The appropriate DTA peak becomes narrower, and the peak temperature of the peak decreases from 160 to 90°C. The endotherm at 165–170°C, which is associated with

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a phase transition in crystalline tetrameric $Co(Acac)_2$ [9], is absent in the DTA curves of the reaction mixtures (Fig. 2).

The IR spectra of the reaction mixtures subjected to mechanical treatment display new absorption bands. which, however, differ from the absorption bands of $Co(Acac)_2$ isolated by sublimation. The IR spectrum of the activated mixture after heating or after the selfpropagating reaction (see below) becomes more like the Co(Acac)₂ spectrum, but contains unsplit absorption bands at 560 and 660 cm⁻¹ instead of doublets. This difference can be attributed to the fact that $Co(Acac)_2$ is a tetramer in the crystal state, while, in the reaction mixture, the product molecules have no possibility of forming tetramers. This can probably explain the above absence of the endothermic effect on the DTA curves of the reaction mixtures. The relationship between the extent of cobalt (II) acetylacetonate association and the nature of the medium was previously noticed in the literature [11].

The residues after the extractive separation of cobalt acetylacetonate from the reaction mixtures by sublimation are pinkish in color. Their IR spectra display absorption bands corresponding to the NaCo(Acac)₃ anionic complex [12]. The maximal yield of $Co(Acac)_2$ is achieved at the stoichiometric ratio between reagents and decreases in an excess of sodium acetylacetonate, whereas the intensities of the absorption bands of NaCo(Acac)₃ in the IR spectra of the residues increase after sublimation. These findings show that, in an excess of sodium acetylacetonate. the mechanical treatment leads to the formation of the NaCo(Acac)₃ anionic complex, probably as a consequence of interaction of an intermediate cobalt acetylacetonate with an excess of the sodium acetylacetone salt. Indeed, the equimolar mixture of cobalt and sodium acetylacetonates after mechanical treatment shows intense absorption bands due to NaCo(Acac)₃; cobalt acetylacetonate was recovered from the mixture in a less than 50% yield. Therefore, it has been shown that mechanical treatment induces not only exchange reactions, but also addition reactions:

 $CoCl_2 + 2NaAcac \longrightarrow Co(Acac)_2 + 2NaCl,$ $Co(Acac)_2 + NaAcac \longrightarrow NaCo(Acac)_3.$

It should be noted that anionic cobalt (II) tris- β -diketonates with alkali metal cations in the outer coordination sphere are of interest in themselves and are the subject for extensive research [13].

To examine the effect of the nature of β -diketone on the course of reaction, we studied mechanochemical interaction of cobalt (II) chloride with sodium and potassium dipivaloylmethanates, in which the volume of the diketonate anion is considerably larger than that of the acetylacetonate anion. To achieve a high yield of the product in this case, a much longer mechanical treatment was necessary. Treatment in the vibratory

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Fig. 1. The parameters of the reaction of cobalt chloride with sodium acetylacetonate vs. the time of mechanical activation: (a) the yield of $Co(Acac)_2$ and (b) the integral intensity I in relative units (a relative unit is equal to the ratio of the peak area to the sample weight) of the exotherm in the range of $60-180^{\circ}C$ on the DTA curves of the activated mixtures.



Fig. 2. DTA curves of the $CoCl_2 + 2.3$ NaAcac reaction mixtures after mechanical activation for (a) 5 min, (b) 10 min, and (c) 45 min; (d) unreacted $CoCl_2$.

mill leads to homogenization of the reaction mixture and formation of a friable, bluish, fine-grained powder. The reaction mixture gradually looses friability over the course of ~1 h and adheres to the balls and the walls of the reactor. According to X-ray diffraction data, the mixture becomes amorphous within the first 10 min: reflections of the initial crystalline phases vanish, and



Fig. 3. Parameters of the reaction of cobalt chloride with potassium dipivaloylmethoxide vs. the time of mechanical activation: (a) the yield of $Co(Acac)_2$ and (b) the integral intensity *I* in relative units (a relative unit is equal to the ratio of the peak area to the sample weight) of the exotherm in the range of 60–130°C on the DTA curves of the activated mixtures.



Fig. 4. The temperature profile of the reaction wave in the mechanically activated mixtures $CoCl_2 + 2.3$ KDPM vs. the duration of mechanical activation: (*a*) 15 min, *b* 30 min, and (*c*) 60 min.

a broad intense peak appears in the region of $2\theta = 20^{\circ}-30^{\circ}$, indicating the presence of an amorphous phase. The X-ray diffraction patterns of the reaction mixtures after a 15-min treatment show reflections of KCl, which gradually grow in intensity.

Heating the reaction mixtures in dynamic vacuum causes the reaction product (cobalt dipivaloylmetha-

nate) to sublime. The yield of the sublimate increases to \sim 90% with increasing duration of the mechanical treatment (Fig. 3, curve *a*). The residue after sublimation consist largely of KCl. The use of sodium dipivaloylmethanate instead of KDPM does not considerably change the yield of the target product. The cobalt dipivaloylmethanate was obtained in these reactions with a yield of up to 85%. Therefore, unlike the reaction with sodium acetylacetonate, the formation of anionic derivatives, causing a decrease in the target product yield, is not observed in the case of dipivaloylmethane. This can be explained by the large volume of the dipivaloylmethanate anion.

Studying the yield of $Co(DPM)_2$ as a function of the ratio between the starting reagents, we found that the highest yield is achieved in the presence of a small potassium dipivaloylmethanate excess compared to its stoichiometric amount. Because of this, we carried out most experiments using the ratio $CoCl_2$: KDPM = 1 : 2.3.

The comprehensive thermal study of the reaction mixtures showed that the mechanical treatment of the mixture of potassium dipivaloylmethanate and CoCl₂ gives rise to a new exotherm in the region of $60-135^{\circ}$ C. The magnitude of this exotherm increases as the duration of treatment increases to ~30 min, after which the integral intensity of this peak gradually decreases (Fig. 3, curve b). By analogy with the solid-phase reaction of chromium β -diketonate formation studied previously [2, 3], we assumed that the exotherm corresponded to interaction of the components of the activated reaction mixture upon heating to form $Co(DPM)_2$. A decrease in the integral intensity of this peak with an increase in the duration of the process is due to the fact that the reaction partially proceeds during the mechanical treatment.

Indeed, the mechanical treatment generates new absorption bands in the IR spectra of the reaction mixtures, which, however, differ from the absorption bands of Co(DPM)₂. The absorption bands of the target product (cobalt dipivaloylmethanate) appear only after heating the reaction mixture or after initiating the self-propagating reaction (see below). Attempts to isolate cobalt dipivaloylmethanate from the activated mixtures by extraction result in only trace amounts of the target product even after prolonged mechanical treatment. These data show that the solid-phase interaction of cobalt (II) chloride with KDPM is a complicated, multistage process and the final product does not form in the course of mechanical treatment. For its formation, subsequent thermal treatment of the activated mixture is required.

The presence of the exotherm in the DTA curves of the activated mixtures of cobalt chloride with alkali metal β diketonates gives grounds to suppose that the reactions under consideration can be carried out in the self-propagating mode [5]. Indeed, heating the end of a cylindrical rod of a compacted activation mixture of

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cobalt chloride with KDPM initiates the self-propagating interaction of the components: in the starting mixture, light blue in color, a zone colored pink appears. The zone propagates from the heated to the cold end gradually extending over the whole sample. As the duration of mechanical treatment increases from 15 to 60 min, the initiation temperature of the process decreases from 120 to 78°C and the maximal temperature in the reaction zone decreases from 133 to 108°C (table). However, an increase in the duration of mechanical treatment has a most pronounced effect on the rate of the temperature increase within the reaction front: a much shorter is time thus needed to reach the maximal temperature from the beginning of the rapid temperature increase (Fig. 4). The linear combustion rate is an extreme function of the mechanical treatment time. The maximal rate is observed after 30-min activation, which corresponds to the maximal integral intensity of the DTA exotherm for these mixtures (Fig. 3). The self-heating of a mixture (the temperature jump) is little affected by the activation time and falls within the range of 74-81°C.

Note that, in almost all cases, we observed a chaotic curvature of the surface of the moving reaction front. Because of this, the measured duration of the process and, correspondingly, the linear propagation rate of the process slightly varied from run to run. However, the linear movement rate of the reaction zone for all cases was in the range 0.9-1.5 mm/s. The curvature of the reaction surface profile in finely dispersed solid mixtures was also observed previously. Even if the combustion looked like it was occurring in the layer-by-layer mode, small-scale curvatures of the profile of the reaction surface are detected [14]. These observations are consistent with the results of a computer simulation of the combustion wave propagation in solid heterogeneous mixtures by cellular automata [15]. The simulation shows that the propagation of the reaction wave in such mixtures can occur not only layer by layer, but also in the form of discrete vortices and channels, depending on the ratio of the active phase to the inert filler in the mixture [16].

The self-propagating self-heated reaction in activated mixtures of cobalt chloride and sodium acetylacetonate can be carried out in a similar way. However, the reproducibility of the combustion parameters for these mixtures is too poor to study this process quantitatively, most likely because of the high hygroscopicity of sodium acetylacetonate.

Therefore, the mechanical activation of nearly stoichiometric mixtures of cobalt chloride with alkali metal β -diketonates promotes the solid-phase interaction of the components with the formation of the appropriate cobalt β -diketonate. The reaction is supported by heat evolution in the course of the reaction.

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