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Solid-state mechanochemical synthesis of ferrocene

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Abstract

Solid-state mechanochemical reactions of iron(II) chloride with cyclopentadienides of alkaline metals or thallium, which lead to the formation of ferrocene, were studied. The dependence of the yield of the product on the parameters of mechanical loading for the reaction with cyclopentadienylthallium was determined. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Earlier we have shown that chlorides of several transition metals can react with ionic cyclopentadienides in the solid state under mechanical loading of mixtures of the starting compounds to form the corresponding cyclopentadienyl derivatives [1]. However, the yields of the products were low. To optimize the conditions of syntheses of metallocenes and investigate processes occurring in the reaction mixtures at mechanical loading, we studied solid-state mechanochemical reactions of iron(II) chloride with cyclopentadienides of alkaline metals or thallium, which led to the formation of ferrocene. The dependence of the yield of the product on the parameters of mechanical loading for the reaction with cyclopentadienylthallium was determined.

2. Experimental

All procedures with anhydrous iron(II) chloride and sodium and potassium cyclopentadienides were carried out in a dry box in a nitrogen atmosphere.

2.1. Starting compounds

Anhydrous iron(II) chloride was prepared by chlorination of an iron wire with hydrogen chloride at a high

temperature [2]. Nickel chloride was prepared by dehydration of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ with heating in vacuum [2]. Sodium and potassium cyclopentadienides (CpNa and CpK) and sodium methylcyclopentadienide (MeCpNa) were prepared by the interaction of cyclopentadiene or methylcyclopentadiene with the corresponding hydroxides [3]. Cyclopentadienylthallium was prepared by the reaction of cyclopentadiene with an alkaline water solution of thallium(I) acetate [4] and sublimed before use.

2.2. Physicochemical investigations

X-ray powder analyses of samples were carried out on a DRON-2 diffractometer (Cu- K_α radiation). IR spectra were recorded on an UR-20 spectrophotometer in the 400–4000 cm^{-1} range. The samples were prepared as suspensions in Nujol. Thermal analyses were carried out on a Q-1000 MOM derivatograph (Hungary) in the 20–500°C temperature interval, the rate of heating was 10° min^{-1} , and the weight of a sample was ~100 mg. Melting points and thermal behavior of samples were determined on a Boetius heating table (Germany).

2.3. Mechanical loading

Mechanical loading was carried out using eccentric vibration ball mills [5] made in our institute. Working frequencies of the mills were 12 and 19.5 Hz and amplitudes of vibrations were 3–11 mm. The reactions were carried out in stainless steel reactors with volumes

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of ca. 80 cm³. Steel balls 4.8, 12.3 and 14.3 mm in diameter were used as activating filling.

To carry out the reactions, a reactor was charged with weighed amounts of starting materials and activating filling, hermetically closed, installed on a vibration ball mill, and subjected to vibrations for scheduled time. After completion of the process, the reactor was opened, the reaction mixture was separated from activating filling and used for physicochemical analyses and isolation of target products.

Isolation of metallocenes from the reaction mixtures was carried out by vacuum sublimation or extraction with benzene. The products obtained were identified according to the data of chemical analyses and physicochemical investigations.

2.4. Preparation of ferrocene by interaction of FeCl₂ and CpTl

A mixture of CpTl (0.7356 g, 2.7 mmol) and FeCl₂ (0.1922 g, 1.5 mmol) was subjected to mechanical loading for 60 min at a frequency of 12 Hz and an amplitude of 11 mm (activating filling, steel balls 4.8 mm in diameter; total weight, 150 g). The reaction mixture became orange. A portion of the reaction mixture (0.5164 g) was transferred into a sublimation apparatus. Sublimation was carried out at a temperature of external heating of 120–140°C in vacuum (0.1 mmHg). Ferrocene was obtained as orange crystals in a yield of 0.1179 g (84%).

Anal. Found, %: C, 65.2; H, 4.94; Fe, 30.15. For C₁₀H₁₀Fe Calc., %: C, 64.56; H, 5.42; Fe, 30.02.

2.5. Preparation of ferrocene by reaction of FeCl₂ and CpK

A mixture of CpK (0.3616 g, 3.47 mmol) and FeCl₂ (0.1380 g, 1.04 mmol) was subjected to mechanical loading for 15 min at a frequency of 12 Hz and an amplitude of 11 mm (activating filling, steel balls 12.3 mm in diameter; total weight, 150 g). A dark orange reaction mixture was obtained. A portion of the reaction mixture (0.367 g) was transferred into a sublimation apparatus. The sublimation was carried out at a temperature of external heating of 120–140°C in vacuum (0.1 mmHg). Ferrocene was obtained as orange crystals in a yield of 0.1725 g (85.2%) and characterized by physicochemical methods.

2.6. Preparation of 1,1'-dimethylferrocene by reaction of FeCl₂ and CH₃C₅H₄Na

A mixture of CH₃C₅H₄Na (0.4390 g, 4.25 mmol) and FeCl₂ (0.2538 g, 2.0 mmol) was subjected to mechanical loading for 30 min at a frequency of 12 Hz and an amplitude of 11 mm (activating filling, steel balls 4.8

mm in diameter; total weight, 150 g). A dark orange reaction mixture was obtained. The weighed amount of the reaction mixture (0.5750 g) was transferred into a sublimation apparatus. Sublimation was carried out at a temperature of external heating of 80–95°C in vacuum (0.1 mmHg). 1,1'-Dimethylferrocene was collected on the cooled part of the sublimation apparatus as orange crystals. The yield was 0.1420 g (90.4%). Anal. Found, %: C, 67.0; H, 6.6; Fe, 25.7. For C₁₂H₁₄Fe Calc., %: C, 67.3; H, 6.59; Fe, 26.09.

2.7. Preparation of nickelocene by reaction of NiCl₂ and CpTl

A mixture of CpTl (0.8940 g, 3.2 mmol) and NiCl₂ (0.2332 g, 1.8 mmol) was subjected to mechanical loading for 60 min at a frequency of 12 Hz and an amplitude of 11 mm (activating filling, steel balls 4.8 mm in diameter; total weight, 150 g). A gray–green reaction mixture was obtained. The weighed amount of the reaction mixture (0.8086 g) was transferred into a sublimation apparatus. Sublimation was carried out at a temperature of external heating of 100–120°C in vacuum (0.1 mmHg). Nickelocene was obtained as dark-green crystals in a yield of 0.198 g (89.5%). The compound was characterized by physicochemical methods.

2.8. Reaction of ferrocene with thallium chloride

A mixture of TlCl (0.6020 g, 2.5 mmol) and ferrocene (0.2334 g, 1.25 mmol) was subjected to mechanical loading for 75 min (filling, steel balls 12.3 mm in diameter; total weight, 150 g). The mixture obtained smelled like cyclopentadiene, which testified to the decomposition of ferrocene. A portion (0.7391 g) of the reaction mixture was transferred into a sublimation apparatus, and ferrocene was sublimed at a temperature of external heating of 120°C in vacuum. Ferrocene was recovered in a yield of 0.1590 g, (68%). The increase of temperature up to 160°C caused sublimation of 0.003 g of pale-yellow cyclopentadienylthallium (yield 0.4%), which was identified by its IR spectrum and diffraction pattern.

3. Results and discussion

Mechanical loading (activation) of mixtures of iron(II) chloride and cyclopentadienides of alkaline metals using a vibration ball mill resulted in the formation of alkaline metal chloride and ferrocene [1]. The study of the dependence of the yield of ferrocene on the ratio of reagents in the reaction with CpK showed that the yield of ferrocene increased with an increase in CpK excess. Conversion of FeCl₂ into ferrocene achieved

85% at the ratio $\text{CpK}:\text{FeCl}_2 = 3.4:1$ after mechanical loading for 15 min at a frequency of 12 Hz and an amplitude of 11 mm. Other conditions being equal, the comparable conversion (80%) was achieved only for 30 min of processing at an amplitude of 7 mm. Only traces of ferrocene were obtained at an amplitude of 3 mm for 15 min, and 7.7% conversion was achieved over 1 h. The yield of the product does not depend on the method of isolation (sublimation or extraction). Thus, an increase of the amplitude within the limits mentioned above led to an increase in conversion of initial substances into ferrocene. Therefore, subsequent experiments were carried out at an amplitude of 11 mm.

It is noteworthy that the results of the reactions under study depend strongly on the identity of organic ligands used. For example, 1,1'-dimethylferrocene was obtained by us with $\sim 90\%$ conversion in the reaction of iron dichloride with sodium methylcyclopentadienide at a stoichiometric ratio of reagents.

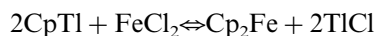
Low yields of ferrocene in the reactions at stoichiometric amounts of the reagents, CpM ($M = \text{K}, \text{Na}$) and FeCl_2 , and darkening of the mixtures during mechanical loading allowed us to assume that a decrease in the yield is due to the oxidation of finely dispersed CpM by traces of oxygen in the reactor. We suggest that the high yield of 1,1'-dimethylferrocene can be explained as follows: some quantity of low melting 1,1'-dimethylferrocene formed at the beginning of the reaction covers the MeCpNa surface and thus prevents its contact with oxygen and oxidation.

To avoid the use of highly oxygen- and moisture-sensitive cyclopentadienides of alkaline metals, we chose the iron(II) chloride-cyclopentadienylthallium system for extensive investigation of the process of the solid-state mechanochemical synthesis of metallocenes. The reactions were carried out at the ratio $\text{CpTl}:\text{FeCl}_2 \sim 1.8$ to prevent contamination of ferrocene with CpTl during sublimation.

The dependence of the yield of ferrocene on the degree of fullness of the reactor with activation filling has a pronounced cupola character with a maximum at about 50% of fullness. A similar dependence was observed by us for syntheses of chromium β -diketonates [6] and described by other authors [7].

An increase in the duration of mechanical loading up to 45–60 min resulted in a growth of the yield of the product (Fig. 1). The reaction mixtures gradually turned orange during activation. Ferrocene was isolated from the mixtures in a yield of 88–90%. After isolation of ferrocene, the residue consisted basically of TlCl , according to the data of chemical analyses and X-ray diffraction data. Further increase of duration of activation led to a gradual decrease in the yield of ferrocene. We assumed that this was related to mechanochemical destruction of ferrocene. In fact, prolonged mechanical loading (75 min and more) of pure ferrocene or its

mixture with thallium chloride resulted in its partial decomposition: the reaction mixtures got a smell of cyclopentadiene. Ferrocene was regenerated from them with a yield of 70–75% only. A small quantity of CpTl was obtained from the mixture of ferrocene with thallium chloride after prolonged activation. The results obtained show that the solid-state reaction of the synthesis of ferrocene is reversible to some extent under conditions of mechanical loading:



Therefore, to avoid destruction of the products, the subsequent reactions were carried out for a duration of activation not longer than 60 min.

Other conditions being the same, an increase in the frequency of mechanical loading from 12 to 19 Hz resulted in some increase in conversion in the initial period of the reaction and to a faster achievement of the maximum conversion. However, the conversion achieved at 19 Hz was somewhat lower than that for 12 Hz (Fig. 1). It is noteworthy that the conversion achieved for a specified duration of loading depended strongly on the ratio of the weight of activating filling to that of the starting materials [6]. The majority of experiments were carried out at a ratio of the weight of filling to that of the starting materials $> 100:1$. An increase in the diameter of filling balls resulted in an increase in the conversion at the initial period of the reaction, but the maximum conversion did not virtually depend on the diameter of filling balls within the limits investigated. For example, the maximum conversion at a frequency of 12 Hz and an amplitude of 11 mm for balls 4.8, 12.3 and 14.3 mm in diameter amounted to 89.5, 87.7, and 88.4%, respectively.

The data on the dependence of the conversion on the parameters of mechanical activation allowed us to carry out mechanochemical synthesis of nickelocene with a high yield (see Section 2).

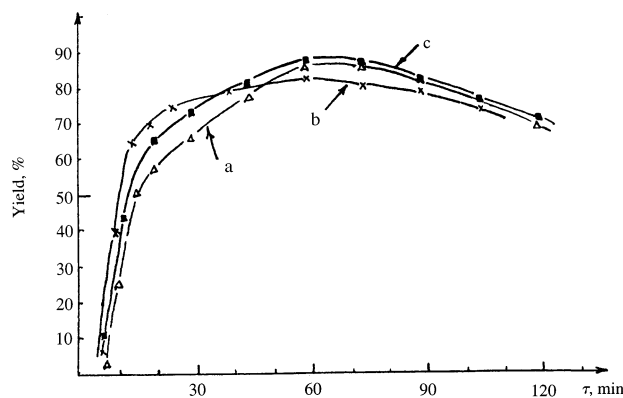


Fig. 1. The dependence of the yield of ferrocene in the reaction of CpTl with FeCl_2 on the duration and conditions of mechanical loading: (a) activating filling 4.8 mm in diameter, frequency 12 Hz; (b) filling 4.8 mm in diameter, frequency 19.5 Hz; (c) filling 12.3 mm in diameter, frequency 12 Hz.

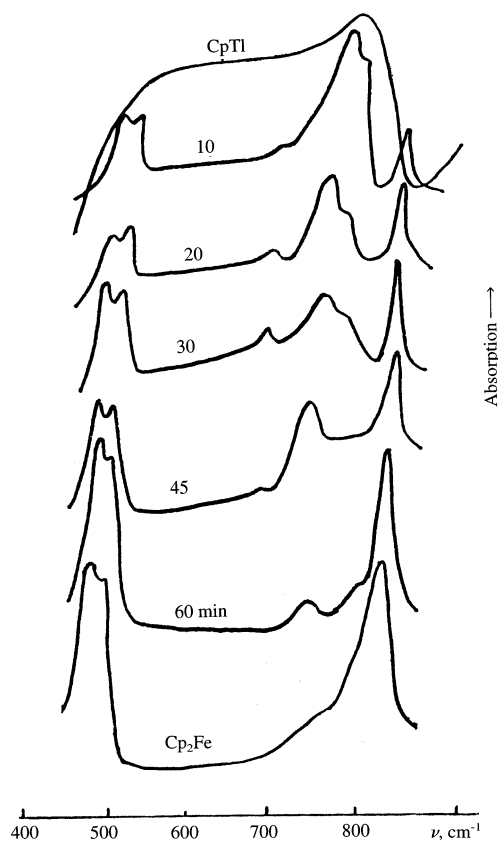


Fig. 2. IR spectra of the mechanically loaded reaction mixtures $1.8\text{CpTi} + \text{FeCl}_2$ at different durations of mechanical loading (frequency of activation, 12 Hz; filling 12.3 mm in diameter).

In the solid-state mechanochemical reaction of CrCl_3 with $3\text{NaC}_5\text{H}_7\text{O}_2$ investigated by us earlier, the formation of an activated mixture only occurred in the initial period of activation, without transformation of the starting materials into the final products [6]. At this stage, extraction of the reaction mixture with organic solvents did not result in isolation of chromium acetylacetonate [6]. By contrast, both extraction and sublimation of mechanically loaded mixtures of CpTi with FeCl_2 at all stages of activation allow one to isolate some quantity of ferrocene. Both methods gave approximately the same yield of the product, which depended on the duration of mechanical loading. These data suggest that the interaction of iron(II) chloride with CpTi is a typical mechanochemical reaction, products of which are formed directly in the process of mechanical loading.

To determine the changes in the reaction mixtures caused by mechanical loading, we investigated the mixtures of CpTi with FeCl_2 after various durations of activation by the means of IR spectroscopy, X-ray diffraction and thermal analyses.

IR spectroscopy data showed that the absorption bands of ferrocene appeared in the IR spectra of the

reaction mixtures immediately during the first minutes of activation (Fig. 2). The intensities of the bands increased to some extent with an increase in the duration of mechanical loading, whereas the bands of CpTi (which was taken in a shortage comparing to FeCl_2) weakened and finally disappeared.

Widened reflexes of TiCl and a broad hump in the area of $2\theta \approx 20\text{--}30^\circ$, which denoted the presence of the amorphous phase, appeared on the X-ray diffraction patterns of the reaction mixtures mechanically loaded for 1–3 min (Fig. 3). Further activation led to a decrease in the intensity of the hump and an increase in intensity and a sharp decrease in the width of the reflexes of TiCl . Their full-width at half-maxima (fwhm) values decreased approximately three times for 1 h of activation and became equal to those for pure crystalline samples of TiCl . These data indicated the reduction of a quantity of the amorphous phase and integration of originally formed finely divided crystals of TiCl . Similar narrowing of TiCl reflexes occurred after separation of ferrocene from the reaction mixtures by sublimation, whereas the reflexes remained broad after extraction with organic solvents at room temperature.

Thermogravimetric investigations of the reaction mixtures activated for several minutes showed that a new exothermic event within the $\sim 115\text{--}150^\circ\text{C}$ interval emerged on the differential thermal analysis (DTA) curves. The exothermic event was followed by endothermic ones at ~ 175 and 240°C , corresponding to the melting and evaporation of ferrocene, respectively. All these events were absent on the DTA curves of the reaction mixtures before activation. The intensities of the endothermic events increased markedly with an increase in the duration of mechanical loading. The intensity of the exothermic events increased with an increase in the duration of activation up to 10–15 min. Then it decreased and the exothermic event disappeared finally when the duration of the mechanical processing increased to ca. 45–60 min. In contrast to the reaction of chromium chloride with sodium acetylacetonate, the yield of ferrocene did not grow after warming up of the activated reaction mixture. Moreover, the exothermic event was observed on the DTA curves of the residues after removal of ferrocene by extraction at room temperature. (The residues consisted basically of thallium chloride, as was specified earlier.)

The presence of the exothermic event on the DTA curves of the activated mixtures allowed us to suppose that the process can be carried out in a self-propagating mode. In fact, the action of a local heat pulse on an end face of a cylindrical specimen made of the activated mixture with broad reflexes of TiCl caused the appearance of a dark-brown zone, which propa-

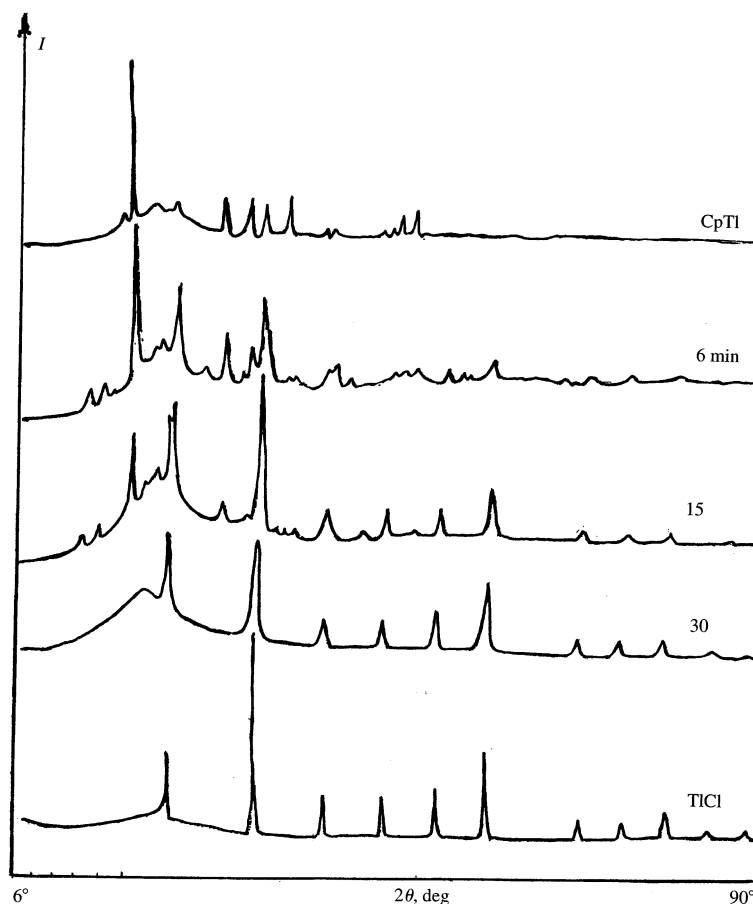


Fig. 3. Diffraction patterns of the mechanically loaded reaction mixtures at different durations of mechanical loading (frequency of activation, 12 Hz; filling 12.3 mm in diameter).

gated along the grey–yellow specimen up to the second end face of the specimen. This implies that we observed a self-propagating process on heating of the mechanically loaded reaction mixture. The rate of propagation can reach $\sim 10 \text{ mm s}^{-1}$ and the temperature in the reaction zone can rise up to $\sim 200^\circ\text{C}$, depending on the conditions of the mechanical loading and organization of the process.

The widths of TiCl_3 reflexes decreased sharply after warming up activated reaction mixtures or after the self-propagating process. The data suggest that the exothermic event on the DTA curves and the self-propagating process in the compacted activated reaction mixtures correspond to crystallization of finely dispersed TiCl_3 formed initially in the course of the exchange reaction between CpTi and FeCl_2 .

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