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Solid-phase mechanochemical synthesis of zirconium tetracarboxylates

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The solid-phase synthesis of zirconium carboxylates $Zr(OOCR)_4$ (R = Alk) by reactions of zirconium tetrachloride with metal carboxylates (isobutyrate, pivalate, and palmitate) (the molar ratio $ZrCl_4$: RCOOM is 1 : (4—5)) under mechanical activation is developed. Further thermal treatment of the reaction mixture and extraction with an organic solvent afford zirconium carboxylates.

Key words: metal carboxylates, zirconium carboxylates, zirconium isobutyrate, zirconium pivalate, zirconium palmitate, mechanical activation, solid-phase synthesis.

Zirconium carboxylates[1—5] are of interest as both the starting compounds for the preparation of zirconium-containing materials possessing unique properties, which are very useful in new technologies and as components of catalysts for various chemical processes. In particular, zirconium tetracarboxylates have found wide application in industrial oligomerization of ethylene.[6,7] Carboxylates of various metals (including zirconium) are produced in an industrial scale by a number of large chemical companies.[8,9] Various types of zirconium carboxylates are known[1—3] that differ in the structure of carboxylic substituents, their number in the coordination sphere of the metal, and the nature of other substituents. Hetero-ligand zirconium carboxylates containing water or hydroxyl groups are studied in most details. Zirconocene carboxylates $(\eta^5\text{-}C_5H_5)_2Zr(OOCR)_2$ are fairly well studied, while information on zirconium tetracarboxylates $Zr(OOCR)_4$ (R = Alk) is scarce.

Reactions of zirconium derivatives with carboxylic acids are usually employed for the preparation of zirconium tetracarboxylates.[1—3] Of them, the reactions of zirconium tetrachloride with carboxylic acids in organic solvents are the most popular.[1—5] These reactions proceed stepwise (Scheme 1).

Scheme 1

$$ZrCl_4 + HOCOR \rightleftharpoons RCOOZrCl_3 + HCl$$

$$RCOOZrCl_3 + HOCOR \rightleftharpoons (RCOO)_2ZrCl_2 + HCl$$

$$(RCOO)_2ZrCl_2 + HOCOR \rightleftharpoons (RCOO)_3ZrCl + HCl$$

$$(RCOO)_3ZrCl + HOCOR \rightleftharpoons (RCOO)_4Zr + HCl$$

Thus zirconium acetate, propionate, *n*-butyrate, and isobutyrate $Zr(OOCR)_4$ were prepared by heating zirconium tetrachloride with an excess of the respective acid in xylene or using acid as a solvent;[1—3] zirconium stearate and palmitate were prepared by heating zirconium tetrachloride with an excess of the respective acid in benzene for 14 h.[10] No data on the possibility of preparation of zirconium tetrapivalate by the reaction of $ZrCl_4$ with pivalic acid or its salts are available.

This approach has some major drawbacks: a low rate and long duration of the reaction; relatively high temperatures (100—150 °C) required to end the process for the lower carboxylates; release of a large amount of corrosive hydrogen chloride; reversibility of the reaction.

The aim of the present work is to study the possibility of application of the solid-phase mechanochemical method for the preparation of zirconium tetracarboxylates, derivatives of aliphatic carboxylic acids. We studied the possibility of the application of the solid-phase (solvent-free) mechanochemical method for the synthesis of this class of compounds by example of zirconium tetracarboxylates from metal carboxylates with primary (palmitate), secondary (isobutyrate), and tertiary (pivalate) alkyl groups.[11]

Experimental

Zirconium tetrachloride and potassium palmitate (both "technical" grade) were used without additional purification. Sodium pivalate and sodium isobutyrate were prepared by dissolving an excess of the respective acid in aqueous sodium hydroxide followed by evaporation of volatiles and drying the residue *in vacuo* with gradual heating from room temperature to 150 °C. Hexane and benzene ("chemically pure" grade) were purified by distillation from $LiAlH_4$ in the presence of cetyltrimethylammonium bromide.

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X-ray phase analysis was performed on a DRON-2 diffractometer (Cu-Kα-radiation). The IR spectra of the starting compounds, reaction mixtures, and reaction products were recorded on a UR-20 spectrophotometer in the range of 400—3600 cm^{-1}. The samples for IR studies were prepared as suspensions in Nujol (a capillary layer between KBr plates). The thermal studies were carried out using a Derivatograph Q-1500M System F. Paulik, J. Paulik, L. Erdey (Hungary) instrument in the range of 20—500 °C, the heating rate was 10 °C min^{-1}, the sample weight was ~100 mg. The integral intensity of the effects on the DTA curves were determined using the area of the respective peak referred to the sample weight.

Mechanical treatment of mixtures of $ZrCl_4$ with metal carboxylates was performed using an eccentric vibration mill[12] with an operating frequency of 12 Hz and an amplitude of 11 mm, a stainless steel reactor of ~85 cm^3 volume. Steel balls (20 pieces with a diameter of 12.3 mm and the total mass of ~150 g were used as the activating filling.

The reaction products were identified by chemical and physicochemical methods of analysis. Chemical analysis was carried out in the Laboratory of Physicochemical Analytical Methods at the Institute of Problems of Chemical Physics RAS. Percentage of carbon and hydrogen was established by elemental microanalysis using a Vario MICROcube (Elemental Analysensysteme GmbH, Germany) CHNS-analyser. Percentage of zirconium was established by titration with a solution of complexon III in 0.25 *M* H_2SO_4 (Xylenol Orange as the indicator).[13]

All operations with air-sensitive compounds were carried out in a dry box under an inert atmosphere.

Zirconium tetraisobutyrate [Zr{Me_2CHCOO}$_4$]. A mixture of zirconium tetrachloride (0.41 g, 1.76 mmol) and sodium isobutyrate (0.83 g, 7.54 mmol) were subjected to mechanical treatment for 2 h. The reaction mixture was separated from the activating filling, heated at 100 °C for 1 h, and extracted with hexane (3×30 mL). Hexane was evaporated to afford zirconium tetraisobutyrate as a white solid. Yield 0.63 g (82%). Found (%): C, 43.86; H, 6.68; Zr, 21.08. $C_{16}H_{28}O_8Zr$. Calculated (%): C, 43.71; H, 6.42; Zr, 20.75. IR, ν/cm^{-1}: 1620 s (ν_{as}(CO)), 1450 s (ν_s(CO)).

Zirconium tetrapivalate [Zr{Me_3CCOO}$_4$]. A mixture of zirconium tetrachloride (0.47 g, 2.01 mmol) with sodium pivalate (1.24 g, 9.96 mmol) were subjected to mechanical treatment for 2 h. The reaction mixture was separated from the activating filling, heated at 150 °C, and extracted with benzene (3×30 mL). Benzene was evaporated to afford zirconium tetrapivalate as a white solid. Yield 0.79 g (80%). Found (%): C, 48.53; H, 7.48; Zr, 18.34. $C_{20}H_{36}O_8Zr$. Caclucated (%): C, 48.47; H, 7.38; Zr, 18.41. IR, ν/cm^{-1}: 1630 s (ν_{as}(CO)), 1455 s (ν_s(CO)), 1340 s and 1320 s (doublet).

Zirconium tetrapalmitate [Zr{$CH_3(CH_2)_{14}COO$}$_4$]. A mixture of zirconium tetrachloride (0.26 g, 1.11 mmol) and potassium palmitate (1.39 g, 4.7 mmol) were subjected to mechanical treatment for 2 h. The reaction mixture was separated from the activating filling, heated at 150 °C, and extracted with warm hexane (3×30 mL). Hexane was evaporated to afford zirconium tetrapalmitate as a white solid. Yield 1.06 g (86%). Found (%): C, 69.16; H, 10.45; Zr, 7.35. $C_{64}H_{124}O_8Zr$. Calculated (%): C, 69.07; H, 11.23; Zr, 8.20. IR, ν/cm^{-1}: 1630 s (ν_{as}(CO)), 1455 s (ν_s(CO)), 1350—1200 w (sept, *trans*-CH_2).

Results and Discussion

The effects of the mechanical treatment on the IR spectra and diffraction patterns of mixtures of solid metal carboxylates with zirconium tetrachloride were studied using a mixture of crystalline sodium pivalate with zirconium tetrachloride (the molar ratio was nearly stoichiometric, 4 : 1) as a model. It was found that the mechanical treatment of the mixture induced the reaction between the reactants. In the diffraction patterns of the reaction mixtures, the intensity of the reflections of the starting compounds gradually decreased and the reflections of sodium chloride appeared, which became stronger and narrower during the mechanical treatment (up to 2 h) (Fig. 1). The well-defined reflections of sodium chloride, weak reflections of the starting compounds, and broad peak (halo) in the range of 2θ = 10—30°, which suggests the presence of an amorphous phase (the reagents and/or the reaction products), appear in the diffraction patterns of the reaction mixtures after mechanical activation for 2 h. In the IR spectra of the reaction mixtures, the intensity of the absorption bands of sodium pivalate (540, 600, 1430, and

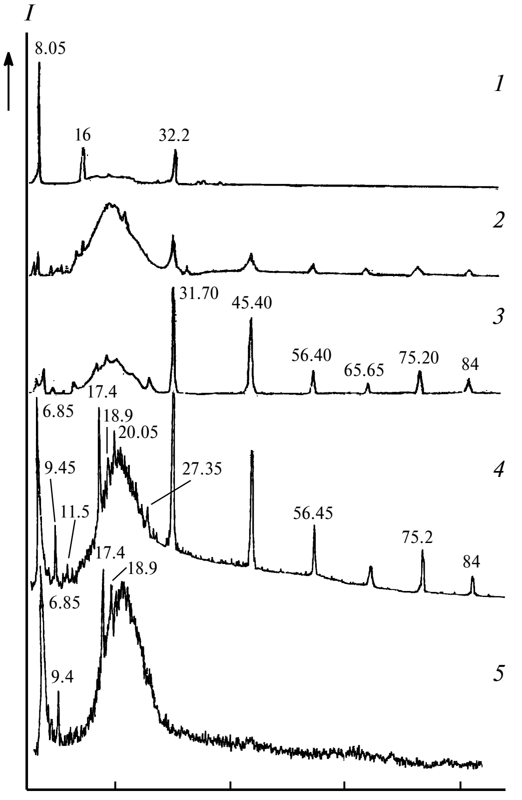

Fig. 1. The diffraction patterns of starting sodium pivalate (*1*), the reaction mixtures ($Me_3CCOONa : ZrCl_4 = 4 : 1$) after mechanical treatment for 60 (*2*), 120 min (*3*), and 30 min with subsequent heating (*4*), and also the mechanochemical reaction product, *i.e.*, zirconium tetrapivalate (*5*).

1580 cm^{-1}) decrease with the increase in the duration of the mechanical treatment, whereas the absorption bands at 430, 575, 625, 1320, 1340, and 1630 cm^{-1} as well as other bands assigned to zirconium tetrapivalate appear (Fig. 2). However, weak absorption bands of sodium pivalate are present in the IR spectra of the reaction mixtures even after mechanical activation for 2 h. The presence of the absorption bands and reflections of the starting materials in the IR spectra and diffraction patterns of the activated mixtures indicate that the exchange reaction does not go to complection over the mentioned time (see Fig. 1, diffraction pattern *3* and Fig. 2, spectrum *4*).

At the same time, the increase in the duration of the mechanical treatment up to more than 3 h results in the appearance of additional absorption bands and reflections in the IR spectra and diffraction patterns of the reaction mixtures, apparently, caused by mechanochemical decomposition of both the reactants and zirconium tetracarboxylate.

To study the possibility of accelerating the reaction and preventing the mechanochemical destruction, we performed the thermographic studies of mixtures of sodium pivalate with zirconium tetrachloride ($RCOONa : ZrCl_4 = (4—4.5) : 1$) at different durations of the mechanical treatment. The thermographic study of the reaction mixtures activated for 30—120 min showed the presence of a strong exothermic effect in the range of 60—160 °C on the DTA curves of these mixtures, which was not accompanied by changes in the sample weight (Fig. 3). It was established that no exothermic effects were observed on the DTA curves of the reactants, nonactivated mixtures, and the reaction products within the temperature range mentioned. The increase in time of the mechanical treatment from 30 to 120 min resulted in a decrease in the temperature corresponding to the maximum of the exothermic effect, while the integral intensity of this effect is diminished (see Fig. 3). In the thermograms of the reaction mixtures that have been mechanically activated and then heated the mentioned thermal effect did not appear. After heating, in the IR spectra of the activated reaction mixtures ($RCOONa : ZrCl_4 = 4 : 1$), the absorption bands of the starting compounds almost disappear with retention of absorption bands of only zirconium tetrapivalate, while in the diffraction patterns the reflections of the starting compounds disappear and the sharp narrowing of the reflections of sodium chloride and zirconium pivalate is observed (see Figs 1 and 2).

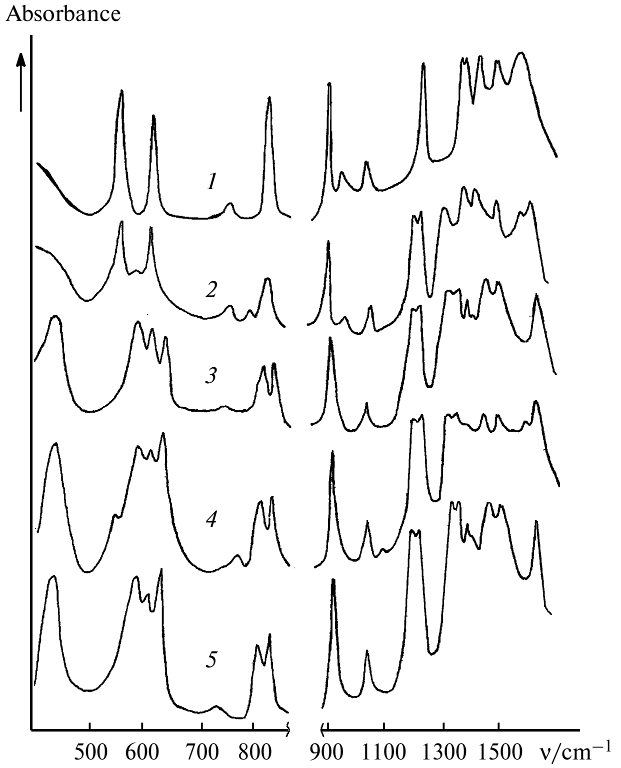

Fig. 2. The IR spectra of $Me_3CCOONa$ (*1*); the reaction mixtures ($Me_3CCOONa : ZrCl_4 = 4 : 1$) after mechanical activation for 60 min (*2*); after mechanical activation for 30 min followed by heating to 150 °C (*3*); after mechanical activation for 120 min (*4*); $Zr(Me_3CCOO)_4$ (*5*).

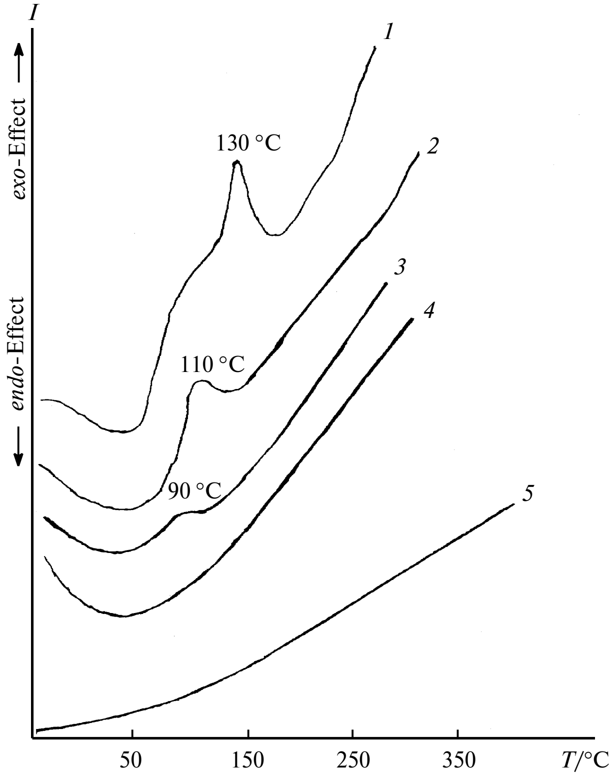

Fig. 3. The DTA curves of the reaction mixtures ($Me_3CCOONa : ZrCl_4 = (4—4.5) : 1$) after mechanical activation for 30 (*1*), 60 (*2*), and 120 min (*3*); after mechanical activation for 30 min followed by heating to 150 °C (*4*). The curve *5* shows the rate of the temperature change during thermogram recording.

As we have shown earlier[14—16] for a number of solid-phase mechnochemical reactions, the emergence of a new exothermic effect that has been absent for a mixture of the starting compounds is due to the fact that the components that were finely dispersed and blended upon a mechanical treatment acquire the ability of an exothermic reaction, which results in the final products with an increase in temperature or continuation of the mechanical treatment. The presence of the exothermic effect on the DTA curves of the activated mixtures shows that the reaction between the solid components of these mixtures can proceed due to thermal energy released during the reaction, *i.e.*, in the mode of self-propagating autothermic reaction.[14—16] The disappearance of the exothermic effect indicates that the reaction is complete.

Mixing of sodium pivalate and zirconium tetrachloride powders in a vibration mill without activating filling (steel balls) for 60 min without heating, as well as with subsequent heating does not result in noticeable change in the diffraction patterns and IR spectra of the mixtures. This implies that the mechanical activation of the mixture of the reactants is the limiting step.[12,14—17]

The considered data of physicochemical studies show that the mechanical activation for 30—120 min followed by heating of the reaction mixture to 150 °C result in completion of the reaction

$$\mathrm{ZrCl_4 + 4\,Me_3CCOONa \longrightarrow Zr[Me_3CCOO]_4 + 4\,NaCl.}$$

Zirconium tetrapivalate can be isolated from the reaction mixture by extraction with organic solvents (for example, hexane or benzene).

Similar results were observed in the case of solid-phase mechanochemical synthesis of zirconium isobutyrate.

Somewhat different reaction patterns were observed by us in exploring the application of the mechanochemical method for the synthesis of zirconium palmitate, $\mathrm{Zr[Me(CH_2)_{14}COO]_4}$, a compound with a long-chain alkyl radical. In contrast to the reactions of sodium isobutyrate and sodium pivalate, no exothermic effect was observed in the range of 20—200 °C on the DTA curves of the reaction mixtures with potassium palmitate. In the range of 60—160 °C, we observed an endothermic effect at about 65 °C, which was present on the DTA curves of the starting potassium palmitate and, apparently, corresponded to variations of conformation of the palmitate fragment. The absence of the exothermic effect on the DTA curves in this case suggests that the reaction of solid-phase synthesis of zirconium tetrapalmitate cannot be performed in the self-propagation mode.[14—16]

The reaction

$$\mathrm{ZrCl_4 + 4\,CH_3(CH_2)_{14}COOK \longrightarrow Zr[CH_3(CH_2)_{14}COO]_4 + 4\,KCl}$$

smoothly proceeds under mechanochemical activation for 2 h followed by heating the reaction mixture to 150 °C. The IR spectra of the mechanically activated reaction mixtures after heating correspond to the IR spectrum of zirconium tetrapalmitate. In the diffraction patterns of the mixtures, the reflections of the starting compounds disappear, while the sharp reflections of potassium chloride appear. Pure zirconium tetrapalmitate was isolated as a white solid upon extraction of the reaction mixture with warm hexane.

The prepared zirconium tetracarboxylates are white fine-crystalline compounds, soluble in saturated, aromatic, and chlorinated hydrocarbons. The preparative reactions of solid-phase synthesis of zirconium tatracarboxylates is reasonable to carry out using a slight excess of salts of an organic acid to simplify the procedure, to achieve complete removal of chlorine, and to increase the yields of the desired compounds. The intensive absorption band at ~1630 $\mathrm{cm^{-1}}$ assigned to the vibrations ν_{as}(COO) of the carboxylic group, which is characteristic of zirconium tetracarboxylates, is observed in the IR spectra of the prepared compounds.[1,4] A set of low-intensive absorption bands in the range of 1350—1185 $\mathrm{cm^{-1}}$ is observed in the IR spectrum of zirconium tetrapalmitate, which is typical of salts of palmitic acid.[18] Zirconium tetracarboxylates are extremely unstable and easily hydrolyzed in air.[4,10,19] As a result, the absorption band of the tetracarboxylate at ~1630 $\mathrm{cm^{-1}}$ in the IR spectra disappears and a low-frequency band (~1560 $\mathrm{cm^{-1}}$) appears. This corresponds to the formation of hydrolysis products apparently with the composition $\mathrm{ZrO(RCOO)_2 \cdot 2H_2O}$.[3,20] Moreover, the narrow absorption band at ~1720 $\mathrm{cm^{-1}}$ appears in the spectrum, which indicates the presence of the aliphatic acid.[18]

Thus, we developed a solid-phase mechanochemical method for the synthesis of zirconium tetracarboxylates, which allows preparing these substances readily and in high yields. Furthermore, the application of this method makes it possible to avoid the release of free corrosive hydrogen chloride and simplification of the technological design of the process.

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