Self-propagating synthesis of chromium acetylacetonate

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After preliminary mechanical activation a mixture of solid chromium(III) chloride and sodium acetylacetonate becomes capable of reacting to form chromium acetylacetonate. The reaction may be carried out in the mode of a self-propagating process.

Key words: self-propagating synthesis, mechanical activation, complex compounds, chromium acetylacetonate.

Reactions of self-propagating high-temperature synthesis (SHS) are well known for systems consisting of simple inorganic compounds and are widely used for obtaining various inorganic materials.[1]

The possibility of self-propagating synthesis of organic compounds was demonstrated earlier by the example of the acid-base reaction between malonic acid and piperazine.[2] The phenomenology and mechanism of this reaction are identical to those for the SHS of inorganic compounds, while such parameters as temperature (100—160 °C), linear velocity (0.5—1.5 mm s^{-1}), and the power of initiating impact (150—200 J) were all below the corresponding values for SHS processes.[3] The preparation of coordination compounds by the method of self-propagating synthesis was not described in the literature.

In this work the self-propagating synthesis of chromium acetylacetonate is carried out by the solid-state interaction of chromium(III) chloride with sodium acetylacetonate.

Results and Discussion

Previously we have shown that the mechanical activation of mixtures of solid 3d metal chloride with sodium acetylacetonate gives rise to acetylacetonate of the corresponding metal.[4] To elucidate the mechanism of the process, we carried out the thermographic study of mixtures of $CrCl_3$ with sodium acetylacetonate (NaAcac) with different durations of mechanical activation.

It was found that the mechanical activation of the mixture resulted in the appearance of endothermic events at 195 and 300 °C corresponding to melting and evaporation of chromium acetylacetonate and exothermic event at ~110 °C which is absent on the DTA curves of the starting materials and final reaction products. The intensity of the events initially increases with increase in the activation time, thereafter the exothermic event disappears while the endothermic events remain as before. The reaction mixture changes its color from pink to violet after disappearance of exothermic event. The extraction of the violet mixture gives chromium acetylacetonate in high yield. The heating of the reaction mixtures at various stages of mechanical activation in vacuum leads to the sublimation of chromium acethylacetonate, and yield of chromium acetylacetonate increases with an increase in the activation time within the limits of Table 1.

Thus, mechanical activation imparts to the mixture of solid $CrCl_3$ and NaAcac the capability of reacting to form chromium acetylacetonate. The presence of an exothermic event on the DTA curves of the activated mixtures allows one to suppose that the reaction may be carried out in a self-propagating mode.

In fact, the local heating of the surface of compacted activated mixture initiates the self-propagating interaction of the reagents.

The results of this study (see Table 1) show that depending on the duration of mechanical activation, τ, the reaction between $CrCl_3$ and NaAcac initiated by thermal impact can proceed in three different modes. At the activation time less than 3 min, the initiation of self-propagating process fails, and the reaction of components proceeds only near impact zone. As the duration of activation increases the components of the mixture become be able to reaction. However, in the interval of $3 < \tau < 5$ min the self-propagating mode is not stable. Its parameters vary from one experiment to another. At $\tau > 5$ min, the self-prapagating process is stable. Its parameters are well reproduced. If the activation time is more than 15 min (the reaction mixture changes its

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Table 1. Dependence of the product yield, temperature, and velocity of burning of the reaction on the duration of mechanical activation

Duration of activation, τ/min	Density of block /g cm^{-3}	Temperature of burning /°C	Velocity of burning /mm cm^{-1}	Yield of $Cr(Acac)_3$ (%)
3	1.20	—	—	16
4	1.30	160	0.23	47
5	1.25	110	0.17	59
5	1.26	140	0.17	64
5	1.29	220	0.18	66
7	1.24	250	0.41	61
10	1.24	260	2.48	80
12	1.21	260	6.90	82
17	1.25	—	—	85

colour and the exothermic event on DTA curve disappears), the self-propagating process cannot be initiated because the synthesis has brought to completion during the mechanical activation.

These data indicate that after preliminary mechanical activation, the reaction between $CrCl_3$ and NaAcac may be initiated by three methods: further mechanical activation, heating the reaction mixture, or local thermal impulse. In the first case the reaction is likely to proceed in the mode of "explosive" mechanochemical synthesis.[5,6] In the third case the reaction is supported by the energy evolving in the course of the process, *i.e.*, this is the self-propagating process.

Hence, we discovered the first example of solid phase synthesis of coordination compounds in the self-propagating mode. A peculiarity of this reaction is that the ability of the reagents to interact arises as the result of mechanical activation and is retained for long time (six months and more) after activation. The reactions of $CrCl_3$ with other sodium β-diketonates may be run analogously.

Experimental

Anhydrous crystalline $CrCl_3$ ("chemical pure" grade) was used as received. Sodium acetylacetonate was obtained by the reaction of a slight excess of acetylacetone with an aqueous solution of NaOH (~10 %). After completion of acetylacetone addition the mixture was stirred for 1 h, water was evaporated in vacuum at ~20 °C, and the residue was dried in vacuum with the temperature gradually increasing from 20 °C to 150 °C. NaAcac was obtained as an off-white powder.

Thermographic investigation of samples was carried out on a Q-1000 MOM derivatograph (Hungary) in quarz vessels in the temperature range 20—500 °C, the velocity of heating 10 deg min^{-1}, the mass of samples *ca.* 100 mg.

The mechanical activation was carried out with a vibrational ball mill with 12 Hz frequency and 11 mm amplitude in the stainless steel reactor (volume 70 cm^3). Steel balls of 12.3 mm diameter were used as the activating filling.

For the investigation of the dependence of the parameters of self-propagating synthesis on the duration of mechanical activation, the reactor was charged in inert atmosphere with 0.40 g (2.53 mmol) of $CrCl_3$, 1.05 g (8.60 mmol) of NaAcac, and 25 activating balls. The reactor was closed hermetically and subjected to vibration for the specified time. After completion of the process the reactor was opened, and the reaction mixture was separated.

For carrying out the reaction as the self-propagating process, the activated mixtures were compacted on a hydraulic hand press at the pressure of 1000 kg cm^{-2} to form cylindrical blocks 7.1 mm in diameter, 14 mm in height, and ~1 g in mass, which were placed in the quartz tubes. The reaction was initiated by the heating of the upper plane of the blocks by the electrically heated nichrome wire. The duration of the burning was recorded with an accuracy of 0.2 s. The temperature in the zone of the burning was measured with an accuracy of *ca.* 5 °C by the Chromel—Alumel thermocouple inserted in the lower plane of the block. The linear velocity of the burning was calculated from the data on the duration of burning and the length of the block. The condensed products of the reaction sintered to a dense mass retaining initial form. Chromium acetylacetonate was sublimated from this mass. Found (%): C, 52.49; H, 6.10; Cr, 14.74. $C_{15}H_{21}O_6Cr$. Calculated (%): C, 51.58; H, 6.06; Cr, 14.88. Melting point 215—216 °C. (Ref. 7 for $Cr(Acac)_3$: 214—216 °C). The yields of $Cr(Acac)_3$ are given in Table 1.

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