

## REACTION OF CHROMOCENE WITH ACETYLACETONE

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Crystalline chromocene reacts with excess liquid acetylacetonone to give chromium(III) acetylacetonate, cyclopentadiene, and hydrogen. The reaction is exothermic and fast as low as at 25°C. The reaction of solid chromocene with acetylacetonone vapours is substantially slower, transient formation of chromium(II) acetylacetonate being observed.

Recently, we dealt in detail<sup>1-3</sup> with study of reactions of chromocene with aliphatic compounds containing OH, OR, NH<sub>2</sub>, and NR<sub>2</sub> groups. These reactions mostly produce very reactive compounds containing Cr(II). This communication attempts to follow the reaction of chromocene with acetylacetonone (2,4-pentanedione) in which one ketonic group is present in its enol form.

## EXPERIMENTAL AND RESULTS

*Reagents.* Preparation and purification of chromocene was described earlier<sup>1</sup>. Macrocrystalline resublimed chromocene was used for the reaction with acetylacetonone. Microcrystalline chromocene with large surface area was used for preparation of the reaction intermediate; this chromocene sample was obtained by thermal decomposition of the aminate<sup>2</sup> formed by reaction of macrocrystalline chromocene with 1-butanamine. The chromocene powder thus prepared is light red and pyrophoric in air. The used 1-butanamine (Fluka, Switzerland) and acetylacetonone (Reachim, U.S.S.R) were dried and purified by fractionation in stream of deoxygenated argon (<5 ppm O<sub>2</sub>). All the reactions were carried out in glass apparatuses without ground glass joints after previous evacuation. Deoxygenated argon was used as protection gas during introduction of the reaction components into the apparatus.

*Analyses.* Chromium content in solid products was determined (after their decomposition by melting with oxidation mixture) colorimetrically (CrO<sub>4</sub><sup>2-</sup>, λ = 400 nm) or gravimetrically (BaCrO<sub>4</sub>). Carbon and hydrogen content was determined by combustion method. Volatile components of the reaction mixtures were detected and identified by gas chromatography (Fractovap GV 200, Carlo Erba, Italy, with flame-ionisation detector; Chrom IV, Laboratorní přístroje, Prague, Czechoslovakia, with heat conductivity detecting element<sup>1</sup>).

*Magnetic measurements.* Oxidation states of chromium in the solid products were distinguished by determination of their magnetic moments. The latter were calculated on the basis of Curie-Weiss equation from temperature dependence of magnetic susceptibilities of the said sub-

stances. The susceptibility was measured with the accuracy of  $\pm 1.5\%$  within temperature interval 90–300 K using a Variable Temperature Gouy Balance apparatus (Newport Instruments, England). The values of magnetic molar susceptibility were corrected by means of the Pascal constants.

*The reaction course.* Addition of excess liquid acetylacetone ( $20 \text{ cm}^3$ ) to crystalline chromocene (1 g) in evacuated apparatus results in a vigorous reaction. Spontaneous heating of the mixture is accompanied by gas evolution. At first the liquid is redbrown, later it is redviolet. The reaction is finished after about 20 min. Violet crystalline solid separates from the solution. If the finely powdered chromocene with large surface area reacts with acetylacetone vapours, the reaction is far slower. A yellowbrown intermediate is formed which is only transformed to violet solid by further action of acetylacetone vapours. The largest amount of the intermediate is present in the reaction mixture after about 70–80 h contact of the reactants.

*Identification of the reaction products.* Gas-chromatographic analysis of the gases present above the liquid reaction mixture proved the presence of acetylacetone, cyclopentadiene, and hydrogen. Some hydrocarbons  $C_1$  to  $C_4$  are present in traces. Composition of the violet product is 51.07% C, 6.24% H, 14.31% Cr, (for chromium(III) acetylacetonate calculated: 51.58% C, 6.06% H, 14.88% Cr). The product is quite stable in air. After recrystallization from hot benzene, melting point of the violet product agrees with the known melting point of chromium(III) acetylacetonate. The yellowbrown intermediate was isolated from the solid reaction mixture by removal of chromocene (sublimation at  $120^\circ\text{C}$  at 10 Pa). It contains 46.90% C, 5.91% H, 20.88% Cr, (for chromium(II) acetylacetonate calculated: 48.00% C, 5.64% H, 20.78% Cr). The intermediate is highly unstable in air.

The magnetic moment found for the violet product is  $\mu(\text{BM})_{293\text{K}} = 3.72$ , the Weiss constant being  $\theta = 0 \text{ K}$  (ref.<sup>3,4</sup> gives for chromium(III) acetylacetonate  $\mu(\text{BM})_{300\text{K}} = 3.86$ ). The yellowbrown intermediate exhibits the magnetic moment  $\mu(\text{BM})_{293\text{K}} = 4.56$  and the Weiss constant  $\theta = 40 \text{ K}$  (ref.<sup>5</sup> gives for chromium(II) acetylacetonate  $\mu(\text{BM})_{300\text{K}} = 4.99$ ).

## DISCUSSION

The given findings allow to express the course of the reaction of crystalline chromocene with excess liquid acetylacetone (acaH) at  $25^\circ\text{C}$  by the following equation:

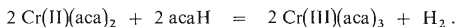
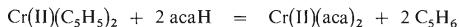


The presence of  $\text{C}_5\text{H}_6$  and  $\text{H}_2$  in the reaction product was proved by gas-chromatographic analysis. By appearance and composition, the violet product corresponds to chromium(III) acetylacetonate and has the corresponding melting point. The found magnetic moment corresponds to the expected value of spin only contribution of three unpaired electrons in Cr(III) atom. The value of the Weiss constant indicates mononuclear structure of the violet substance.

The same overall reaction course is observed on contact of chromocene with acetylacetone vapours at  $25^\circ\text{C}$ . However, the reaction leads to a yellowbrown product whose composition, appearance and chemical behaviour indicate the presence of chromium(II) acetylacetonate. The found magnetic moment confirms the presence

of four unpaired electrons of Cr(II) atom. Magnitude of the Weiss constant suggests magnetic coupling of paramagnetic centres in a layered structure<sup>5</sup> of chromium(II) acetylacetonate.

The both partial steps of the reaction are expressed by the equations:



The first step is analogous to the process taking place in the previously studied<sup>1</sup> interaction of chromocene with aliphatic alcohols. The second step consists in oxidation Cr(II)→Cr(III) and formation of elementary hydrogen.

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