Note

PREPARATION OF CHROMIUM(III) SPINELS BY THE SOLID STATE REACTION BETWEEN POTASSIUM DICHROMATE AND HYDRATED METAL CHLORIDES

M.R. UDUPA

Department of Chemistry, Indian Institute of Technology, Madras-600 036 (India)

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The solid state reaction between two solid reactants to give a solid product is usually governed by the ability of the reactant to migrate through the reactant–product interphase. Thus, the mobility and the diffusivity of the reactant phase control the reaction rate. It has been reported [1] that inorganic chromites are obtained by heating potassium dichromate and anhydrous metal chloride mixtures at 1100°C. In order to understand the nature and mechanism of the reaction, we have taken up the thermogravimetric decomposition studies of intimate mixtures of potassium dichromate and divalent metal chlorides. The decomposition products were characterized by chemical, X-ray and IR spectral analyses.

EXPERIMENTAL

Commercially available reagent grade $K_2Cr_2O_7$, $MgCl_2 \cdot 6\ H_2O$, $MnCl_2 \cdot 6\ H_2O$, $CoCl_2 \cdot 6\ H_2O$, $NiCl_2 \cdot 6\ H_2O$, $CuCl_2 \cdot 2\ H_2O$, $ZnCl_2 \cdot 2\ H_2O$ and $CdCl_2 \cdot 2\ H_2O$ were used without further purification. Equimolar amounts of $K_2Cr_2O_7$ and the hydrated metal chlorides were taken in an agate mortar and intimately mixed by grinding for 15–20 min. About 200 mg of the samples were placed in a platinum crucible container and heated in air continuously at the rate of 6°C min^{-1} from room temperature to 1200°C on a Stanton recording thermobalance. The X-ray powder patterns were obtained using a Philips X-ray unit. The IR spectra of the intermediate chromate residues were obtained using a Perkin-Elmer 257 spectrometer.

RESULTS AND DISCUSSION

The thermogravimetric plots of mixtures of $K_2Cr_2O_7$ and the chlorides of Mg, Mn, Co, Ni, Cu, Zn and Cd are given in Fig. 1. The final products obtained in all cases are found to be insoluble in water and showed the

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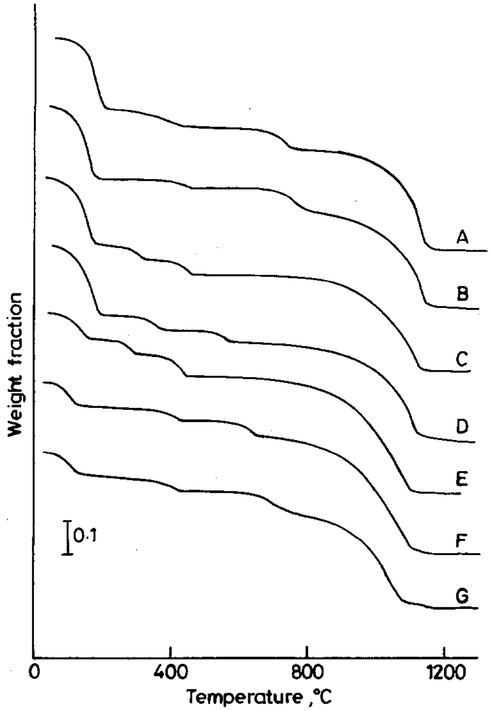

Fig. 1. TG curves of equimolar mixtures of $K_2Cr_2O_7$ and chlorides of Mg(A), Mn(B), Co(C), Ni(D), Cu(E), Zn(F) and Cd(G).

absence of chloride. The weight losses observed at 1100°C correspond to the formation of metal(II) chromites(III) except for the $CuCl_2$–$K_2Cr_2O_7$ system, in which case it was found to be a mixture of copper(I) chromite(III) and chromium(III) oxide. This observation was confirmed by the X-ray powder patterns of the residues [2].

The thermogravimetric data tabulated in Table 1 include the observed and the calculated weight losses at various states of decomposition. The TG curves suggest that there are four stages of decomposition for all the systems. The first stage occurs in the temperature range 100–200°C, and is attributed to the dehydration process as the calculated weight loss for the removal of water molecules from the chloride mixtures agreed with the observed values. Further, on cooling to room temperatures from 200°C, these mixtures rehydrate.

At higher temperatures the anhydrous mixtures undergo thermal reduction in two steps. The first step corresponds to the formation of a mixture of metal chromates, Cr_2O_3 and KCl according to reaction (1). In the subsequent step

$$K_2Cr_2O_7 + MCl_2 \rightarrow MCrO_4 + \tfrac{1}{2}\ Cr_2O_3 + 2\ KCl + \tfrac{3}{4}\ O_2 \qquad (1)$$

$$MCrO_4 + \tfrac{1}{2}\ Cr_2O_3 \rightarrow MCr_2O_4 + \tfrac{3}{4}\ O_2 \qquad (2)$$

TABLE 1

Thermogravimetric data on the decomposition of equimolar ratios of potassium dichromate and hydrated metal(II) chlorides

Metal chloride	Dehydration			Thermal reduction			Volatilization of KCl		
	Temp. (°C)	wt. loss (%)		Temp. (°C)	wt. loss (%)		Temp. (°C)	wt. loss (%)	
		Found	Calcd.		Found	Calcd.		Found	Calcd.
Mg	100–200	22.0	22.7	300–420	26.0	26.5	800–1100	61.0	61.4
				650–750	31.0	31.4			
Mn	90–180	22.0	20.5	360–520	25.0	25.0	800–1100	58.0	57.8
				700–800	29.0	28.8			
Co	90–180	20.0	20.3	250–350	25.0	24.8	800–1100	57.0	57.4
				450–480	29.0	28.6			
Ni	90–180	20.0	20.3	300–380	25.0	24.8	800–1100	50.0	50.2
				500–600	29.0	28.6			
Cu	100–140	8.0	7.8	250–320	13.0	12.9	700–1100	52.0	51.8 [a]
				400–500	18.0	18.1			
Zn	100–140	8.0	7.7	350–450	12.0	12.0	800–1080	50.0	49.9
				600–650	18.0	18.0			
Cd	100–120	7.0	7.0	400–500	11.0	10.9	800–1080	46.0	46.4
				570–800	16.0	16.4			

[a] Calculated weight loss for the formation of $Cu_2Cr_2O_4$ and Cr_2O_3 according to reaction (3).

the metal chromates and Cr_2O_3 interact to give metal chromites as in (2). In separate experiments, heating was interrupted at the end of each stage, and the products were characterized by X-ray and IR studies. The appearance of characteristic IR bands around 900 cm^{-1} due to Cr–O stretching vibrations confirmed [3] the formation of chromates. The X-ray powder patterns of the residues around 750°C gave characteristic lines due to KCl and the cubic spinel structure [2]. The final stage of the weight loss process is attributed to the removal of KCl due to volatilization. Although free KCl is reported [4] to undergo sublimation around 1500°C in the presence of mixed oxide spinels, this temperature is drastically reduced, probably due to the catalytic influence of the oxides.

It is known [5] that $CuCr_2O_4$ undergoes reduction at 700°C, and thus the weight loss occurring in the temperature range 700–1100°C is attributed to both the decomposition of $CuCr_2O_4$ and the evaporation of KCl according to reaction (3)

$$2\,CuCr_2O_4 + KCl \rightarrow Cu_2Cr_2O_4 + Cr_2O_3 + \tfrac{1}{2}\,O_2\uparrow + KCl\uparrow \qquad (3)$$

The facile formation of chromates during the solid state reaction between potassium dichromate and metal chloride is probably due to the ease of migration of Cr(VI) through the reactant–product interphase.

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