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Note

THERMAL AND SPECTROSCOPIC BEHAVIOUR OF $K_2Cr_2O_7$—MoO_3 AND K_2CrO_4—MoO_3 REACTIONS

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It is well known that most hetero- and isopolyions can be prepared from solutions under controlled experimental conditions. An alternative method of preparation is the solid—solid reactions at high temperatures, where substitution or addition processes may take place. Some hetero- and polyheteroions such as $(CrWO_7)^{2-}$, $(CrSO_7)^{2-}$, $(CrMo_3O_{13})^{2-}$ and $(CrP_2O_{10})^{4-}$ were proposed to be formed cryoscopically in $K_2Cr_2O_7$ melt through substitution reactions [1—4]. The basic principle of such cryoscopic studies is the extremely dilute molten salt-mixture solutions. However, an increase in concentration and treatment at different temperatures may lead to a different result. Therefore, the present work is aimed at investigating the reactions of $K_2Cr_2O_7$ and K_2CrO_4 with MoO_3 at equimolar concentrations.

EXPERIMENTAL

Materials

$K_2Cr_2O_7$, K_2CrO_4 and MoO_3 were Merck, P.A. products. $K_2Mo_2O_7$ was prepared and analyzed.

Procedure

Two mixtures of x $K_2Cr_2O_7$—y MoO_3 (mole ratio $x/y = 1$ and $1/3$) were heated at 400—450° C (m.p. of $K_2Cr_2O_7$ = 400° C) for 72 h. The samples were quenched, ground and then re-heated every 24 h. A brown water-insoluble product was isolated in the sample with $x/y = 1$, whereas the other with $x/y = 1/3$, was completely insoluble in water. The equimolar reaction mixture K_2CrO_4—MoO_3 was treated thermally at 400—420° C as in the above two reactions. Moreover, it melted further at about 425° C. An X-ray diffractometer, IR-Beckman and Carl Zeiss DMR 21 spectrophotometers, together with a Stanton TR-1 thermobalance with a heating rate of 2° C min^{-1} were used in the identification. In addition, chemical analysis of the brown phase in the dichromate systems was carried out.

RESULTS AND DISCUSSION

The results of TG are plotted in Fig. 1. Figure 2 shows the IR spectra of $K_2Cr_2Mo_3O_{13}$, 1 : 1 K_2CrO_4—MoO_3 (melted) and 1 : 1 $K_2Cr_2O_7$—$K_2Mo_2O_7$ (melted), whereas the electronic absorption spectrum of $K_2Cr_2Mo_3O_{13}$ is shown in Fig. 3. Table 1 includes some experimental data on the two systems.

$K_2Cr_2O_7$—MoO_3 system

Bradbury [5] isolated and chemically analyzed a brown compound, $K_2Cr_2Mo_3O_{13}$, obtained on melting 1 mole $K_2Cr_2O_7$ with 1 mole MoO_3 at 500°C. Chemical analysis of the isolated brown, water-insoluble product (Table 1) showed that the same compound, potassium chromium(III) trimolybdate, is formed, not only by an equimolar reaction but also at a different mole ratio of 1/3. Moreover, the formation of this product seemed to pass through an intermediate compound during the reduction process of Cr(VI) to lower oxidation states, such as Cr(III) and Cr(V), as the results of TGA (Fig. 1) illustrate.

Previous results of thermal decomposition studies of CrO_3 and $(NH_4)_2Cr_2O_7$ showed the presence of Cr(V) and other lower oxidation states at different temperatures [6]. Such results may confirm the formation of Cr(V) as one of the lower oxidation states of Cr(VI) during the thermal decomposition of $K_2Cr_2O_7$ in the presence of MoO_3 in the studied systems. The actively formed dissociation products react simultaneously with MoO_3, leading to the formation of the compound K_2Cr(III) Cr(V) Mo_3O_{14}, and finally $K_2Cr_2Mo_3O_{13}$ at a lower temperature, in comparison with the known compound $Cr_2Mo_3O_{12}$ formed from its corresponding oxides at 700°C [7].

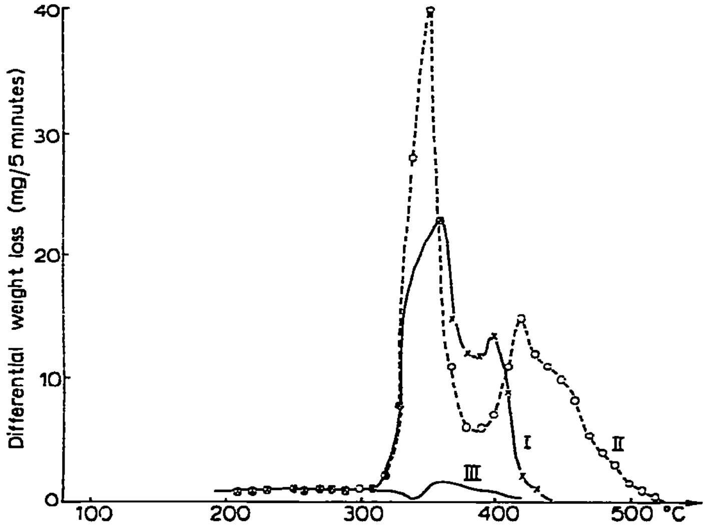

Fig. 1. Thermogravimetric analysis of I, $K_2Cr_2O_7$—MoO_3 (1 : 1); II, $K_2Cr_2O_7$—MoO_3 (1 : 3); and III, K_2CrO_4—MoO_3 (1 : 1).

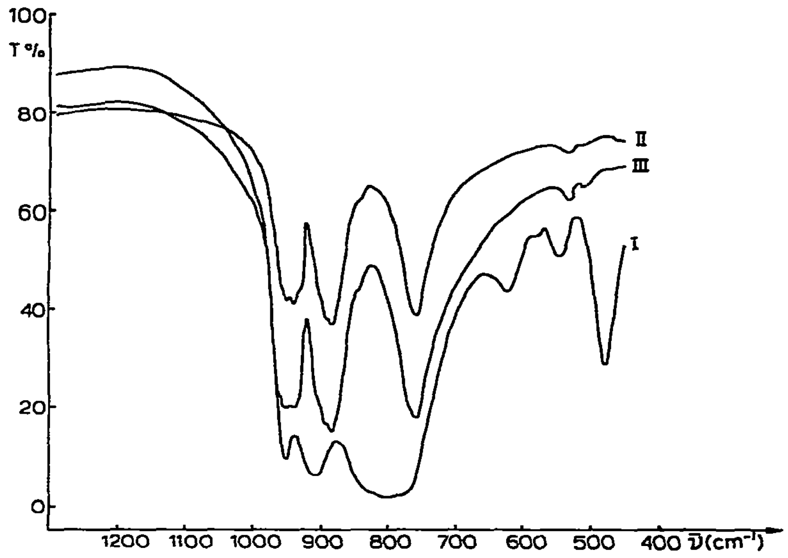

Fig. 2. IR absorption spectra of I, $K_2Cr_2Mo_3O_{13}$; II, K_2CrO_4—MoO_3 (1 : 1, melted); and III, $K_2Cr_2O_7$—$K_2Mo_2O_7$ (1 : 1, melted).

TGA (Fig. 1) confirms such an assumption and shows a similar behaviour in the case of dichromate systems at different mole ratios. The rate of gas evolution (decomposition of $K_2Cr_2O_7$) begins to increase at 320°C, with a maximum at 355—360°C. The minimum at 385°C may be due to the formation of an intermediate compound, which loses weight on raising the temperature passing through a maximum at 400—420°C. According to the calculated and found weight losses, the following reaction equations may be formulated.

$$3\,K_2Cr_2O_7 + 3\,MoO_3\ (1:1) \rightarrow K_2Cr(III)Cr(V)Mo_3O_{14} + O_2 + 2\,K_2Cr_2O_7 \qquad (1a)$$

(Weight loss: calcd. = 2.43%, found = 2.2%)

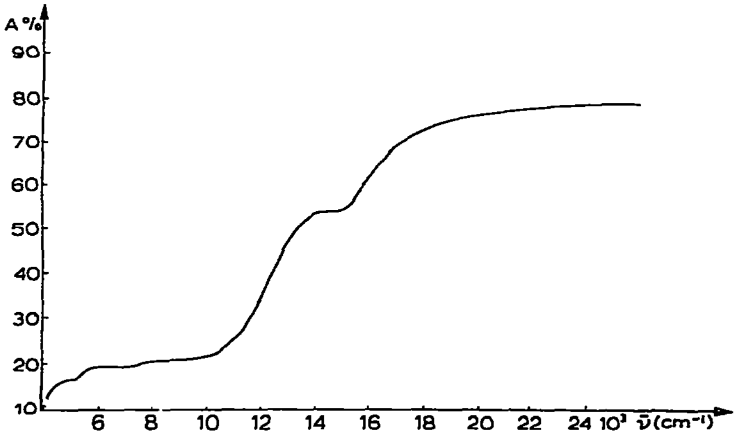

Fig. 3. Electronic absorption spectrum of $K_2Cr_2Mo_3O_{13}$.

TABLE I

Some experimental data on $K_2Cr_2O_7$—MoO_3 and K_2CrO_4—MoO_3 systems

System (mole ratio)	Thermal treatment		X-ray analysis	Microscopic examination	Chemical analysis	
	(°C)	(h)			Found (%)	Calcd. (%)
$K_2Cr_2O_7$ + MoO_3 (1 : 1)	400—450	24 24 24	$K_2Cr_2Mo_3O_{13}$ + $K_2Cr_2O_7$	Crystalline, homogeneous and anisotropic phase $K_2Cr_2Mo_3O_{13}$	K = 11.8 Cr = 15.5 Mo = 42.4	11.5 15.3 42.4
$K_2Cr_2O_7$ + MoO_3 (1 : 3)			$K_2Cr_2Mo_3O_{13}$			
K_2CrO_4 + MoO_3 (1 : 1)	400—420 425 (melted)	24 24 24	$K_2Cr_2O_7$—$K_2Mo_2O_7$ mixed crystal	Crystalline, homogeneous and anisotropic phase		

$$K_2Cr(III)Cr(V)Mo_3O_{14} + 2\,K_2Cr_2O_7 \rightarrow K_2Cr_2Mo_3O_{13} + 2\,K_2Cr_2O_7 + 0.5\,O_2 \tag{1b}$$

(Weight loss: calcd. = 1.25%, found = 1.0%)

$$K_2Cr_2O_7 + 3\,MoO_3\ (1:3) \rightarrow K_2Cr(III)Cr(V)Mo_3O_{14} + O_2 \tag{2a}$$

(Weight loss: calcd. = 4.4%, found = 3.8%)

$$K_2Cr(III)Cr(V)Mo_3O_{14} \rightarrow K_2Cr_2Mo_3O_{13} + 0.5\,O_2 \tag{2b}$$

(Weight loss: calcd. = 2.3%, found = 2.3%)

The X-ray patterns of the brown phase from the two reactions were found to be the same. No lines of free Cr_2O_3 or MoO_3 were observed. Diffracted lines of excess unreacted $K_2Cr_2O_7$ were detected only in the reaction products with mole ratio 1/1.

The IR spectrum of $K_2Cr_2Mo_3O_{13}$ (Fig. 2) is characterized by the absence of both Cr—O and Cr—O—Cr bond vibrations at 890 and 760 cm^{-1}, which occur in K_2CrO_4 and $K_2Cr_2O_7$, respectively. The Mo—O—Mo bond vibration at 700—740 cm^{-1} in $K_2Mo_2O_7$ and $K_2Mo_3O_{10}$ [8] is also absent. However, the spectrum does show a broad band at 800 cm^{-1} similar to a general Mo—O bond vibration within $(MoO_4)^{2-}$ groups. The range of such Mo—O frequency differs from one structure to another, e.g., K_2MoO_4 (838 cm^{-1}), $K_2Mo_2O_7$ (860 cm^{-1}) and $K_2Mo_3O_{10}$ (898 cm^{-1}). The absorption bands at 622 and 550 cm^{-1} can be related to Cr(III) in octahedral coordination, in confirmation of the behaviour of Cr(III)-containing oxidic compounds [9]. The electronic absorption spectrum (Fig. 3) shows an absorption band which can be assigned to the electronic transition: $^4A_{2g} \rightarrow {}^4T_{2g}$ within the energy level diagram of Cr(III). The second transition $^4A_{2g} \rightarrow {}^4T_{1g}$ at higher frequency is masked by self-absorption of the compound due to the absorption of Mo^{6+} in the same region. Generally, the ligand field strength, Δ, is relatively small in comparison with known Cr(III)-containing oxidic compounds [10].

K_2CrO_4—MoO_3 system

The mechanism of an equimolar reaction in this system is different from that with $K_2Cr_2O_7$. Some properties of the melted reaction product are: (a) light orange colour, (b) complete solubility in water, (c) relative lower melting point ($\simeq$ 425°C) than that of the corresponding starting components (K_2CrO_4 = 890°C and MoO_3 = 700°C), (d) crystalline homogeneous phase. It did, however, give the same X-ray pattern and IR spectrum as those of a melted equimolar mixture $K_2Cr_2O_7$—$K_2Mo_2O_7$, which was prepared for the sake of comparison (Fig. 2). According to these results, the reaction can be formulated as

$$K_2CrO_4 + MoO_3\ (1:1) \xrightarrow{400\text{—}420^\circ C} K_2Cr_2O_7 + K_2Mo_2O_7$$

$$K_2Cr_2O_7 + K_2Mo_2O_7 \xrightarrow[\text{melted}]{425^\circ C} K_2Cr_2O_7\text{—}K_2Mo_2O_7 \text{ (mixed crystal) or}$$

$$2(K_2CrMoO_7)$$

Thermogravimetric analysis (Fig. 1) confirms the overall reaction without loss in weight. The present assumption of the intermediate formation of $K_2Cr_2O_7$ and $K_2Mo_2O_7$ is in agreement with the IR spectrum of the unmelted equimolar K_2CrO_4—MoO_3 reaction product [11]. On the other hand, the mixed crystal formation of $K_2Cr_2O_7$ and $K_2Mo_2O_7$ agrees with the well-known fact that the two compounds form a continuous mixed crystal [12].

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