

Silver(III): The state of oxidation of silver(III) can also be stabilised by co-ordination with some nitrogen containing organic bases⁵, and three inorganic anions: fluoride, per-iodate and tellurate. Curiously enough, all these complexes separate out with several molecules of hydration water, usually 7-18 H₂O. The oxidation with K₂S₂O₈ of a cold aq. solution of a mixture of biguanide sulphate and AgNO₃ at pH 6.5-7.0 has in fact been claimed to yield sparingly soluble brown crystals of Ag(C₂H₇N₅)(OH)(SO₄).7H₂O⁶. All these compounds are diamagnetic.

Thermogravimetric analyses of the silver complex revealed that there was gradual loss of water molecules starting from a temperature of 60° with complete loss of water at 140°; further rise in temperature resulted in thermal decomposition of the anhydrous complex.

The compound was diamagnetic and oxidised two equivalents of iodide per gram-atom of silver. In this complex silver showed a co-ordination number six, which is rather uncommon for this group of ter-valent ions.

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Thermal Decomposition Studies on Chromium(III) Complexes with Hydroxamic Acids

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SEVERAL workers have studied transition metal complexes thermogravimetrically including chromium(III)¹ to establish their thermal properties. This communication deals with the thermal decomposition studies of few tris(hydroxamato) chromium(III) complexes.

Results and Discussion

The thermal decomposition curve of tris(salicylhydroxamato)-chromium(III) indicated that the complex was stable upto 70° and after that it suffered decomposition. Two breaks were observed at 220° and 360° respectively. The break observed at 220° corresponded to the loss of two-third ligand molecule.

(Found: 0.2190 g.; calcd: 0.22006 g.). The decomposition of the latter compound began at 360° giving a residue of Cr₂O₃ beginning at 500° (Fig I, curve b). The decomposition may be represented as:

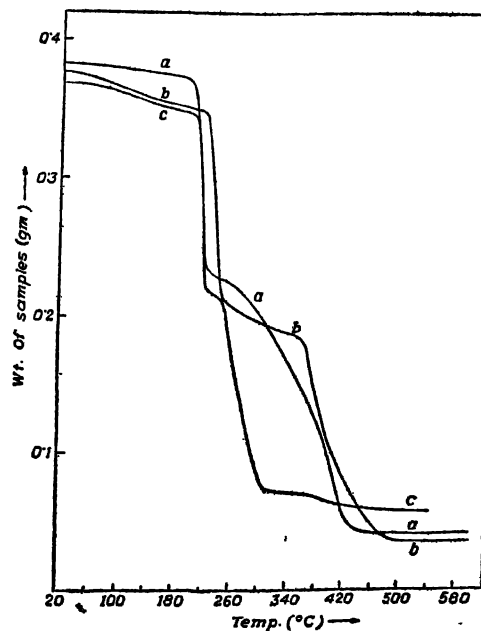
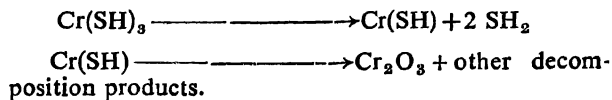


Fig. 1

The thermograms for tris(phenylacetylhydroxamato) chromium(III) (Fig I, Curve a) showed that the complex suffered no loss upto 80° and after that a break was observed at 220° which corresponded to the two-third loss of the ligand (Found; 0.2350 g., calcd.: 0.2302 g.). However, no break was observed for the loss of the remaining ligand molecule as found in case of tris(salicylhydroxamato) chromium(III). The residual product of the pyrolysis was Cr₂O₃ beginning at 460°.

The weight-loss curve of tris(benzohydroxamato) chromium(III) (Fig. I, Curve c) indicated that there was no appreciable loss of the compound upto 70° and after that it suffered decomposition. Although two breaks were noted in the curve at 300° and 420° respectively, no definite stoichiometry could be assigned to these. The terminal product, however, was Cr₂O₃.

No attempt has been made to formulate the intermediates in any case.

Experimental

The syntheses, characterisation spectral data, i.r. and magnetic properties have been described earlier². The thermograms were recorded in air on a Stanton thermobalance (high temperature model, 1mg. sensitivity) from 0° to 600°. Heating rate was 10° per minute.

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Studies on Thermal Properties of Cadmium tungstate catalyst

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CADMIUM tungstate is reported to have effective catalytic activity for a number of industrial reactions at the temperature range 250°-425°¹⁻⁵. Literature on the physicochemical properties of this tungstate is extremely meagre. In the present note the results on the method of preparation, differential thermal analysis (DTA), thermogravimetry (TG), X-ray diffraction (XRD) and magnetic susceptibility of fresh cadmium tungstate and its various thermal transition products have been presented.

Experimental

Preparation and chemical analysis of the catalyst :

100 ml. of cadmium sulphate octahydrate (12.8 g. per 100 ml. of water) saturated at room temperature was added slowly (5 ml. at a time) to a saturated solution of sodium tungstate dihydrate (16.5 g./100 ml. water) followed by digestion for 45 min. at 70°-80°. The substance was allowed to settle, filtered off, washed with hot water and ultimately dried in an air-oven at 110° for 24 hr. The catalyst was pure white. W⁶ in solution was analysed as WO₃ by precipitation with HCl and HNO₃ (50 : 50) in presence of quinine and calcination at 700°-800°. Cd²⁺ in solution was analysed as cadmium molybdate by precipitation with ammonium molybdate solution in feebly acetic acid medium at 90° and calcination at 120°. The amount of water was determined by estimating hydrogen using Coleman Carbon-Hydrogen Analyzer.

Procedure :

The experimental set up and the procedure followed by the authors were the same as described by Bhattacharyya et al. ^{6,7} previously. The X-ray diffraction patterns of samples obtained by heating the fresh tungstate at 250°, 440° and 900° (for 2 hours in

each case) were taken. Magnetic susceptibilities of these samples were measured by Faraday method at 24° using Hg [Co (NCS)₄] as calibrant.

Results and Discussion

The chemical composition of cadmium tungstate is established as CdWO₄ · 1.1/2 H₂O (Cd-29.05%, W-47.78%, H₂O-6.75%).

DTA and TG curves are shown in Fig. 1. The DTA curve shows a sharp endothermic peak at 195° followed by an endothermic change at 315° and a baseline drift within 440°-850°. The TG curve registers a total weight loss amounting to 7.62% within 110°-850°. The weight loss up to 250° is 4.1% which corresponds to removal of one molecule of water from one molecule of CdWO₄ · 1.1/2H₂O. The rest water, however, is lost within 260°-860°.

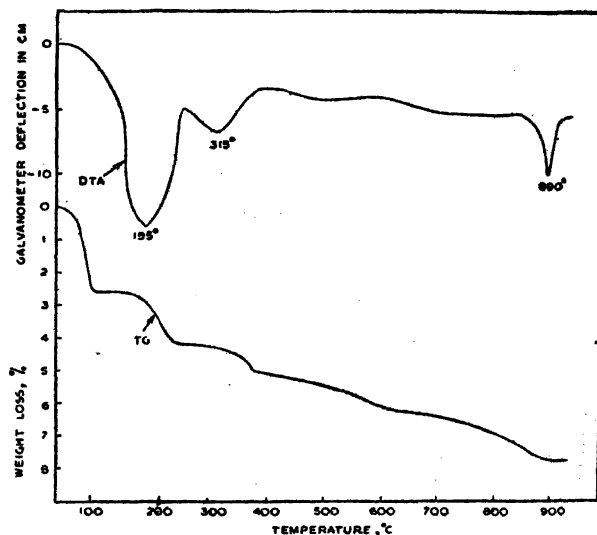


Fig. 1. DTA and TG of Cadmium tungstate

X-ray analysis of the catalyst samples heated at 110° and 250° exhibits the same XRD patterns with the relevant lines at $d = 3.787, 3.050$ (characteristic), 2.547, 1.910, 1.806, 1.762, 1.546 Å. The XRD patterns of the 440° preheated sample appear to be more distinct than observed in the preceding cases. The characteristic d -values calculated are 3.819, 3.050, 2.533, 1.806, 1.756, 1.546, 1.523, 1.457, 1.398 Å. Thus, the structure of the fresh sample is crystalline and the removal of the adsorbed water molecules from the large tungstate molecule does not cause any change in the crystal structure of the system. The characteristic d -values, e.g., 3.81, 3.050, 2.533 Å, etc. compare excellently to those reported for standard patterns of CdWO₄ (A.S.T.M. Card 1-0488).

The original catalyst sample is diamagnetic and this property remains unaffected upto melting.

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