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Note

THERMAL DECOMPOSITION OF OXALATOCUPRATES(II)

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The thermal decomposition of oxalato metal complexes has been studied by several workers [1–6]. It has been observed that during the decomposition of trivalent cobalt [3,4] and trivalent iron [6] complexes a change in their valence states occurs. There seems to be a greater influence of the gaseous environment which affects the course of decomposition. After dehydration, potassium bis(oxalato)cuprate(II) dihydrate decomposes as if it were a mixture of copper(II) oxalate and potassium oxalate. In this investigation, we report the thermal decomposition of oxalatocuprates(II) of morpholinium, $(morphH)_2Cu(C_2O_4)_2$; ethylenedimorpholinium, $(EDMH_2)Cu(C_2O_4)_2 \cdot 4\,H_2O$; hydrazinium, $(N_2H_5)_2Cu(C_2O_4)_2 \cdot 2\,H_2O$; and ethylenediammonium, $(enH_2)Cu(C_2O_4)_2$. The studies are followed by thermogravimetry and differential thermal analysis and the products of decomposition are examined by chemical analysis and X-ray powder patterns.

EXPERIMENTAL

The oxalatocuprate(II) complexes were prepared according to the reported method [7] by the addition of a known amount of hot copper sulphate solution to a solution of the corresponding amine-onium oxalate taken in required proportions.The resulting solution was cooled to 10°C and the crystalline precipitate obtained was filtered, washed with acetone and dried.

The thermogravimetric analyses were made using a Stanton thermobalance at a heating rate of 6°C min^{-1}. Differential thermal analyses were carried out on a Netzsch differential thermal analyzer and a set-up of our own. The heating rate of the furnace was kept at 10°C min^{-1}. Both the studies were made in air and flowing nitrogen atmosphere. The X-ray powder patterns were taken using $Cu\,K_\alpha$ radiation on a Philips X-ray diffractometer.

RESULTS AND DISCUSSION

The TG and DTA curves of $(morphH)_2Cu(C_2O_4)_2$, $(EDMH_2)_2Cu(C_2O_4)_2 \cdot 4\,H_2O$, $(N_2H_5)_2Cu(C_2O_4)_2 \cdot 2\,H_2O$ and $(enH_2)Cu(C_2O_4)_2$ in air are given in Fig. 1. It

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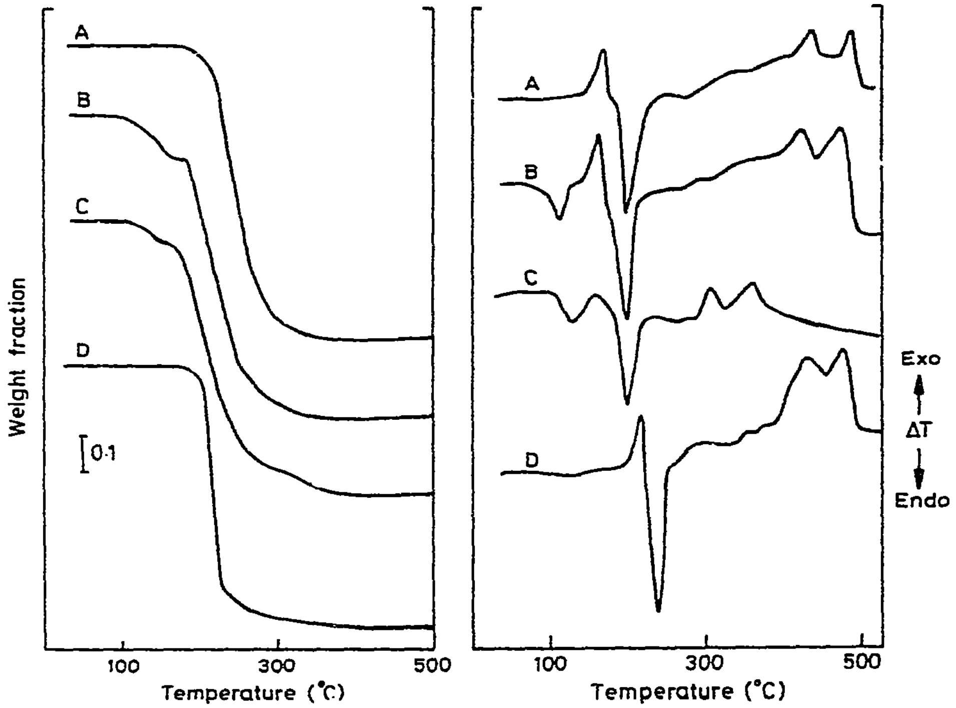

Fig. 1. TG and DTA plots of A, $(morphH)_2Cu(C_2O_4)_2$; B, $(EDMH_2)Cu(C_2O_4)_2 \cdot 4\ H_2O$; C, $(N_2H_5)_2Cu(C_2O_4)_2 \cdot 2\ H_2O$; and D, $(enH_2)Cu(C_2O_4)_2$ in air.

is clear that $(EDMH_2)Cu(C_2O_4)_2$ dehydrates in the temperature range 80–180°C. The observed weight loss of 14% corresponds to the removal of all the four molecules of water, as the calculated weight loss was found to be 13.9%. However, $(N_2H_5)_2Cu(C_2O_4)_2 \cdot 2\ H_2O$ loses only one molecule of water in the temperature range 80–150°C, as seen from the observed weight loss of 5% as compared with the calculated value of 5.3%. The remaining water molecule is lost along with other gaseous products since there is no indication of any break in the TG curve above 180°C. This suggests that the two water molecules are held differently in the complex.

The oxalate and the amine-onium groups of the complexes decompose above 180°C and the decomposition is complete at 400°C for hydrazinium and at 500°C for other cuprates. The observed weight losses of 81%, 85%, 77% and 79% are in good agreement with those calculated for the formation of CuO from $(morphH)_2Cu(C_2O_4)_2$ (80.9%), $(EDMH_2)Cu(C_2O_4)_2 \cdot 4\ H_2O$ (80.6%), $(N_2H_5)_2Cu(C_2O_4)_2 \cdot 2\ H_2O$ (76.8%) and $(enH_2)Cu(C_2O_4)_2$ (78.6%), respectively. This has been further confirmed by wet chemical analysis and the X-ray powder diffraction patterns of the end products.

The DTA curves exhibit endothermic effects at 130 and 120°C for ethylenediammonium and hydrazinium complexes which are attributed to the dehydration process. $(N_2H_5)_2Cu(C_2O_4)_2 \cdot 2\ H_2O$ shows an endothermic effect at 198°C and other complexes show an exothermic effect which is immediately followed by a

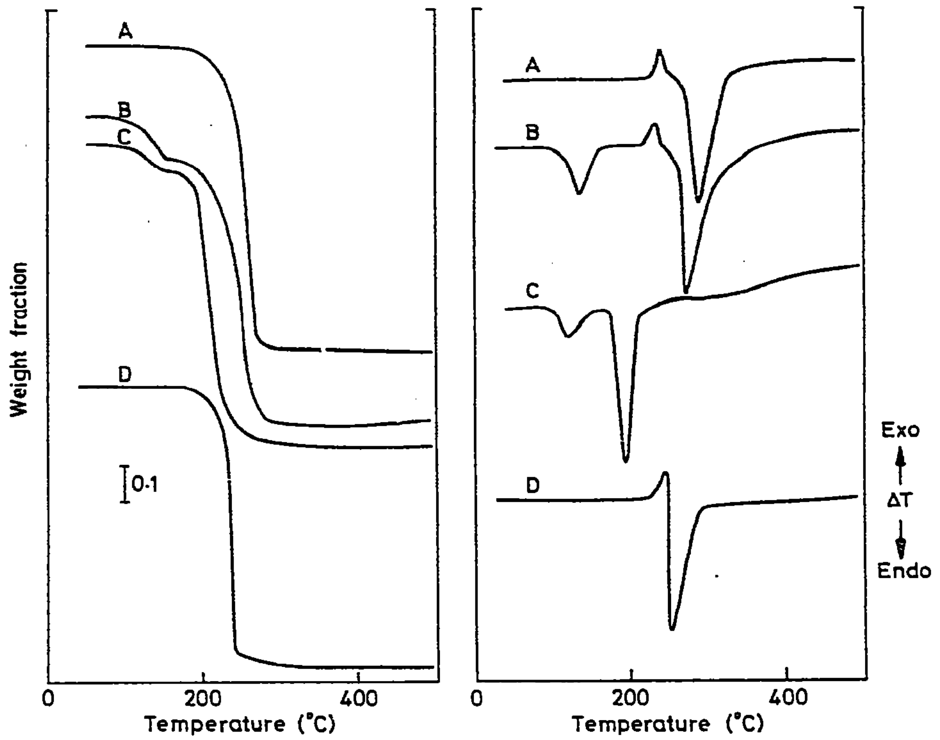

Fig. 2. TG and DTA plots of A. $(morphH)_2Cu(C_2O_4)_2$; B. $(EDMH_2)Cu(C_2O_4)_2 \cdot 4\ H_2O$; C. $(N_2H_5)_2Cu(C_2O_4)_2 \cdot 2\ H_2O$; and D. $(enH_2)Cu(C_2O_4)_2$ in nitrogen.

strong endothermic reaction in the temperature range 220–250°C. Copper(II) oxalate is known to decompose exothermally [8] and as such, the initial exothermic effect in the three oxalato complexes is probably due to the rupture of the Cu-oxalate framework, and the endothermic reaction is the combined effect of the decomposition of the oxalate and the cation. In the case of the hydrazinium complex, the exothermic affect is probably masked by the endothermic effect due to the almost simultaneous removal of the second molecule of water and the decomposition of the oxalate and hydrazinium groups.

The two exothermic peaks at 305 and 363°C of hydrazinium and those in the temperature range 420–480° for other complexes are attributed to the oxidation process to give CuO. In fact, in all the cases the residue obtained around 300°C is found to be a mixture of Cu, Cu_2O, CuO and carbonaceous matter.

Thermal plots of the complexes in nitrogen are given in Fig. 2. The course of dehydration of ethylenedimorpholinium and hydrazinium is similar to that observed in air. The TG curves indicate that the decomposition process is complete at 300°C for all the complexes and the weight loss corresponds to the formation of elemental copper. The observed weight losses of 85%, 88%, 81% and 79% for $[morphH]^+$, $[EDMH_2]^{2+}$, $[N_2H_5]^+$ and $[enH_2]^{2+}$ cuprates agree well with the calculated values of 84.7%, 87.7%, 81.4% and 78.0%, respectively.

The DTA traces exhibit an endothermic peak at 198°C for $[N_2H_5]^+$ and an exotherm followed by an endotherm in the temperature range 200–300°C for other complexes, as observed in air around this temperature range.

The energies of activation, estimated for the decomposition of the oxalate and cation, based on the Coats and Redfern equation [9] are 36, 45, 13 and 60 kcal mole^{-1} in air and 32, 40, 11 and 53 kcal mole^{-1} in nitrogen for morpholinium, ethylenedimorpholinium, hydrazinium and ethylenediammonium bis(oxalato)-cuprates(II). The low value for $(N_2H_5)_2Cu(C_2O_4)_2 \cdot H_2O$ suggests that the course of decomposition is different from that of other cuprates, which is also evidenced by the DTA plots.

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