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A THERMAL STUDY ON ISOMORPHOUS METAL FORMATES *

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ABSTRACT

The thermal behaviour of some isomorphous hydrated formates was investigated by thermal, X-ray and IR methods from ambient temperature to complete decomposition. The results show that thermal dehydration and decomposition occur in various steps and involve structural changes. In the DSC thermograms, there are also peaks corresponding to no weight losses; these are attributed to crystallisation of the amorphous anhydrous phase obtained directly from the dihydrates.

INTRODUCTION

Some years ago, research undertaken in our laboratory on the IR spectroscopic and thermal behaviour of a series of crystalline isomorphous nickel, iron(II), cobalt, manganese, magnesium, zinc and cadmium formates [1–3] provided further evidence of the close similarity in the IR spectroscopic behaviour of the formate and hydration water bands [4,5]. We pointed out that changing the cation caused only slight differences in band shape and position. This close similarity persisted when deuteration was carried out, showing that different types of water molecules are present in the crystal lattice.

These compounds formed an anhydrous phase when heated; a second anhydrous phase was revealed in some cases by the IR spectra recorded as a function of temperature for both these and other formates. After dehydration, decomposition to carbonate, oxide or metal (according to the cation and the experimental conditions adopted) was observed at temperatures not exceeding 500 ° C.

The similarity was attributed to the close correspondence of the cell parameters of the monoclinic lattice, as reported in the literature relating to the crystal structure determination [6,7]. Attention has now been directed to the changes induced by heating the hydrated salts from ambient temperature to 500 ° C, in particular the crystallographic transformations caused by dehydration. DSC and TG techniques were employed, together with X-ray

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diffraction of the powders obtained in the different situations. The reaction and transition kinetics involved were also studied for the purpose of comparison.

EXPERIMENTAL

DSC measurements were carried out both in air and under a nitrogen stream, at a heating rate of 5 K min^{-1}, using a Perkin–Elmer DSC-4 calorimeter in the range 25–500 °C and on samples of about 3 mg. Temperature calibration was obtained with an indium standard and the kinetic parameters were computed with a standard program. Simultaneous TG and DTG data were obtained with a Netzsch STA 409 thermobalance using powdered samples of about 100 mg in covered alumina crucibles under a static atmosphere, at the same rate as the DSC runs.

Structural changes in the formates were monitored by powder X-ray diffraction recorded with a Philips PW 1050/25 diffractometer in the 2θ range from 10 to 32 degrees, using Cu $K\alpha$ radiation.

The isomorphous formates were K & K products, used without prior grinding.

RESULTS AND DISCUSSION

The DSC and TG measurements are summarised in Table 1. The TG, DTG and DSC curves recorded on a magnesium formate dihydrate sample are shown in Fig. 1. From the table, it can be seen that three peaks are present in some DSC curves, whereas only two peaks, those pertaining to the first and third transformations, were recorded in the TG curves. A fair agreement can be observed between our data and those of Masuda and Shishido [8].

TABLE 1

Enthalpies (kJ mol^{-1}), temperatures (°C) and activation energies (kJ mol^{-1}) for the transitions observed in the DSC and TG curves

Formate	ΔH_1	T_1	E_a	ΔH_2	T_2	E_a	ΔH_3	T_3	E_a
Mg	63	182	76	−13.8	285	433	−1784	444	321
Fe	37	100	113				−1730	280	290
Co	57	155	81				−1931	315	343
Ni	60.2	188	82	−0.8	263	484	−1630	294	251
Mn	54	122	130				−1726	286	292
Zn	57.3	102	84	−2.5	166	353	−1933	285	110
Cd	43	68	77				−1534	299	358

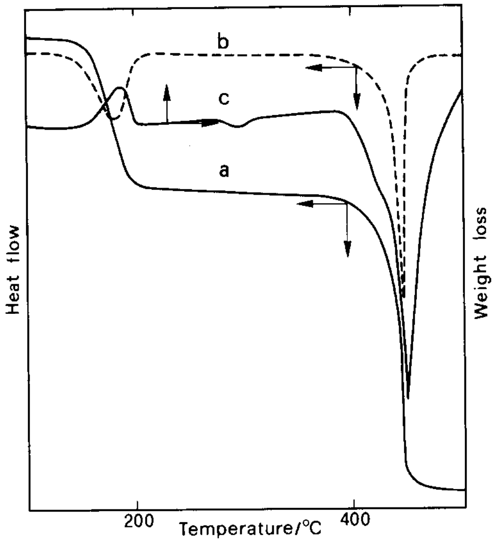

Fig. 1. TG (a), DTG (b) and DSC (c) curves recorded on a magnesium formate dihydrate sample.

The first peak is readily attributable to the dehydration step. The calculated weight loss closely corresponds to the removal of two water molecules in all cases, with the exception of the commercial cadmium formate and the freshly prepared iron(II) formate whose composition did not correspond to the stoichiometric formulae. The first had a lower water content, and the second tended to oxidise very quickly in air to a tervalent compound. Their behaviour was, therefore, analysed in detail by recrystallising the cadmium salt and heating the iron salt in an inert atmosphere. Their behaviour and their DSC and TG values then approached those of the other formates.

The second peak is always weak and exothermic in all cases. It corresponds to the transition between the α and β forms of iron(II) formate [7]. Correspondingly, the spectra show a change in band multiplicity and wavenumbers at about the same temperatures.

The third peak relates to thermal decomposition of the formate, with formation of oxide in air and of metal in nitrogen. For example, in the case of magnesium formate dihydrate, the weight loss measured in the decomposition step is 48.50%, in fair agreement with the theoretical value of 49.20% calculated on the assumption of formation of magnesium oxide. No changes were observed above the decomposition temperature.

The enthalpies and activation energies of the processes involved also display interesting trends. The dehydration enthalpies are in the range expected, and in all cases a first-order reaction takes place. The peak, however, is not simple and a two-step process can be assumed (compare, e.g., ref. 9). The complex peak divides into two as the recording rate is

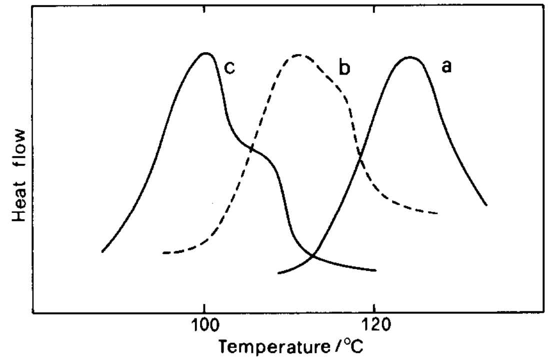

Fig. 2. DSC curves recorded on a manganese formate dihydrate sample heated at the rate of: a, 5; b, 3; and c, 1 K min^{-1}.

lowered (Fig. 2). The decomposition peak displayed an even clearer separation into two components as the heating rate was lowered.

The peak following the dehydration is of greater interest. Spectral changes without weight losses are observed in TG in the same temperature interval, indicating that some transformations are taking place without loss of species.

Two anhydrous phases, confirmed by X-ray diffraction [7], have so far been reported for iron(II) formate only. Our DSC data have now identified this transition for Mg, Zn and Ni salts as well. Indeed, the existence of more than one phase appears to be part of a general pattern for this kind of compound, as two different spectra have also been recorded for other formates [10]. The two or more anhydrous forms described for certain formates not belonging to the isomorphous series [5,11,12] have been related to different crystalline structures.

The crystalline nature of these forms, however, has never been questioned. A series of X-ray measurements was therefore carried out on heated samples to ascertain the nature of the phase obtained from dehydration and the subsequent transformation, and thus to interpret the behaviour of this series of formates.

Ground samples of the salts were heated in the range 200–260 ° C for various times; portions of the products were then subjected to X-ray diffraction. Figure 3 illustrates the diffraction patterns for a magnesium formate sample heated to 225 ° C as a function of time. Figure 4 shows some IR spectra recorded on original and heated magnesium formate. As the heating time increases, the main features of the hydrated salt rapidly decrease and disappear, while no new bands appear in the spectra. At 225 ° C, the disappearance of the strongest lines (at 4.92, 4.55, 3.66 and 3.40 Å) is complete after 10 min. The pattern, therefore, corresponds to an amorphous phase. Subsequently, a new crystalline phase is slowly formed. After about 30 min, some broad lines appear at positions different from those of the dihydrated sample: strong lines appear at 5.27 and 6.38 Å. Their

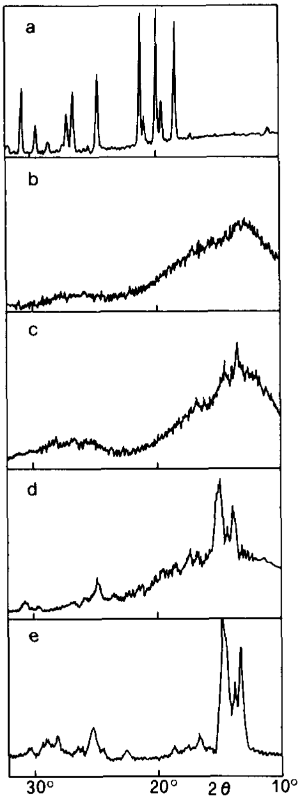

Fig. 3. X-ray diffraction patterns of a magnesium formate dihydrate sample heated to 225 ° C for: a, 1; b, 10; c, 60; d, 300; and e, 1440 min.

intensities increase with time, more quickly at higher temperatures. At 210 ° C, for example, formation of the amorphous phase is slow and recrystallisation of the anhydrous form even slower. At 260 ° C, on the other hand, the new crystalline form appears while the lines of the hydrate are still disappearing.

The known crystal structure of the dihydrated formates serves to explain the transitions observed in these thermograms. Two kinds of octahedra are present in the monoclinic lattice, one with the metal surrounded by six oxygens from formate ions, the other surrounded by two oxygens from formate ions and four from water molecules [6,13,14]. Only the latter could be eliminated during dehydration. This would take place in different ways, depending on their positions relative to the crystal lattice.

Dehydration does not perturb the first kind of octahedra, but destroys the second. Rearrangement of the lattice must therefore be expected. However, this transformation has a low enthalpy but a high activation energy, and hence can only take place a number of degrees after dehydration and not during dehydration. This variability explains why the rearrangement peak is

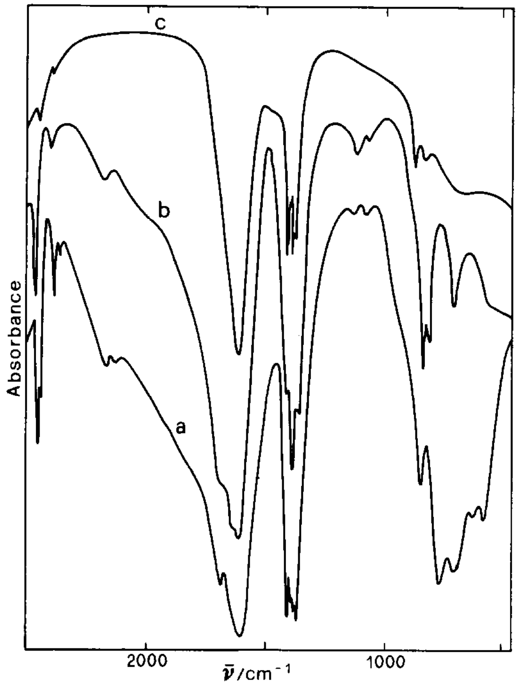

Fig. 4. IR spectra (3000–450 cm^{-1}) of a magnesium formate sample: a, dihydrate; b, heated to 230 °C; and c, heated to 330 °C.

not observed in some cases. We believe that the transition may be overlapped by the dehydration or the decomposition peak and thus is not observed as a distinct peak. In the case of the nickel salt, in fact, it occurs just a few degrees before decomposition, whereas in the case of the zinc and magnesium salts, it is well separated from both the dehydration and decomposition.

CONCLUSIONS

Measurements on a series of crystalline hydrated formates using a variety of experimental techniques show that the dehydration process is complex. Owing to their particular crystal structure, formates lose water without an immediate collapse of the lattice. After the formation of an amorphous phase, a slow reorganisation leads to the formation of a new crystalline phase. While this is clear in some cases, in others overlapping of exothermic recrystallisation and endothermic dehydration or exothermic decomposition takes place. Further research will ascertain the kinetics of recrystallisation of the anhydrous form and identify the conditions for observation of the intermediate amorphous phase. IR spectra at constant temperature as a function of time could help in the interpretation of the process involved.

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