

THERMAL DECOMPOSITION OF FORMATES. PART VIII. THERMAL DEHYDRATION OF Dy(III), Ho(III), Er(III), Tm(III), Yb(III) AND Lu(III) FORMATE DIHYDRATES

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ABSTRACT

The thermal dehydration of some rare earth metal formate dihydrates were studied by means of thermogravimetry, differential thermal analysis and differential scanning calorimetry.

The dehydration took place successively as a one step reaction for all of the formate dihydrates examined. The reaction order of dehydration was found to be $2/3$ for all of the salts examined, which indicated that the rate of dehydration was controlled by a chemical process at a phase boundary.

The values of the activation energy, frequency factor and the enthalpy change of dehydration for all of the dihydrates were 108–142 kJ mole⁻¹, 10^{16} – 10^{17} min⁻¹ and 109–147 kJ mole⁻¹, respectively.

Both the temperature at which the dehydration occurred and the enthalpy change increased as the reciprocal of the radius of the metallic ion increased.

INTRODUCTION

Although the thermal decomposition of formates has been studied extensively, the thermal dehydration of formates and their kinetic and calorimetric studies have scarcely been reported. The thermal dehydration reactions of first transition metal formate dihydrates were described in a previous paper [1].

This paper is a systematic study of the thermal dehydration of rare earth metal formate dihydrates by means of thermogravimetry, differential thermal analysis and differential scanning calorimetry. Basic kinetic constants such as the order of reaction, enthalpy change and activation energy were determined. These kinetic and calorimetric parameters were compared with those obtained for the dehydration of first transition metal formate dihydrates.

EXPERIMENTAL

Materials

All compounds were prepared by the reaction of formic acid and rare earth metal oxide. The purity of the rare earth metal oxide used was 99.9% (purchased from Mitswa Pure Chemical Co., Osaka, Japan). The oxides were combined with a large excess of aqueous formic acid solution and the mixture held at a temperature just below its boiling point with stirring until the oxide had dissolved. The crystals obtained when the solution was evaporated slowly were kept in a desiccator.

The results of the elemental analysis for C, H and metal are given in Table 1.

Measurements

Each sample was pulverized in a mortar with a pestle and sieved to a narrow fraction of 250–300 mesh in order to carry out the dehydration process under the same conditions for all of the salts.

The TG–DTA curves were simultaneously recorded on a Rigaku Thermoflex TG-DTA M8075 at a heating rate of 5 K min⁻¹ in air. About 10 mg of specimen were weighed into an aluminium crucible and measured by use of α -alumina as a reference material.

The enthalpy change (ΔH) for the dehydration was determined from the DSC curve recorded on a Rigaku Thermoflex DSC 8055 at a heating rate of 5 K min⁻¹. The instrument was calibrated by measuring the heat of transition of KNO₃ ($\Delta H = 5.414$ kJ mole⁻¹ at 401 K).

The IR spectra in the frequency region 250–4000 cm⁻¹ were measured with a Hitachi 295 spectrophotometer by the KBr disk method.

TABLE 1
Elemental analysis for rare earth metal formate dihydrates

Ln(HCO ₂) ₃ ·2 H ₂ O	C(%)		H(%)		Ln(%)	
	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.
Dy	10.79	10.53	2.10	2.20	48.72	49.45
Ho	10.71	10.54	2.08	2.09	49.09	48.99
Er	10.64	10.39	2.07	2.11	49.44	48.87
Tm	10.59	10.65	2.06	2.15	49.69	50.37
Yb	10.47	10.61	2.03	2.07	50.30	51.07
Lu	10.40	10.63	2.02	2.08	50.57	50.87

The X-ray diffraction pattern of powder was obtained by a Rigaku Geigerflex diffractometer using CuK_α or MoK_α radiation.

RESULTS AND DISCUSSION

The TG and DTA curves of rare earth metal formate dihydrates are shown in Fig. 1. The temperature range of successive dehydration, the peak temperature of DTA curves (T_p) and the weight loss after complete dehydration are listed in Table 2. The smoothness of the curves and agreement between the calculated and observed weight loss values suggest that dehydration takes place successively as a one-step reaction without any intermediate hydrate for all of the formate dihydrates examined.

The activation energy and the order of reaction for the dehydration calculated by the Freeman and Carroll method are given in Table 2. The order of reaction seems to be $2/3$ for all of the salts examined. These values

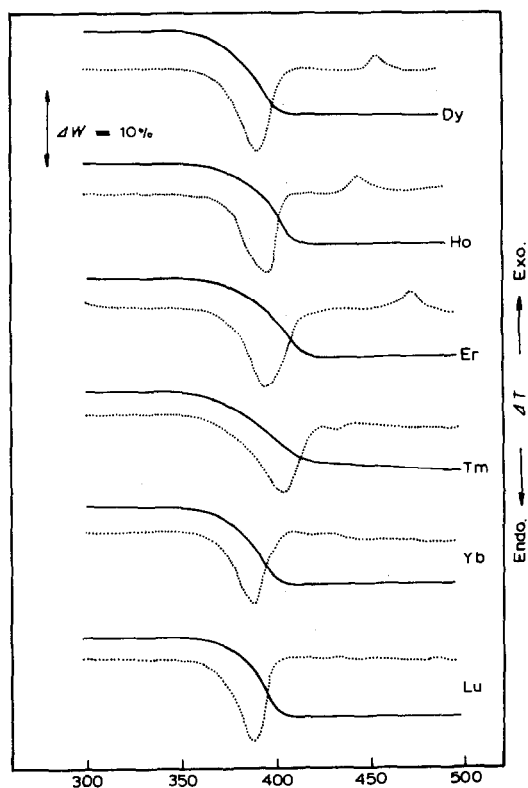


Fig. 1. TG (solid line) and DTA (broken line) for the dehydration of rare earth metal formate dihydrates.

TABLE 2

Temperature range, peak temperature of DTA curve (T_p) and weight loss value for the dehydration

Ln(HCO ₂) ₃ · 2 H ₂ O	Temp. range (K)	T_p (K)	Weight loss (%)	
			Calcd.	Obs.
Dy	350–415	408	10.8	10.1
Ho	354–413	401	10.7	10.0
Er	356–414	397	10.6	10.6
Tm	353–407	391	10.6	10.2
Yb	354–418	390	10.5	10.6
Lu	362–405	394	10.4	10.4

were checked by the Coats and Redfern method. Figure 2 shows the Coats–Redfern plots for the dehydration of Ho(HCO₂)₃ · 2 H₂O.

When the order of reaction, n , was assumed to be 2/3, the plot gave a straight line to yield an activation energy of 119.2 kJ mole⁻¹, which agreed

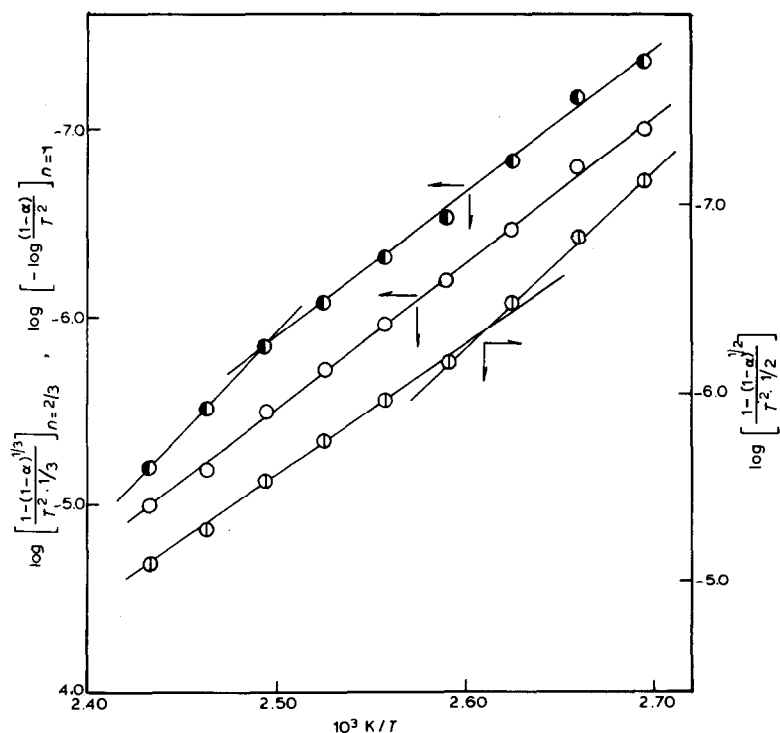


Fig. 2. Plots using the Coats–Redfern method for the dehydration of Ho(HCO₂)₃ · 2 H₂O. ●, $n = 1$; ○, $n = 2/3$; ⊙, $n = 1/2$.

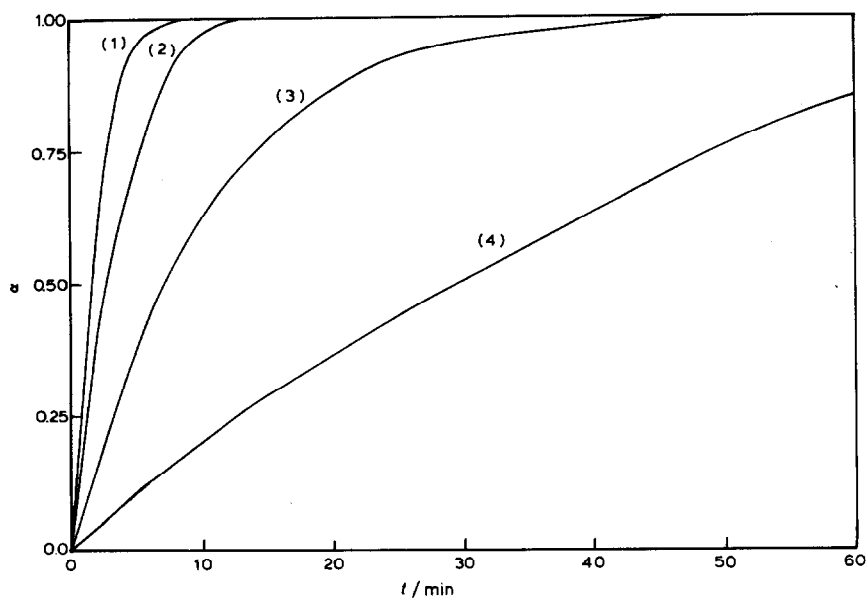


Fig. 3. α - t curves for the dehydration of $\text{Yb}(\text{HCO}_2)_3 \cdot 2 \text{H}_2\text{O}$ at (1) 393 K, (2) 386 K, (3) 377 K, and (4) 370 K.

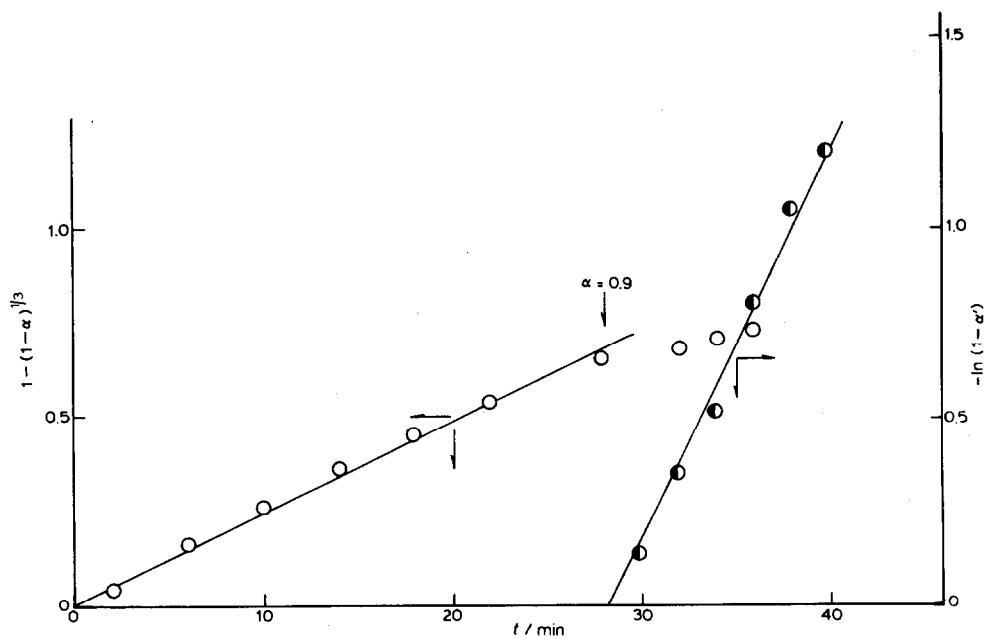


Fig. 4. Plots of $1-(1-\alpha)^{1/3}$ vs. time and $\ln(1-\alpha')$ vs. time for the dehydration of $\text{Yb}(\text{HCO}_2)_3 \cdot 2 \text{H}_2\text{O}$ at 377 K.

closely with that determined by the Freeman–Carroll method ($115.5 \text{ kJ mole}^{-1}$). This result was similar to that for the dehydration of the first transition metal formate dihydrates [1,2]. Consequently, the most reasonable reaction order decided by the above method was $2/3$, which indicated that the mechanism of the dehydration was a phase boundary-controlled reaction [5].

In recent years, Criado and Molrales [6,7] and several other authors [8] pointed out that the reaction mechanism could not be deduced from a single TG diagram and the result obtained from the single diagram must be checked by the isothermal experiment or other methods. For the above reason, the dehydration reaction was studied in more detail under isothermal conditions.

Figure 3 shows the relation between the fraction of dehydration (α) and the time of reaction (t) for the isothermal dehydration of $\text{Yb}(\text{HCO}_2)_3 \cdot 2 \text{H}_2\text{O}$. Analyzing the α - t curves, the dehydration reaction shows a similar feature to those for the dehydration of first transition metal formate dihydrates. That is to say, the reaction was confirmed to be a phase boundary-controlled reaction [5] in the range $0 < \alpha < \sim 0.9$ and to be a first-order reaction in the range $\alpha \geq \sim 0.9$ (Fig. 4).

This transition from the phase boundary reaction to the first-order reaction may be interpreted in a similar manner described in the previous paper [1,2]. Consequently, the dehydration mechanism was found to be a phase boundary-controlled contracting-interface reaction.

Table 3 shows the pre-exponential factor and the activation energy ob-

TABLE 3

Reaction order (n), activation energy (E), frequency factor (A) and enthalpy change (ΔH) for dehydration

$\text{Ln}(\text{HCO}_2)_3 \cdot 2 \text{H}_2\text{O}$	n	E (kJ mole^{-1})			A (min^{-1})	ΔH (kJ mole^{-1})
		F-C ^a	R-C ^b	Iso ^c		
Dy	0.67	108.3	115.1	126.8	2.0×10^{17}	108.8
Ho	0.65	115.5	119.2	128.6	2.5×10^{16}	114.2
Er	0.75	119.2	122.6	129.3	7.9×10^{15}	131.4
Tm	0.61	135.5	137.7	130.5	3.2×10^{16}	141.8
Yb	0.80	137.6	142.2	137.2	1.6×10^{17}	145.6
Lu	0.71	133.1	139.7	138.1	4.0×10^{17}	146.9
Y ^d	0.63	115.0		119.0	1.1×10^{17}	115.0

^a Freeman–Carroll method.

^b Coats–Redfern method.

^c Isothermal method.

^d Ref. 14.

tained from the Arrhenius plot. The activation energy determined by isothermal methods were in rough agreement with those by the Freeman–Carroll and Coats–Redfern methods.

It has been known that the dihydrates of the formates of Y, Ho and Er are all orthorhombic and isostructural [9–11,13] and the metal ion is coordinated by eight oxygens (two of them are associated with water and the other six with three formate groups) in a distorted D_{4d} square antiprism. Although the structure of Dy formate dihydrate is not known, it seems to be isostructural with yttrium-type salts, since its powder diffraction pattern resembles theirs.

On the other hand, the dihydrates of the formates of Tm, Yb and Lu are triclinic [10]; however, the coordination structures have not been determined.

In both the orthorhombic and triclinic salt series, the temperature at which the weight loss began increased with increasing reciprocal radius of the metallic ion ($1/r_M$).

After dehydration, an exothermic peak was found in the DTA curves of yttrium type salts. This exothermic peak is attributed to the recrystallization of amorphous formate anhydride [14]. Unlike the yttrium-type dihydrates, no exothermic peak following dehydration was recognized in the DTA curve of thulium-type salts, which suggested that the positions of the metal and the formic group in the hydrated and the anhydrous salts were similar. The similarity of these two structures were so similar that the Russian workers have thought them equivalent [10,12].

The enthalpy change (ΔH) for the dehydration of the first transition metal formate dihydrates increased in the order of Irving–Williams, which revealed that the stabilities of these salts increase in this order and these stabilities may be accounted for in terms of crystal field stabilization energies.

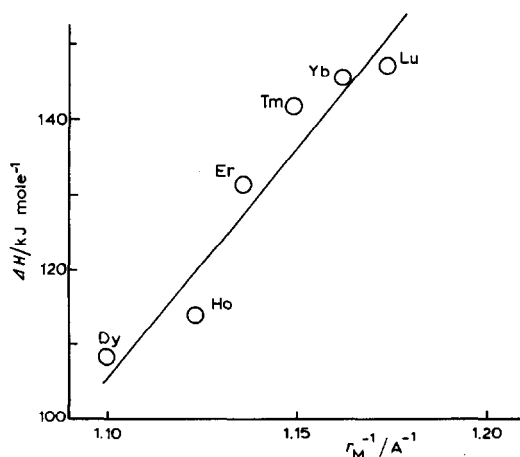


Fig. 5. Relationship between ΔH and $1/r_M$.

However, the information of the ligand field effect could not be obtained from the value of ΔH for the dehydration reaction of rare earth formate dihydrates.

The relation between ΔH and $1/r_M$ showed an approximate linearity (Fig. 5), which suggests that the Ln-OH₂ bond depends on the electrostatic force between the metallic ion and the water molecule.

In the case of colored samples, the dehydration of the first transition metal formate dihydrates was accompanied by a drastic color changes. On the other hand, the color changes were scarcely apparent for the dehydration of rare earth formate dihydrates.

The above-mentioned experimental results can be ascribed to the fact that the *f* electrons of the rare earth ions are uninfluenced by the ligand fields, unlike the *d* electrons of the first metal ions.

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