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KINETIC ANALYSIS OF TG DATA. THERMAL DEHYDRATION OF Ni(II), Co(II) AND Mg(II) ACETATE TETRAHYDRATES

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ABSTRACT

A study has been made of the kinetic behaviour of three tetrahydrated acetates undergoing dehydration.

Differential kinetic analysis was used to discriminate between models. A two-step model, namely two-dimensional nuclei growth and phase boundary reaction in cylinders, is required to describe the course of the dehydration of the three solids.

If the Coats–Redfern method is used to fit the kinetic data to any of the models used, the E and A values obtained depend on the heating rate. A model with more than one step must be used.

INTRODUCTION

Although the thermal decomposition of most compounds has been analysed in terms of one-step models [1–4], the kinetics of decomposition of many solids are better described using more complex models, i.e. two-step models.

In an earlier paper [5], the kinetics of calcium oxalate dehydration were described using a two-step model. When a one-step model is used [6], the values of kinetic parameters obtained depend on the heating rate.

The present paper gives three examples of thermal dehydration which have to be analysed in terms of a two-step model. All three of the salts used had the same number of water molecules and the same monoclinic crystalline form.

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The Coats–Redfern method did not allow discrimination between models, and for each model probed, the values of kinetic parameters observed were dependent on the heating rate.

Discrimination was achieved through a differential kinetic analysis, taking into account the experimental reaction rate.

EXPERIMENTAL

The manufacturers' specifications of the salts used in the decomposition studies are listed in Table 1.

The dehydration behaviour of solid samples weighing 10 ± 0.05 mg, randomly distributed in the sample pan, was observed using a DuPont Model 951 thermogravimetric analyser connected to a nitrogen flow control system which maintained a flow rate of 2 cm^3 s^{-1}. This gives an approximate linear velocity of 0.71 cm s^{-1} in the reaction chamber. The same conditions were maintained during all the experiments in order to avoid the influence of macrokinetic parameters.

The sample temperature was measured using a chromel–alumel thermocouple placed only a few millimetres from the sample.

The weight variation of the sample was recorded as a function of sample temperature. The derivative of this curve was also recorded.

The decomposition experiments for the three salts were carried out at five different heating rates (0.5, 1, 2, 5 and 10 K min^{-1}). These heating rates were chosen in order to give a wide temperature range for the experimental α–T curves, and to provide sufficient experimental data for both constant temperature and conversion studies. The heating rates were also chosen to be low enough to avoid thermal gradients within the sample and between the sample and the external fluid.

RESULTS AND DISCUSSION

Experimental α–T data are shown in Figs. 1–3.

If the Coats–Redfern method is used, plotting $\ln[g(\alpha)/T^2]$ vs. $1/T$, we obtain straight lines for each of the models listed in Table 2; and, for a given

TABLE 1

Sample compositions

Compound	Source	Assay (% wt. min.)
$Ni(CH_3{-}COO)_2 \cdot 4H_2O$	BDH GPR	98.0
$Co(CH_3{-}COO)_2 \cdot 4H_2O$	Carlo Erba RPE	99.0
$Mg(CH_3{-}COO)_2 \cdot 4H_2O$	Carlo Erba RPE	99.0

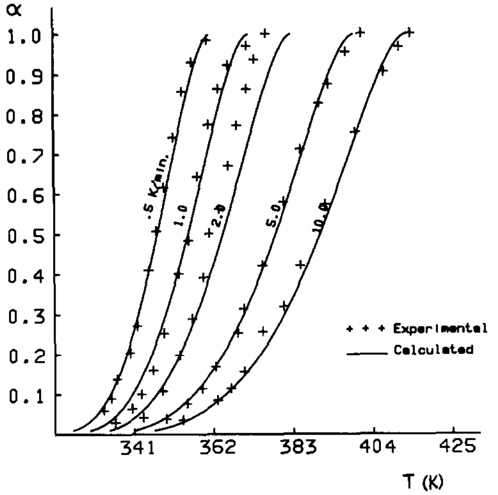

Fig. 1. Experimental and calculated $\alpha - T$ data: nickel acetate dehydration.

$g(\alpha)$, the slope of the lines depends on the heating rate. Table 3 shows, as an example, the values of kinetic parameters obtained for nickel acetate dehydration, using the R2 model. As can be seen from Table 3, the higher the heating rate, the lower the values of the kinetic parameters obtained. It is for this reason that the decomposition temperatures and the influence of the low activation energy step increase with increasing heating rate. Using the same method with other models yields similar results. The variation in the values of kinetic parameters obtained for different heating rates indicates that a two-step model should be used.

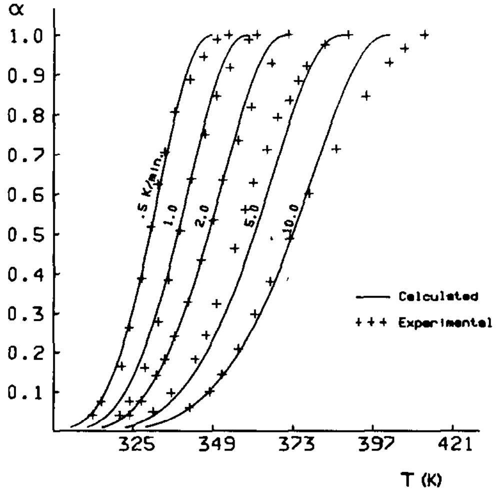

Fig. 2. Experimental and calculated $\alpha - T$ data: cobalt acetate dehydration.

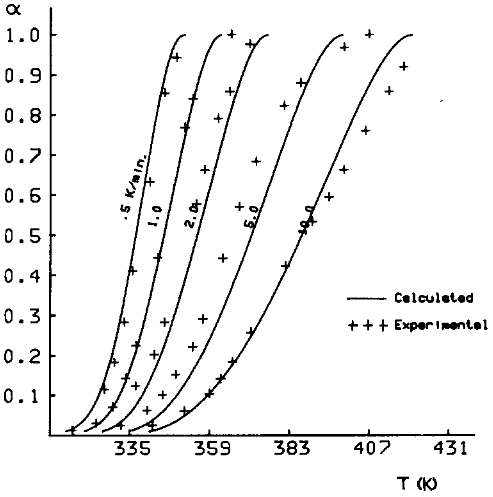

Fig. 3. Experimental and calculated $\alpha - T$ data: magnesium acetate dehydration.

The experimental reaction rates shown in Table 4 were calculated from DTG curves. If the two steps of the model are connected in series, the reaction rate has the expression [5]

$$\frac{1}{r} = \frac{1}{A_1 \exp(-E_1/RT) f_1(\alpha)} + \frac{1}{A_2 \exp(-E_2/RT) f_2(\alpha)} \tag{1}$$

TABLE 2

Conversion functions of the different steps probed

Rate mechanism	$f(\alpha)$	$g(\alpha)$	Symbol
Nucleation and nuclei growth			
(a) Random nucleation	$1-\alpha$	$-\ln(1-\alpha)$	F1
(b) Two-dimensional nuclei growth	$2(1-\alpha)\{-\ln(1-\alpha)\}^{1/2}$	$-\{\ln(1-\alpha)\}^{1/2}$	F2
(c) Three-dimensional nuclei growth	$3(1-\alpha)\{-\ln(1-\alpha)\}^{2/3}$	$-\{\ln(1-\alpha)\}^{1/3}$	F3
Diffusion			
(a) One-dimensional transport	α^{-1}	$\alpha^{2/2}$	D1
(b) Two-dimensional transport (cylindrical geometry)	$\{-\ln(1-\alpha)\}^{-1}$	$(1-\alpha)\ln(1-\alpha)+\alpha$	D2
(c) Three-dimensional transport (spherical geometry)	$\{(1-\alpha)^{-1/3}-1\}$	$3/2\{1-2\alpha/3-(1-\alpha)^{3/2}\}$	D3
Phase boundary reaction			
(a) One-dimensional (zero order)	Constant	α	R1
(b) Two-dimensional (cylindrical geometry)	$(1-\alpha)^{1/2}$	$2\{1-(1-\alpha)^{1/2}\}$	R2
(c) Three-dimensional (spherical geometry)	$(1-\alpha)^{2/3}$	$3\{1-(1-\alpha)^{1/3}\}$	R3

TABLE 3

Nickel acetate dehydration: influence of heating rate on kinetic parameters obtained using the Coats–Redfern method [a]

Heating rate (K min^{-1})	0.5	1.0	2.0	5.0	10.0
E (kcal mol^{-1})	28.3	28.1	26.3	20.3	17.4
A (min^{-1})	1.0×10^{16}	4.9×10^{15}	3.2×10^{14}	5.3×10^{10}	9.0×10^{8}

[a] Probed model is R2.

and six unknowns must be determined by non-linear regression. The method would be tedious because 27 combinations of f_1 and f_2 would have to be considered in order to test the nine steps of Table 2.

TABLE 4

Experimental reaction rates

$Ni(CH_3-COO)\cdot 4H_2O$

T (K)

350		355		360		365		370	
α	r	α	r	α	r	α	r	α	r
0.025	0.028	0.040	0.045	0.065	0.069	0.100	0.100	0.160	0.131
0.045	0.035	0.080	0.050	0.135	0.073	0.210	0.100	0.315	0.125
0.140	0.043	0.250	0.066	0.410	0.087	0.625	0.099	0.870	0.092
0.280	0.043	0.475	0.055	0.750	0.056	0.900	0.029	0.990	0.010
0.675	0.034	0.900	0.017	0.980	0.008				

$Mg(CH_3-COO)_2\cdot 4H_2O$

T (K)

340		350		360		370		380	
α	r	α	r	α	r	α	r	α	r
0.020	0.022	0.050	0.051	0.110	0.095	0.240	0.168	0.390	0.192
0.060	0.036	0.160	0.073	0.350	0.132	0.610	0.134	0.805	0.083
0.100	0.039	0.415	0.067	0.735	0.074	0.910	0.022	0.970	0.010
0.335	0.043	0.715	0.049	0.925	0.013	0.975	0.006	0.998	0.004
0.605	0.027	0.950	0.004	0.955	0.003				

$Co(CH_3-COO)_2\cdot 4H_2O$

T (K)

340		350		360		370		380	
α	r	α	r	α	r	α	r	α	r
0.050	0.057	0.125	0.122	0.265	0.205	0.450	0.250	0.625	0.205
0.132	0.076	0.315	0.140	0.600	0.167	0.810	0.079	0.955	0.012
0.297	0.060	0.565	0.071	0.805	0.038	0.985	0.007	0.999	0.002
0.540	0.047	0.840	0.017	0.990	0.003				
0.855	0.010	0.985	0.012						

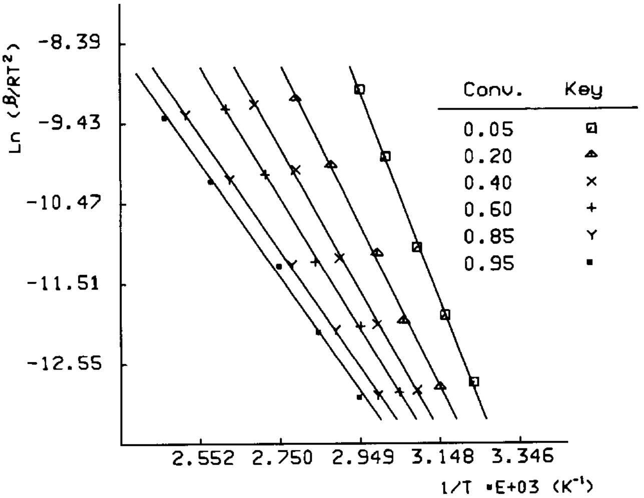

Fig. 4. Integral analysis at constant temperature of nickel acetate dehydration.

If the analysis is carried out at constant temperature, to study the conversion influence separately, there is only an experimental r–α value for each experiment and the range of conversion at a given temperature is small, as can be seen from Table 4. Correlating experimental data obtained at constant temperature is therefore difficult. The discrimination would be easier if the approximate kinetic parameters were known. These can be obtained from the results of an integral analysis at constant conversion [7]. In fact, using eqn. (2) to correlate α–T data, the values of kinetic parameters obtained depend on the true values of the kinetic parameters and the relative influence of each step at each conversion level.

$$\ln\frac{\beta}{RT^2} = \ln\frac{A/E}{g(\alpha)} - \frac{E}{RT} \tag{2}$$

Figure 4 shows, as an example, experimental data obtained for nickel acetate dehydration, plotted according to eqn. (2). The slopes of the supposed straight lines vary with varying conversion level. Assuming that only one step controls the reaction at the beginning and at the end of the process, then the values of E and A can be obtained from those calculated from eqn. (2) at different conversion levels by extrapolation to $\alpha = 0$ and $\alpha = 1$. Using the approximate kinetic parameters obtained in this way together with eqn. (1), it is possible to find out what functions ($f_1(\alpha)$ and $f_2(\alpha)$) can correlate the experimental reaction rates. Table 5 shows the approximate kinetic parameters obtained. In all cases, the kinetic model is a combination of two-dimensional nuclei growth and phase boundary reaction in cylinders.

Having established the kinetic model, the optimal kinetic parameters were obtained by multiple non-linear regression analysis on the whole range of r–α–T data given in Table 2. Table 6 shows the optimal E and A values

TABLE 5

Approximate kinetic parameters

Compound	Parameters			
	A_1 (min^{-1})	E_1 (kcal mol^{-1})	A_2 (min^{-1})	E_2 (kcal mol^{-1})
$Ni(CH_3\text{-}COO)_2 \cdot 4H_2O$	2.6×10^{20}	31.79	2.0×10^{7}	14.21
$Mg(CH_3\text{-}COO)_2 \cdot 4H_2O$	6.4×10^{17}	26.43	8.1×10^{3}	9.73
$Co(CH_3\text{-}COO)_2 \cdot 4H_2O$	1.7×10^{18}	28.81	8.9×10^{6}	13.21

TABLE 6

Optimal kinetic parameters

Compound	Parameters			
	A_1 (min^{-1})	E_1 (kcal mol^{-1})	A_2 (min^{-1})	E_2 (kcal mol^{-1})
$Ni(CH_3\text{-}COO)_2 \cdot 4H_2O$	1.0×10^{20}	32.78	2.0×10^{7}	14.40
$Mg(CH_3\text{-}COO)_2 \cdot 4H_2O$	2.0×10^{15}	25.23	6.9×10^{3}	8.34
$Co(CH_3\text{-}COO)_2 \cdot 4H_2O$	1.6×10^{18}	28.41	8.9×10^{6}	13.41

obtained. Figures 1–3 indicate the agreement between the calculated and experimental $\alpha - T$ data.

In conclusion, when the Coats–Redfern method is used to fit the $\alpha - T$ data and the values of the kinetic parameters obtained depend on the heating rate for any given model, it is necessary to use a two-step model.

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