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KINETIC STUDIES ON THE THERMAL DECOMPOSITION OF TETRAHYDRATED COBALT(II) METHANESULPHONATE

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ABSTRACT

A kinetic study of the dehydration and decomposition of tetrahydrated Co^{II} methanesulphonate has been carried out in an argon flow by TG at constant temperature as well as with a linearly rising temperature. The thermal dehydration occurs in two steps regulated by random nucleation, A_2 and A_3, while the decomposition of the anhydrous salt follows first-order kinetics, F_1, where the rate-controlling step is a nucleation process in which there is equal probability of nucleation at each active site. The kinetic parameters obtained at three heating rates are in good agreement; however, the values of kinetic parameters estimated isothermally are smaller than those estimated dynamically.

INTRODUCTION

In an increasing number of areas of technology and, hence, industry, progress is recognized as being directly related to understanding the factors influencing the reactivity of solids and how they react and interact in specific environments. In general, the reactions, which include solid reactions, are very complex from the kinetic standpoint as they involve several physical and chemical steps [1].

Many thermal techniques have been applied as valuable tools for studying the kinetics of thermal solid decomposition [2]. In analysing the kinetic data it is true that the conventional isothermal method is important for estimating the kinetic model and parameters, but the dynamic method has some advantages over it in several respects [2]. The present work was designed to study the kinetics of the dehydration and decomposition of tetrahydrated

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cobalt(II) methanesulphonate, $Co(MS)_2 \cdot 4H_2O$, by TG using both isothermal and non-isothermal methods. Since Co^{II} is easily oxidized in air, the thermal decomposition rate was followed in argon atmosphere. In the literature, there are a small number of works concerning the thermal stability of metallic salts of sulphonic acid [3–6], but few of them deal with the kinetics of their thermal decomposition.

EXPERIMENTAL

Hydrated cobalt(II) methanesulphonate, $Co(MS)_2 \cdot 4H_2O$, was prepared in aqueous solution by the reaction between cobalt carbonate and methanesulphonic acid. The solution was concentrated until solid product was obtained on cooling. The product was then filtered off and recrystallized.

To establish the composition of the compound, cobalt was determined by atomic absorption spectrophotometry, and carbon and hydrogen determinations were carried out by elemental analyses. Thermogravimetric (TG) and differential thermal analysis (DTA) were recorded simultaneously using a DT-30 thermal analyser (Shimadzu) using samples of about 5 mg to ensure a linear heating rate for the sample. The heating rates were 5, 8 and 10 K min^{-1}.

RESULTS AND DISCUSSION

TG and DTA curves of $Co(MS)_2 \cdot 4H_2O$ in flowing argon are shown in Fig. 1. The TG curve shows that the dehydration takes place in two successive steps, each corresponding to the elimination of two water molecules in the temperature range 71–189 °C. The weight losses observed were 11.4% and 11.2% for the first and second steps respectively, which are in agreement with the theoretically calculated dehydration (11.2%). In the DTA curve, the endothermic peaks associated with the two dehydration steps can be seen at 98 °C and 176 °C. Also, the DTA curve for the anhydrous salt, $Co(MS)_2$, shows an endothermic peak at 370 °C before the decomposition of the salt. This DTA peak is not accompanied by a loss in weight in the TG curve and may refer to the melting of the compound before its decomposition. The TG curve shows that the decomposition of anhydrous salt $Co(MS)_2$ started at about 380 °C leading to Co_9S_8 (experimental weight loss, 64%; calculated, 64.9%) as identified by X-ray diffraction.

The kinetic model functions $g(\alpha)$ listed in Table 1 were examined for each of the dehydration and decomposition steps by conventional isothermal analysis. Under isothermal conditions, the rate constant, k, is independent of reaction time and so $g(\alpha) = kt$. A plot of $g(\alpha)$ versus time should thus give a straight line if the correct form of $g(\alpha)$ is used. The isothermal α–t

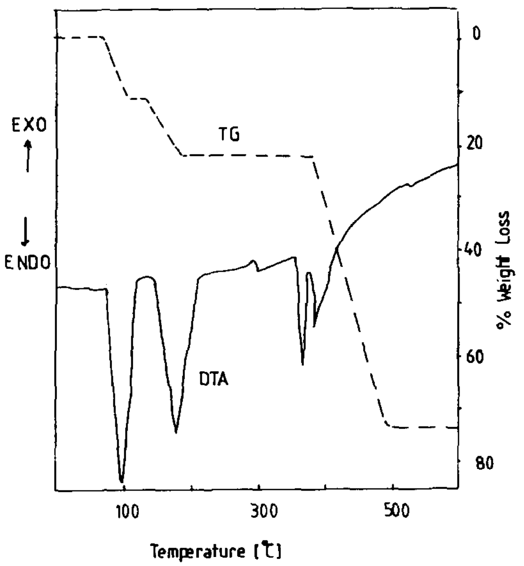

Fig. 1. DTA (———) and TG (— — —) curves for $Co(MS)_2 \cdot 4H_2O$.

data were analysed according to the various kinetic models by regression analysis. The best fit of the dehydration data was obtained by a random nucleation process: A_3 model for the first dehydration step and A_2 model for the second dehydration step. According to this mechanism the nucleation of the reactant is a random process. As nuclei grow larger, they must eventually impinge on one another, so that growth ceases where they touch.

TABLE 1

Kinetic model functions for solid decomposition

$g(\alpha)$	Symbol	Rate-controlling process
α^2	D_1	One-dimensional diffusion
$\alpha + (1-\alpha)\ln(1-\alpha)$	D_2	Two-dimensional diffusion
$[1-(1-\alpha)^{1/3}]^2$	D_3	Three-dimensional diffusion (Jander function)
$(1-2\alpha/3)-(1-\alpha)^{2/3}$	D_4	Three-dimensional diffusion (Ginstling–Brownshtein function)
$\ln[\alpha/(1-\alpha)]$	A_u	Autocatalytic reaction (Prout–Tompkins function)
$1-(1-\alpha)^{1/n}$	R_n	Phase-boundary reaction; $n = 1$, 2 and 3 (one-, two- and three-dimensional respectively)
$[-\ln(1-\alpha)]^{1/m}$	A_m	Random nucleation and its subsequent growth; $m = 2$, 3 and 4 (Avrami–Erofeev function)
$-\ln(1-\alpha)$	F_1	First-order kinetics

TABLE 2

Kinetic parameters for dehydration and decomposition of $Co(MS)_2 \cdot 4H_2O$ calculated according to isothermal and dynamic methods

Reaction type	TG analysis	Heating rate (K min^{-1})	E (kJ mol^{-1})	A (s^{-1})	ΔS (J mol^{-1} K^{-1})	Kinetic model	Correlation coefficient
1st	Isothermal		81.9	7.1×10^{8}	−77.32	A_3	0.994
dehydration	Dynamic	5	87.8	1.6×10^{9}	−70.56		0.972
step		8	88.9	2.2×10^{9}	−67.91		0.981
		10	90.2	2.4×10^{9}	−67.20		0.991
2nd	Isothermal		123.7	8.0×10^{11}	−20.47	A_2	0.992
dehydration	Dynamic	5	129.9	1.9×10^{12}	−13.28		0.981
step		8	131.8	2.3×10^{12}	−11.69		0.976
		10	134.2	2.5×10^{12}	−11.00		0.979
Decompo-	Isothermal		280.9	2.1×10^{18}	99.33	F_1	0.996
sition	Dynamic	5	301.2	3.4×10^{18}	103.34		0.991
step		8	305.1	3.5×10^{18}	103.58		0.987
		10	307.2	3.9×10^{18}	105.80		0.986

However, the regression analysis method showed that the decomposition of the anhydrous salt, $Co(MS)_2$, takes place according to a first-order mechanism (F_1 model), where the rate-determining step is a nucleation process and there is equal probability of nucleation at each active site. The results of the calculation of the kinetic parameters are given in Table 2. Typical plots of the corrected form of $g(\alpha)$ against time are shown in Figs. 2–4.

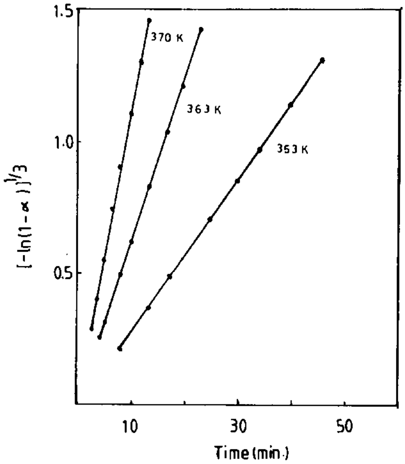

Fig. 2. Isothermal reaction for the first dehydration step of $Co(MS)_2 \cdot 4H_2O$ according to the random nucleation (A_3) model.

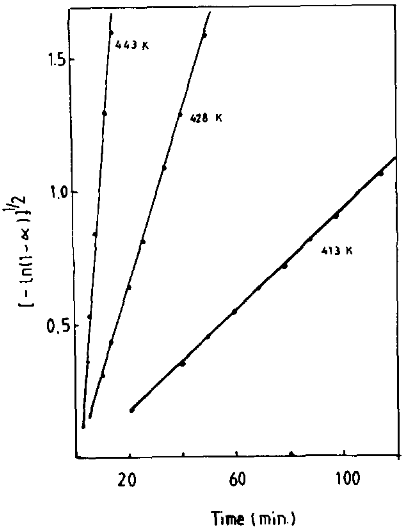

Fig. 3. Isothermal reaction for the second dehydration step of $Co(MS)_2 \cdot 4H_2O$ according to the random nucleation (A_2) model.

In order to obtain reliable kinetic parameters from the rising temperature method, three different heating rates, 5, 8 and 10 K min^{-1}, were employed using a small mass ($\approx$ 5 mg). Several methods can be used for the calculation of kinetic parameters from non-isothermal TG data. In the present case,

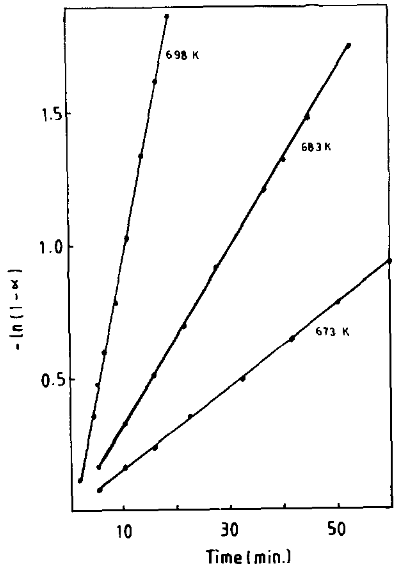

Fig. 4. Isothermal decomposition of $Co(MS)_2$ according to the first-order mechanism (F_1 model).

the Coats–Redfern [7] method was used. For calculation of the activation energy (E) according to this method, the following equation is applied

$$-\ln g(\alpha)/T^2 = -\ln(AR/\beta E)(1 - 2RT/E) + (E/RT) \qquad (1)$$

where A is the frequency factor, β is the rate of temperature change, T is the absolute temperature and R is the gas constant. In view of the conclusions from isothermal studies, the random nucleation models (A_2 and A_3) and the first-order kinetic model (F_1) were used for $g(\alpha)$ in eqn. (1) to analyse the results for the dehydration and the decomposition process respectively. By plotting the left side of eqn. (1) against $1/T$, the activation energy (E) and the frequency factor (A) were calculated from the slopes and intercepts of these plots respectively and are listed in Table 2. The entropy, ΔS^{*}, of activation was calculated using the relation

$$A = (K_b T_p/h)\exp(\Delta S^{*}/R) \qquad (2)$$

where K_b is the Boltzmann constant, h is the Planck constant and T_p is the peak temperature of the decomposition. The values of ΔS^{*} are also given in Table 2. The negative values of the entropy of activation obtained for each of the dehydration steps indicate that the activated complexes formed during the dehydration processes are more ordered than the reactants, while the positive values of ΔS^{*} obtained for the decomposition of $Co(MS)_2$ indicate a higher ordering of the $Co(MS)_2$ than of the activated complex during the decomposition process. Table 2 shows a close agreement in the kinetic parameters obtained using the three heating rates which demonstrates internal consistency. On the other hand, the observed difference in the kinetic parameters obtained from the dynamic and isothermal methods may be attributed to the change in the dynamic decomposition mechanism or to the kinetic compensation effect [8–10].

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