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Note

The kinetics of thermal dehydration of $FeC_4H_4O_6 \cdot 2.5H_2O$ employing DSC traces

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Abstract

The non-isothermal dehydration kinetics for the loss of coordinated water of the hydrated ferrous tartrate $FeC_4H_4O_6 \cdot 2.5H_2O$, have been studied by DSC technique under nitrogen atmosphere with varying heating rates. The specific reaction rate constant determined by employing the Flynn–Wall–Ozawa method is found to increase linearly with increase in heating rate. However, there is no effect on specific reaction rate with variation in sample mass.

Keywords: Dehydration; DSC; Ferrous tartrate; Iron tartrate; Kinetics; Non-isothermal

1. Introduction

The kinetic study of the thermal dehydration of metal carboxylates is interesting because they act as model compounds in the understanding of the kinetics and mechanism of thermal dehydration processes [1–3]. The kinetic study is usually performed by isothermal or non-isothermal methods [3, 4]. Here we report the non-isothermal kinetic study for the thermal dehydration of $FeC_4H_4O_6 \cdot 2.5H_2O$, using a 910 Du Pont differential scanning calorimeter under nitrogen atmosphere, with four different heating rates (5, 10, 15 and 20 K min^{-1}); the rate of nitrogen

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purge was 25 ml min^{-1}. The nature of the thermal dehydration of this compound under different atmospheres, namely dynamic air, dynamic nitrogen and static air, employing TGA, DTG, DTA, and electrical conductivity techniques is reported in our earlier study [5]. It was apparent from the DSC traces that there is an initial loss of $0.5H_2O$ ($<100°C$) and a further loss of $2.0H_2O$ molecules ($<200°C$). The loss of $0.5H_2O$ corresponds to absorbed water and the further loss of $2.0H_2O$ corresponds to coordinated water, from the temperatures of the liberation of these water molecules [5]. We report here the reaction kinetics for the thermal dehydration of the $2.0H_2O$, i.e. the coordinated water molecules, as represented in Eq. (2) below. The thermal dehydration reaction for $FeC_4H_4O_6 \cdot 2.5H_2O$ is thus

$$FeC_4H_4O_6 \cdot 2.5H_2O \xrightarrow{<100°C} FeC_4H_4O_6 \cdot 2H_2O + 0.5H_2O \quad (1)$$

$$FeC_4H_4O_6 \cdot 2.5H_2O \xrightarrow{<200°C} FeC_4H_4O_6 + 2.0H_2O \quad (2)$$

The Flynn–Wall–Ozawa (FWO) [6] method was employed to evaluate the activation energy E_a (J mol^{-1}), and other kinetic parameters, namely the specific factor Z (min^{-1}) and the half time $t^{1/2}$ (min). This FWO method is found to be the most straightforward technique when DSC is employed with a variable program rate [6, 7]. The Du Pont DSC is found to suit this method (FWO) well, due to its linear program rates, high degree of baseline stability and its ability to measure directly the sample temperature via a thermocouple located close to the sample [7].

2. Calculations

The log program (heating) rate ($\log \beta$) is plotted against the reciprocal peak temperature for evaluation of the kinetic parameters, namely, activation energy E_a, pre-exponential factor z, specific reaction rate constant k, and half time $t^{1/2}$, as described in Eqs. (3)–(6)

$$E_a = 2.19R \frac{\mathrm{d} \log \beta}{\mathrm{d}(1/T)} \quad (3)$$

where E_a is the activation energy in J mol^{-1}, R the gas constant (8.317 J mol^{-1} K), T the peak temperature in K (near the middle of the range) and

$$Z = \frac{\beta E_a e^{E_a/RT}}{RT^2} \quad (4)$$

where Z is the pre-exponential factor (Arrehenius frequency factor) in min^{-1}, and

$$K = Ze^{-E_a/RT} \quad (5)$$

where K is the specific reaction rate constant in min^{-1}, and

$$t^{1/2} = \frac{0.693}{K} \quad (6)$$

where $t^{1/2}$ is the half time.

Table 1
Kinetic parameters evaluated by the FWO method for thermal dehydration of $FeC_4O_6 \cdot 2.5H_2O$ employing DSC traces under N_2 atmosphere

$\beta/(K\ min^{-1})$	T/K	Z/min^{-1}	K/min^{-1}	$t^{1/2}/min$
5	385.23	7.19×10^6	–	–
10	395.20	1.77×10^{10}	6.08×10^{-1}	1.14
15	401.35	1.78×10^{10}	8.79×10^{-1}	0.79
20	406.27	1.74×10^{10}	1.7×10^0	0.405

$d \log \beta / d(1/T) = 4.35 \times 10^3\ K^2\ min^{-1}$. Activation energy $E_a = 79.20\ kJ\ mol^{-1}$. (The plot of $\log \beta$ vs. $1/T$ for $\beta = 5\ K\ min^{-1}$ is non-linear, but linear for other values.) $Z_{avg} = 1.76 \times 10^{10}\ min^{-1}$ (the Z value for $\beta = 5\ K\ min^{-1}$ is quite low and hence is neglected).

3. Results and discussion

An activation energy value of 79.2 kJ mol^{-1} is obtained for reaction (2), employing different heating rates. These, together with other kinetic parameters, are shown in Table 1. It is observed that the value of Z is almost constant, with an average value of $1.76 \times 10^{10}\ min^{-1}$ (Z_{avg}). Calculation of the K values employing Z_{avg} indicates that the specific reaction rate constant increases progressively with increase in heating rate. It is also noticed from the table that as the heating rate increases the peak temperature also increases linearly, and the half time $t^{1/2}$ of the reaction decreases. These changes in specific reaction rate constant and half-time values indicate that the rate of thermal dehydration of $FeC_4H_4O_6 \cdot 2.0H_2O$, i.e. for the coordinated water molecules, is fast at higher heating rates under nitrogen atmosphere. However at lower heating rates (5 K min^{-1}), deviation from linearity is observed. Variation in sample mass has no influence on the values of kinetic parameters.

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