NOTE

Kinetics of Thermal Decomposition of Potassium Sodium Tartrate Tetrahydrate

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Kinetic analyses were performed on potassium sodium tartrate tetrahydrate ($KNaC_4H_4O_6 \cdot 4H_2O$) using TG/DTA measurement in N_2. The thermal behaviour and the effect of heating rate on the kinetics were investigated. To estimate the activation energy E of decomposition, the Ozawa and Kissinger iso-conversional method were applied. All stages of dehydration are governed by nucleation model F1 [$g(\alpha) = (1-\alpha)^{-1}$].

Key Words: Potassium sodium tartrate tetrahydrate, Thermal decomposition, Kinetics.

Potassium sodium tartrate is a white crystal with exceptional and unique properties. In recent years, it has received a considerable amount of attention because of many applications in printing, electroplating, pharmaceutical, telecommunications and glass industry[1-5]. The behaviour of potassium sodium tartrate tetrahydrate under heating is of great value for the industrial applications.

In the present work, the objective is to determine potassium sodium tartrate tetrahydrate decomposition kinetics in nitrogen atmosphere and to evaluate whether kinetic parameters are influenced by the procedural variables used in this study.

The potassium sodium tartarate tetrahydrate used in this study was commercial analyzed reagent. All the experiments were performed on Shimadzu simultaneous thermal analyzer DTG-60 device. All the samples were placed in ceramic crucibles. All the experiments were conducted under nitrogen as the purge gas. The flow rate of the gas was 30 mL min^{-1}. The range of temperature was from 25-500 ℃, at the heating rates of 2, 5, 10 and 20 ℃ min^{-1}. Sample mass was 6.6 ± 0.2 mg.

Theoretical method: The commonly used equation in the non-isothermal decomposition kinetics is presented as:

$$\frac{d\alpha}{dt} = \frac{A}{\beta} e^{-E/RT} f(\alpha) \tag{1}$$

where α is the fraction decomposed at time t, $d\alpha/dt$ is the rate of the reaction, A is the pre-exponential factor, E is the apparent activation energy and $f(\alpha)$ or $g(\alpha)$ is an expression describing the kinetic model[6]. The possible kinetic models and the expressions of $f(\alpha)$ or $g(\alpha)$ are listed in literature[7]. The purpose

of kinetic analysis in thermal analysis is to obtain conclusions about the mechanism of a reaction or to extract reference values of certain parameters, such as activation energy E. The apparent activation energy of the decomposition process in non-isothermal conditions can be calculated by iso-conversional method. The iso-conversional method avoids the use of explicit kinetic models. Iso-conversional method of Ozawa and Kissinger are applied on thermal analysis data[8]. They start from eqns. 2 and 3:

$$\ln \frac{\beta}{T_p^2} = \ln \left[\frac{RA}{E} \right] - \frac{E}{R} \cdot \frac{1}{T_p} \tag{2}$$

$$\log \beta = -0.4567 \frac{E}{RT} + \text{Constant} \tag{3}$$

In eqn. 2, the slope of log β *vs.* 1/T for the same value of a gives the value of apparent energy. In eqn. 3, the slope of ln (β/T_p^2) *vs.* $1/T_p$ for the same value of a gives the value of apparent energy. The most probable mechanisms of thermal decomposition can be achieved following Coats and Redfern eqn. 4[9].

$$\ln \left[\frac{g(\alpha)}{T^2} \right] = \left[\ln \frac{AR}{\beta E} \cdot \left(1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT} \tag{4}$$

The thermal analysis curves of $KNaC_4H_4O_6 \cdot 4H_2O$ (β = 10 ℃ min^{-1}) are shown in Fig. 1 and the analysis data are summarized in Table-1. The TG curve shows a continuous mass loss around 29.41-258.02 ℃ indicating that the tartrate hydrates formed at this temperature are unstable in the study
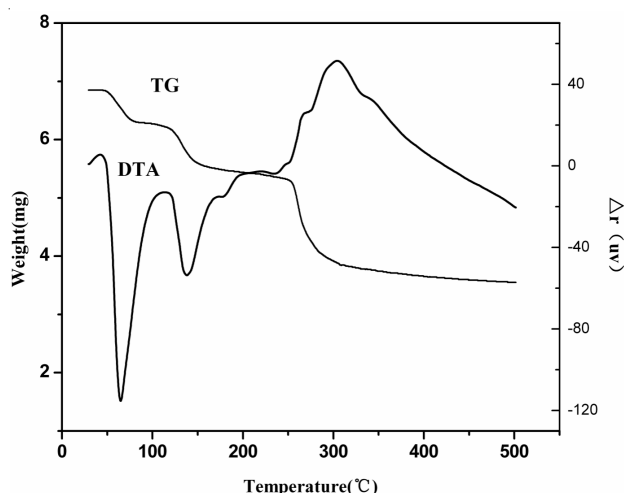
Fig. 1. TG/DTA curve of $KNaC_4H_4O_6 \cdot 4H_2O$ ($\beta = 10$ °C min^{-1})

TABLE-1
THERMAL ANALYSIS DATUM OF
$KNaC_4H_4O_6 \cdot 4H_2O$ ($\beta = 10$ °C min^{-1})

Stage	Range (°C)	DTA, peak (°C)	TG, mass loss (%)	
			Found	Theory
1	29.41-71.35	64.93	6.45	6.38
2	71.35-258.02	138.01	19.26	19.13
3	258.02-498.10	304.27	22.42	22.32

conditions. The TG and DTA curves exhibit two endothermic steps of dehydration. The first, between 29.41-71.35 °C is generally interpreted as being caused by the loss of 1 mol of water (mass loss of 6.45 %, theoretically 6.38 %), in the second stage 3 mol of crystal water are lost between 71.35-258.02 °C. The two steps are associated with a total mass loss of 25.71 %. The weight is stabilized at *ca.* 258 °C where anhydrous potassium sodium tartrate is formed. Finally, between 258.02 and 498.01 °C, a separate step connected with the formation of $C_3H_4NaO_4 \cdot$, with a mass loss of 22.42 %. Future work will be concentrated on exploring the exact course of the detailed change of this stage these are not discussed in this paper. On the basis of our study the following reactions were assumed to occur in the course of the thermal decomposition of $KNaC_4H_4O_6 \cdot 4H_2O$.

Dehydration process of potassium sodium tartrate tetrahydrate:

$$KNaC_4H_4O_6 \cdot 4H_2O \rightarrow KNaC_4H_4O_6 \cdot 3H_2O + H_2O$$
$$KNaC_4H_4O_6 \cdot 3H_2O \rightarrow KNaC_4H_4O_6 + 3H_2O$$
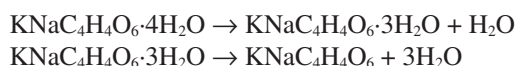
Decomposition process of potassium sodium tartrate:
$$KNaC_4H_4O_6 \rightarrow NaC_3H_4O_4 \cdot + \cdot COOK$$

The experiments were carried out with different heating rates in order to determine the effect of changing the experimental variables on the kinetics. Table-2 summarizes the peak characteristics for the DTA curves at different heating rates. It is evident that the apparent temperature of reaction become higher with increasing heating rate and the amplitude of the DTA peak temperature decreases with decreasing heating rate.

The kinetic parameters (the activation energy E, the pre-exponential factor A and the correlation coefficient r) were evaluated using the Ozawa method and Kissinger method by applying eqns. 2 and 3. The calculated results are given in

TABLE-2
PEAK TEMPERATURES OF THE DTA
CURVE AT DIFFERENT HEATING RATES

Heating rate (°C min^{-1})	DTA, peak (1) (°C)	DTA, peak (2) (°C)	DTA, peak (3) (°C)
2	58.64	133.41	246.34
5	60.50	136.36	266.64
10	64.93	138.01	304.27
20	68.79	144.35	394.63

Table-3. The activation energies E calculated by these two methods were in good agreement and all of the correlation coefficient r are larger than 0.99. In the first stage of dehydration process, E is 192.49 KJ mol^{-1}, A is 3.56×10^{15} and in the second stage E is 280.33 KJ mol^{-1}, A is 1.18×10^{18}.

TABLE-3
KINETIC PARAMETERS OF THE
DEHYDRATION STAGES OF $KNaC_4H_4O_6 \cdot 4H_2O$

Stage	E (kJ mol^{-1})			A	r	
	Ozawa	Kissnger	Average		Ozawa	Kissnger
1	191.91	193.06	192.49	3.56×10^{15}	0.9913	0.9907
2	280.51	280.14	280.33	1.18×10^{18}	0.9915	0.9926

The kinetic analysis of experimental TG curve ($\beta = 10$ °C min^{-1}) recorded under non-isothermal conditions was carried out by means of an integral method by applying the eqn. 4. The most probable mechanisms of thermal decomposition were obtained. All stages of dehydration are governed by nucleation model F1 [$g(\alpha) = (1 - \alpha)^{-1}$].

Conclusion

The thermal decomposition of potassium sodium tartrate tetrahydrate occurs in three steps under the conditions applied in this study. The first reaction, in which a water molecule is given off, the average activation energy E is 192.49 KJ mol^{-1}, the most probable mechanisms of thermal decomposition is F1 [$g(\alpha) = (1 - \alpha)^{-1}$]. The second reaction, in which three water molecule are given off, the average activation energy E is 280.33 KJ mol^{-1}, the most probable mechanisms of thermal decomposition is F1 [$g(\alpha) = (1 - \alpha)^{-1}$].

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