Thermochimica Acta 552 (2013) 60–64

Contents lists available at SciVerse ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

# Thermal decomposition kinetics of glycine in nitrogen atmosphere

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ARTICLE INFO

*Article history:*
Received 14 May 2012
Received in revised form 8 November 2012
Accepted 9 November 2012
Available online 19 November 2012

*Keywords:*
Glycine
Thermal decomposition
Kinetics
Thermodynamical analysis

ABSTRACT

The non-isothermal decomposition kinetics of glycine was investigated using analyzer DTG-60. TG experiments were carried out under dynamic nitrogen atmosphere of 30 mL min$^{-1}$ with heating rates of 10, 14, 18 and 22 K min$^{-1}$. The kinetic parameters such as activation energy ($E$), exponential factor ($A$) and reaction order ($n$) were evaluated by Flynn–Wall–Ozawa, Doyle, Kissinger and Šatava-Šesták methods. The results show that the non-isothermal decomposition mechanism of glycine corresponds to nucleation and growth, following the Avrami–Erofeev equation with $n = 1/3$. Moreover, thermodynamic properties of the non-isothermal decomposition process such as the change in the values of enthalpy ($\Delta H$), entropy ($\Delta S$) and Gibbs free energy ($\Delta G$) were calculated.

## 1. Introduction

Glycine (aminoacetic acid, CAS RN 56-40-6) is a kind of white crystalline powder (chemical formula: $NH_2CH_2COOH$) [1]. Glycine is one of the major inhibitory neurotransmitter in posterior areas of the vertebrate central nervous system. In the spinal cord and brain stem, glycinergic interneurones provide an inhibitory feedback mechanism that controls the motor rhythm generation during movement and they also play an important role in the coordination of spinal reflex activity [2,3]. In recent years, it has been widely used in many fields such as pesticide, medicine, food, feed, and so on [4]. Glyphosate is one of the herbicides with major interest in the farm chemical industry beacause of its broad-spectrum, low-toxic, efficient and security. Glycine is one of the raw materials to produce glyphosate, and thus its thermodynamic properties need to be studied. The standard mole combustion enthalpies of glyphosate and glycine measured by oxygen-bomb calorimeter have been reported [5]. The solubility data of α-glycine and γ-glycine in pure water from 288.15 to 353.15 K were measured by laser dynamic method [6]. Although glycine has been widely studied [4–9], its thermal decomposition process and kinetics have not been reported. In this paper, we report the thermal decomposition kinetics of glycine. Kinetic parameters such as activation energy, $E$, and apparent pre-exponential factor, $A$, were calculated using Flynn–Wall–Ozawa (FWO), Doyle, Kissinger and Šatava-Šesták methods. The kinetic equation of the thermal decomposition was established by the Šatava-Šesták method. The thermodynamic data, such as enthalpy ($\Delta H$), entropy ($\Delta S$) and Gibbs free energy($\Delta G$) for the non-isothermal decomposition process, were calculated. These data play an active role in understanding the physico-chemical interactions and the thermodynamic properties for glycine at high temperatures.

## 2. Experimental

### 2.1. Materials

Crystalline glycine, provided by a chemical factory in Zhejiang Province, China, was purified by recrystallization with mixed solvents of ethanol and water to obtain the purity of 99.5% (mass fraction) by high performance liquid chromatography. Indium (99.99%) and zinc (99.99%) are used to calibrate the apparatus, and α-$Al_2O_3$ powder is used as TG-DTA standard material, were provided by the Shimadu Company in Japan.

### 2.2. Instrument and methods

The TG-DTA analyzer (type DTG-60, Shimadzu Corporation, Japan) was used to determine the TG-DTA curves of the samples. SPN-500-type nitrogen generator (Hewleet-Packard, Beijing Institute of Technology, China) was used to provide a nitrogen atmosphere for the experimental system of thermal analysis. The thermal analysis apparatus was calibrated by measuring a standard specimen, such as indium (purity = 99.99%, $T_m = 429.78$ K, $\Delta_m H = 28.45$ J g$^{-1}$) or zinc (purity = 99.99%, $T_m = 419.58$ K,

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http://dx.doi.org/10.1016/j.tca.2012.11.006

| | |
|---|---|
| $A$ | exponential factor ($\text{min}^{-1}$) |
| $E$ | activation energy ($\text{kJ mol}^{-1}$) |
| $f(\alpha)$ | differential form of kinetic mechanism function |
| $g(\alpha)$ | integral form of kinetic mechanism function |
| $G$ | Gibbs free energy ($\text{kJ mol}^{-1}$) |
| $H$ | enthalpy ($\text{kJ mol}^{-1}$) |
| $m$ | mass of the glycine (mg) |
| $n$ | reaction order |
| $R$ | gas constant, $8.314\,\text{J}\,(\text{mol K})^{-1}$ |
| $S$ | entropy, $\text{J}\,(\text{mol K})^{-1}$ |
| $t$ | time (s) |
| $T$ | absolute temperature (K) |
| *Greek symbols* | |
| $\alpha$ | conversion degree |
| $\beta$ | heating rate ($\text{K min}^{-1}$) |

$\Delta_m H = 100.50\,\text{J g}^{-1}$), before the glycine sample was analyzed. α-$Al_2O_3$ (standard material, Japan Shimadzu Co.) was used as reference sample in the process of the analysis.

The thermogravimetric measurements were carried out at different heating rates (10, 14, 18, 22 $\text{K min}^{-1}$) from room temperature to 1173.15 K under nitrogen atmosphere (30 $\text{mL min}^{-1}$), using about 4–5 mg of powdered samples. Kinetic parameters were obtained from the thermogravimetric (TG) data using Flynn–Wall–Ozawa(FWO), Doyle, Kissinger and Šatava-Šesták methods.

### 2.3. Theoretical analysis

The kinetic analysis of solid-state thermal decomposition is usually given by Eq. (1) [10]:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

where $d\alpha/dt$ is the rate of conversion. $\alpha$ is the conversion of the reaction which is defined as $\alpha = (m_0 - m_t)/(m_0 - m_f)$, where $m_0$ and $m_f$ are the initial and final masses of the sample at each stage of decomposition, respectively, and $m_t$ is the mass of the sample at time $t$ (or temperature $T$). $f(\alpha)$ is a mathematical model function of kinetics which depends on the reaction type and reaction mechanism. $k(T)$ is the temperature dependent rate constant, which can be described by the Arrhenius Eq. (2):

$$k(T) = Ae^{-E/RT} \tag{2}$$

where $A$ is the pre-exponential factor ($\text{min}^{-1}$), $R$ is the gas constant ($8.314\,\text{J}\,(\text{mol K})^{-1}$), $E$ is the apparent activation energy ($\text{kJ mol}^{-1}$) and $T$ is the absolute temperature (K). By combining Eqs. (1) and (2), moreover, taking into account the heating rate $\beta = dT/dt$ under non-isothermal condition, the kinetic analysis of solid-state thermal decomposition is described by Eq. (3) [11–15]. Based on TG data, kinetic parameters can be obtained from Eq. (3).

$$\frac{d\alpha}{dt} \equiv \beta\frac{d\alpha}{dT} = Ae^{-E/RT}f(\alpha) \quad or \quad \frac{d\alpha}{dT} = \frac{A}{\beta}e^{-E/RT}f(\alpha) \tag{3}$$

Its integral form

$$g(\alpha) = \frac{A}{\beta}\int_0^T e^{-E/RT}dT \tag{4}$$

where

$$g(\alpha) = \int_0^\alpha \frac{1}{f(\alpha)}d\alpha \tag{5}$$

is the integral form of the model function that does not depend on the heating rate used.

#### 2.3.1. Flynn–Wall–Ozawa (F-W-O) method

This method [15] is an integral method, which can determine the activation energy $E$ without the knowledge of reaction order for given values of conversion. The integral form of F-W-O method is represented by Eq. (6).

$$\ln\beta = \ln\left(\frac{AE}{Rg(\alpha)}\right) - 5.330 - 1.0516\frac{E}{RT} \tag{6}$$

Since the value of $\ln(AE/(Rg(\alpha)))$ is approximately constant when the values of $\alpha$ are the same at the different heating rate $\beta_i$, the plot $\ln\beta$ versus $1/T$ is approximately linear. Thus by plotting $\ln\beta$ against $1/T$ at certain conversion rates, the slope ($-1.0516\,E/R$) leads to the activation energy $E$.

#### 2.3.2. Doyle method

The Doyle method [16] is an approximate integral method. It is necessary to get more than three groups of experimental data at different heating rates. The equation is given by Eq. (7).

$$\ln\beta = \ln\left[\frac{AE}{Rg(\alpha)}\right] - 2\ln\frac{E}{RT} - \frac{E}{RT} \tag{7}$$

when $\alpha$ is a constant value, $\ln(AE/(Rg(\alpha)))$ is also a constant value. And the value of $2\ln(E/RT)$ change little, so $\ln\beta$ can be regarded as linear with $1/T$ at different heating rates $\beta$ as long as selecting the same $\alpha$, the $E$ value can be calculated from the slope.

#### 2.3.3. Kissinger method

Kissinger method [11,12,17,18] is expressed by Eq. (8)

$$\ln\frac{\beta_i}{T_{pi}^2} = \ln\left(\frac{A_k R}{E_k}\right) - \frac{E_k}{R}\frac{1}{T_{pi}} \tag{8}$$

where $i = 1$–4,. . . . . . By plotting $\ln(\beta_i/T_{pi}{}^2)$ versus $1/T_{pi}$, $E_k$ and $A_k$ can be calculated based on the slope ($-E_k/R$) and intercept ln ($A_k R/E_k$), respectively.

#### 2.3.4. Šatava-Šesták method

The expression form of Šatava–Šesták method [19] is given by Eq. (9)

$$\ln g(\alpha) = \ln\frac{A_s E_s}{R\beta} - 5.330 - 1.0516\frac{E_s}{RT} \tag{9}$$

where $g(\alpha)$ comes from one of 30 forms of integral formula in the literature [20]. These forms of integral formula are shown in Table 1. For fixed $\beta_i$ ($i = 1, 2, 3, 4, \ldots$), the values of $E_s$ and $A_s$ can be obtained using Eq. (9) at any selected $g(\alpha)$. The calculating steps in detail are: (i) choose the same $\alpha_j$ for each heating rate $\beta_i$, and estimate the corresponding $g(\alpha_{ij})$, (ii) find out the corresponding absolute temperature $T_{ij}$ according to $\alpha_{ij}$,. (iii) describe the sketch of $\lg(\alpha)$ versus $1/T_{ij}$ for each fixed $\beta_i$, and calculate the values of both $E_s$ and $\ln(A_s)$ according to the slope ($-1.0516E_s/R$) and intercept ($\ln(A_s E_s/R\beta_i) - 5.330$) of the line, respectively. (iv) determine the mechanism function of the reaction. Generally, the mechanism functions are kept as long as meeting the condition of $0 < E_s < 400\,\text{kJ mol}^{-1}$. Then the values of $E_s$ and $\ln(A_s)$ obtained based on the mechanism functions compare with the values of $E_0$ and $\ln(A_k)$, respectively. If the values of $E_s$ and $\ln(A_s)$ meet with $\left|(E_0 - E_s)/E_0\right| \leq 0.1$ and $\left|(\ln A_s - \ln A_k)/\ln A_s\right| \leq 0.46$, in which $E_0$ and $\ln(A_k)$ come from Flynn–Wall–Ozawa or Doyle method and Kissinger method, respectively, the $g(\alpha)$ will be an integral form of the most probable mechanism function of the reaction.