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Study on thermal decomposition and the non-isothermal decomposition kinetics of glyphosate

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Abstract The thermal decomposition process and non-isothermal decomposition kinetic of glyphosate were studied by the Differential thermal analysis (DTA) and Thermogravimetric analysis (TGA). The results showed that the thermal decomposition temperature of glyphosate was above 198 °C. And the decomposition process was divided into three stages: The zero stage is the decomposition of impurities, and the mass loss in the first and second stage may be methylene and carbonyl, respectively. The mechanism function and kinetic parameters of non-isothermal decomposition of glyphosate were obtained from the analysis of DTA–TG curves by the methods of Kissinger, Flynn–Wall–Ozawa, Distributed activation energy model, Doyle and Šatava-Šesták, respectively. In the first stage, the kinetic equation of glyphosate decomposition obtained showed that the decomposition reaction is a Valensi equation of which is two-dimensional diffusion, 2D. Its activation energy and pre-exponential factor were obtained to be 201.10 kJ mol^{-1} and 1.15×10^{19} s^{-1}, respectively. In the second stage, the kinetic equation of glyphosate decomposition obtained showed that the decomposition reaction is a Avrami–Erofeev equation of which is nucleation and growth, and whose reaction order (n) is 4. Its activation energy and pre-exponential factor were obtained to be 251.11 kJ mol^{-1} and 1.48×10^{21} s^{-1}, respectively. Moreover, the results of thermodynamical analysis showed that enthalpy change of $\Delta H^{\neq}$, entropy change of $\Delta S^{\neq}$ and the change of Gibbs free energy of $\Delta G^{\neq}$ were, respectively, 196.80 kJ mol^{-1},107.03 J mol^{-1} K^{-1}, and 141.77 kJ mol^{-1} in the first stage of the process of thermal decomposition; and 246.26 kJ mol^{-1},146.43 J mol^{-1} K^{-1}, and 160.82 kJ mol^{-1} in the second stage.

Keywords Glyphosate · Thermal decomposition · Non-isothermal decomposition kinetics · Thermogravimetric analysis

Abbreviations

A	Pre-exponential factor of the Arrhenius equation, s^{-1}
E	Activation energy, kJ mol^{-1}
$f(\alpha)$	Differential form of kinetic mechanism function
$G(\alpha)$	Integral form of the kinetic mechanism function
n	Reaction order
R	Universal gas constant, 8.3145 J K^{-1} mol^{-1}
t	Time, s
T	Absolute temperature, K
m	Mass of the glyphosate, %
α	Fractional conversion
β	Heating rate, °C min^{-1}
Subscript, i	i-set of experimental data
k	Action rate constant, s^{-1}

Introduction

Glyphosate (*N*-carboxy methyl phosphonic glycine, CAS RN 1071-83-6) is a highly effective herbicide, widely used in agricultural production [1]. Glyphosate formula is $(HO)_2P(O)CH_2NHCH_2COOH$, experimental formula is

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$C_3H_8NO_5P$, the relative molecular mass of glyphosate is 169.1. It has such characteristics and properties of white crystalline, non-volatile, insoluble in ethanol, ether and benzene, and other organic solvents. And its isopropylamine salt dissolves in water. To study the process of thermal decomposition and deduce the possible mechanism of thermal decomposition model and get the dynamic equation of thermal decomposition, the DTA-TG curves of glyphosate were investigated in temperature programmed with thermal gravity-differential thermal analysis. Although glyphosate is widely used, several of its important thermodynamic and kinetic data are scarce, and the research of the thermal decomposition process and its kinetics has not been reported. Therefore, this study can be used for further development and provide basic data for glyphosate.

Experiment

Experimental apparatus

DTG-60 coupled with thermogravimetric-differential thermal analyzer and DSC-60 differential scanning calorimeter (Japan Shimadzu Corporation); SPN-500-type nitrogen generator (Hewlett-Packard, Beijing Institute of Technology).

Experimental drugs

95% purity of glyphosate (from a factory in Zhejiang, China); α-Al_2O_3(α-Al_2O_3 Power for DTG Standard Material, Japan Shimadzu Corporation).

Experimental conditions

The measurements were made under fixed conditions of which was the constant heating rate of β (2, 4, 6, 8 °C min^{-1}) from room temperature to 500 °C, and the sample was 1.7–2.7 mg, under nitrogen atmosphere (20 mL min^{-1}). α-Al_2O_3 (standard material, Japan Shimadzu Co.)was used as reference sample in the process of the analysis. Before the samples were analyzed, the DTG-60 was calibrated with indium (purity = 99.99%, $T_m = 429.78$ K, $\Delta_m H = 28.45$ J g^{-1}) and zincum (purity = 99.99%, $T_m = 419.58$ K, $\Delta_m H = 100.50$ J $g^{-1)}$ (Japan Shimadzu Co.). Data acquisition and online processing were done with TA-60WS Collection Monitor software.

Theoretical part

Assume that the initial amount of the sample is m_o, the mass becomes m when that is decomposed at a time of t at a heating rate of β (°C min^{-1}), then the decomposition rate can be expressed by Eq. 1 [2–7]:

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

Where $\alpha = (m_o - m)/(m_o - m_\infty)$ is the degree of decomposition at the time of t, namely the conversion rate; m_∞ is the residual mass(mg) in the end of thermal decomposition of the sample; E is the activation energy(J mol^{-1}); A is frequency factor, namely the pre-exponential factor (min^{-1}); R is the gas constant (J $(\text{mol K})^{-1}$); T is the absolute temperature(K); $f(\alpha)$ is the kinetic function model, whose function depends on the reaction type and reaction mechanisms.

Flynn–Wall–Ozawa (F–W–O) method

The F–W–O equation of integral formula [2–6, 8] is showed in Eq. 2:

$$\lg\beta = \lg\left(\frac{AE}{RG(\alpha)}\right) - 2.315 - 0.4567\frac{E}{RT} \tag{2}$$

The method has the advantage of which obtains directly E values. Therefore, F–W–O method is often used to test the activation energy values of which is obtained by other methods that need assume the reaction mechanism functions. It is notable that the value of E/RT is not less than 13, when the F–W–O method was used to calculate the E.

Doyle method

Doyle method [9] is an approximate integral method and requires more than three β values. Finishing the original equation can be obtained by Eq. 3:

$$\ln\beta = \ln\left[\frac{AE}{RG(\alpha)}\right] - 2\ln\frac{E}{RT} - \frac{E}{RT} \tag{3}$$

When α is a constant, $f(\alpha)$ is a constant and the value of $2\ln\frac{E}{RT}$ change little, so lnβ is linear with $1/T$ in different heating rates β as long as selecting the same α, the activation energy E can be calculated by the slope.

Distributed activation energy model (DAEM)

DAEM [10, 11] based on the following two assumptions: (i) Reaction system consists of numerous independent composition, and these reactions have different activation energy, that is, assuming infinite parallel reaction; (ii) Each response shows some continuous distribution for the function forms of activation energy, namely the activation energy distribution hypothesis. The original equation simplified [11] is given with Eq. 4:

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\frac{k_0 R}{E} + 0.6075 - \frac{E}{RT} \tag{4}$$

E and k_0 can be obtained by plotting of $\ln(\frac{\beta}{T^2})$ vs. $1/T_0$

Kissinger method

This expression formula of Kissinger method is given in Eq. 5 [2, 3, 12, 13]

$$\ln\frac{\beta_i}{T^2_{\max i}} = \ln\left(\frac{A_k R}{E_k}\right) - \frac{E_k}{R}\frac{1}{T_{\max i}} \tag{5}$$

where $i = 1, 2,\ldots,4$ (or 5, 6). E_k and A_k can be calculated by plotting of $\ln\frac{\beta_i}{T^2_{\max i}}$ vs. $\frac{1}{T_{\max i}}$.

Šatava-Šesták method [14–16]

The original equation changed is given by the general formula

$$\lg G(\alpha) = \lg\frac{A_\mathrm{s} E_\mathrm{s}}{R\beta} - 2.315 - 0.4567\frac{E_\mathrm{s}}{RT} \tag{6}$$

In the Eq. 6, $G(\alpha)$ comes from one of 30 forms of integral formula in literature [18]. For every fixed β_i ($i = 1, 2, 3,\ldots,\mathrm{L}$) and each mechanism functions $G(\alpha)$, E_s and A_s can be calculated using Šatava-Šesták method, respectively. In general, only by meeting condition of $0 < E_\mathrm{s} < 400$ kJ mol^{-1}, those of G(α) are kept; and it is necessary that E_s calculated compare with E_0 calculated by Flynn–Wall–Ozawa method, respectively. If E_s meets with the condition of $\left|\frac{E_0 - E_\mathrm{s}}{E_0}\right| \leq 0.1$, the E_s is acceptable; and those lg (A_s) calculated need to be compared with E_0 those calculated by Kissinger method, if lg (A_s) meets with the conditions of $\left|\frac{\lg A_s - \lg A_k}{\lg A_k}\right| \leq 0.2$, so is the lg ($A_\mathrm{s}$). If $G(\alpha)$ meets the requirements above-mentioned, then the correlation coefficient and residual variances can be calculated.

Calculation of parameters of thermodynamic model

After E and A is obtained by using non-isothermal method, the thermodynamic parameters of them can be calculated with Eqs. 7–9 [16, 17]:

$$A\mathrm{e}^{\left(-\frac{E}{RT}\right)} = \nu\mathrm{e}^{\left(-\frac{\Delta G^{\neq}}{RT}\right)} = \frac{kT}{h}\mathrm{e}^{\left(-\frac{\Delta G^{\neq}}{RT}\right)} \tag{7}$$

$$\Delta H^{\neq} = E - RT \tag{8}$$

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \tag{9}$$

where ν is Einstein vibration frequency; k is Boltzmann constant, 1.3807×10^{-23}; T is the absolute temperature (K); h is Planck constant, 6.625×10^{-34} J s^{-1}. $\Delta H^{\neq}$, $\Delta S^{\neq}$, and $\Delta G^{\neq}$ are the enthalpy change, entropy change, and the change in Gibbs free energy in the thermal decomposition process, respectively.

Results of data processing and discussion

Discussion of thermal decomposition of glyphosate

Figure 1 shows the curves of DTA and TG of glyphosate, in which the heating rate is 6 °C min^{-1} for example. And it reveals that the process of thermal decomposition have four stags (0–3 stages). The digital signature of them was written successively: the zero endothermic peak, the first endothermic peak, the second exothermic-endothermic conversion peak, and the third exothermic peak. The total percentage (wt%) of decomposition was less than 65% as the maximum temperature was lower than 500 °C. The curves of DTA and TG of glyphosate showed that were obviously incomplete in the temperature range so the third stage peak was left out of account.

From Table 1, the results show that the thermal behavior is:

i. The zero stage could be determined to be the decomposition process of mass lost of impurities in the sample of glyphosate. The reasons are that the melting temperature of glyphosate is nearly 230 °C, but the experiment result showed that there was a stage of mass loss in the temperature among of 190–220 °C. On the other hand, the purity (95%) of glyphosate sample

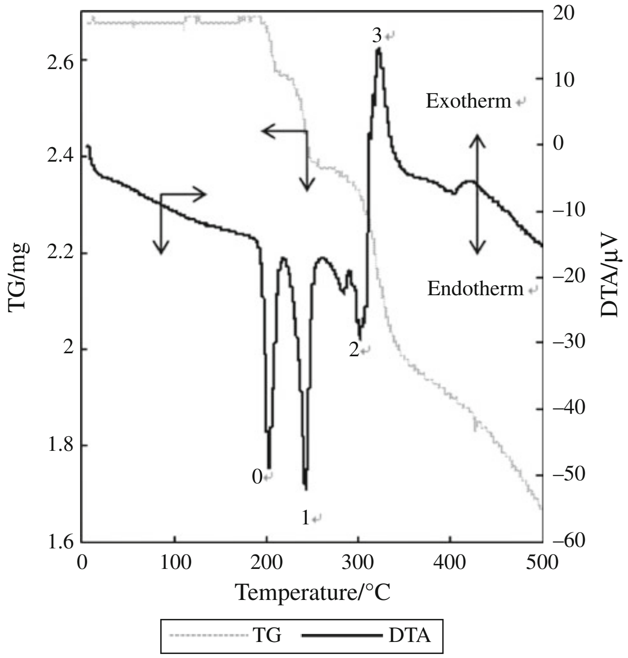

Fig. 1 Thermal analysis results of DTA and TG for glyphosate

Table 1 The experimental data of mass loss in the different heating rates

Heating rate	2 °C min^{-1}	4 °C min^{-1}	6 °C min^{-1}	8 °C min^{-1}	Average	ΔT/°C
Zero stage/%	4.036	4.259	4.247	4.469	4.253	198–220
First stage/%	8.386	8.518	7.750	7.186	7.960	230–253
Second stage/%	15.776	15.886	15.797	15.700	15.790	261–349

The purity of glyphosate is 95%

used, and the experimental data of mass loss of 5% met well with the amount of impurities.

ii. In the first stage of hot mass loss, the initial temperature was at around 230 °C, so the result demonstrated that the decomposing phenomenon occurred with the melting process of glyphosate. By analyzing the infrared spectrum of the sample which is processed by rising temperature to 260 °C at the heating rate of 6 °C min^{-1}, the most possible group loss in this stage may be methylene. Moreover, the mass loss in the first stage by TGA is in accordance with the mass loss of a group of methylene in the molecular of glyphosate.

iii. With the temperature increased, the second stage appeared the exothermic peak after a smaller main endothermic peak, and the lost mass had continued, which indicated that this stage might occur burning phase, thus exothermic phenomenon occurred. By analyzing the infrared spectrum of the sample which is processed by rising temperature to 360 °C at the heating rate of 6 °C·min^{-1}, the most possible group loss in this stage may be the group of carbonyl. Moreover, the mass loss in the second stage by TGA is in accordance with the mass loss of a carbonyl in the molecular of glyphosate.

Determination of kinetic parameters of thermal decomposition process

The thermal kinetic behavior of the first and second stages was investigated in this article, and it was calculated with the methods of Kissinger, F–W–O, DAEM, and Doyle by the value interval on level decomposition, respectively. And Šatava-Šesták method was used to optimize the mechanism equation of each process of hot lost mass. In the process of thermal decomposition, the kinetic parameters of glyphosate are given in Table 2 by Kissinger method and in Table 3 by the methods of F–W–O, DAEM, and Doyle, respectively. The results showed that the activation energy values is between 197.11 and 207.60 kJ mol^{-1} in the first stage, and the activation energy decreased with the conversion rate of glyphosate increasing. The activation energy and pre-exponential factor of which all of these mechanism functions in literature [18] were calculated by Šatava-Šesták method for each stage. By comparing E and ln$A$ in the table, the most probable mechanism function could be identified.

Table 2 The activation energy and pre-exponential factor by Kissinger method

Peak number	E_k/kJ mol^{-1}	lg (A)	R^2
First peak	307.73	31.06	0.9953
Third peak	124.49	10.38	0.9625

Kissinger method uses the third peak in the second stage

By comparing all of these activation energies calculated by three methods could be found that the values of activation energy by Doyle method were slightly higher than DAEM method, and results of DAEM method were slightly higher than the F–W–O method. And the correlation coefficients (R^2) were better. In the first stage, by comparison with average of activation energy calculated in Table 3 and the values of activation energy calculated by Šatava-Šesták method, the fact was gotten that the thermal behavior of glyphosate in the stage may be consistent with the thermal decomposition mechanism of which is the Valensi equation in literature [18]. So the mechanism can be described as the two-dimensional diffusion, 2D, and the forms of integral and differential for the mechanism function are given by $f(\alpha) = -[\ln(1-\alpha)]^{-1}$ and $G(\alpha) = \alpha + (1-\alpha)\ln(1-\alpha)$, respectively. And the results list in Table 4.

In the second stage, by comparison with average of activation energy calculated in Table 3 and the values of activation energy calculated by Šatava-Šesták method, the results listed in Table 4, showed that the thermal decomposition mechanism of glyphosate in the second stage may be a Avrami–Erofeev equation, of which is nucleation and growth, and its reaction order n is 4, $f(\alpha) = \frac{1}{4}(1-\alpha)[-\ln(1-\alpha)]^{-3}$ and $G(\alpha) = [-\ln(1-\alpha)]^{4}$

Compensation effect of non-isothermal decomposition kinetic of glyphosate

Usually, the phenomenon of a linear relationship between ln$A$ and E is known as kinetic compensation effect. The mathematical expression [4, 7]:

Table 3 The activation energy by F–W–O, DAEM, and Doyle method

Stages	F–W–O method		DAEM method		Doyle method		Average
	E/kJ mol^{-1}	R^2	E/kJ mol^{-1}	R^2	E/kJ mol^{-1}	R^2	E/kJ mol^{-1}
First	197.11	0.9837	199.12	0.9827	207.60	0.9841	201.28
Second	269.09	0.9984	273.29	0.9983	282.98	0.9984	274.89

Table 4 The results of the activation energy and pre-exponential factor by Šatava-Šesták method for the first and the second stages

Stages	Name of function	$\beta = 2$ °C min^{-1}			$\beta = 4$ °C min^{-1}			$\beta = 6$ °C min^{-1}			$\beta = 8$ °C min^{-1}			Average	
		E	lg$A$	R^2	E	lg$A$	R^2	E	lg$A$	R^2	E	lg$A$	R^2	E	lg$A$
First	Valensi equation	188.85	17.18	0.9874	196.19	17.74	0.9844	217.18	19.78	0.9857	209.95	18.80	0.9754	203.04	18.38
Second	Avrami–Erofeev, $n = 4$	181.89	14.76	0.9789	222.81	18.34	0.9912	279.51	23.33	0.9882	231.51	18.55	0.9888	228.93	18.75

Table 5 The parameters of kinetic compensation effect

Stages		a	b	R^2
Second	Šatava-Šesták method	0.0003	−12.207	0.9987
	DAEM method	0.0003	−19.853	1.0000
Third	Šatava-Šesták method	0.00009	−1.2868	0.9936
	DAEM method	0.0002	−0.0836	1.0000

Table 6 Thermodynamic parameters for the decomposition stage of Glyphosate

Stages		E_a/kJ mol^{-1}	lg (A)	$\Delta S^{\neq}$/J (mol K)$^{-1}$	ΔG/kJ mol^{-1}	$\Delta H^{\neq}$/kJ mol^{-1}
First	Šatava-Šesták method	203.04	18.38	94.10	150.37	198.76
	DAEM method	199.12	19.73	119.95	133.17	194.84
	Average	201.10	19.06	107.03	141.77	196.80
Second	Šatava-Šesták method	228.93	18.75	100.04	165.70	224.08
	DAEM method	273.29	23.59	192.81	155.93	268.44
	Average	251.11	21.17	146.43	160.82	246.26

$$\ln A = aE + b \tag{10}$$

where a and b is thought of as the compensation parameters, the unit of a is J mol^{-1}.

In order to investigate the relationship between ln$A$ and E, the values of a and b in Eq. 10 were obtained using least-square method for linear fitting, and are showed in Table 5.

Thermodynamic analysis

From Table 6, it shows that the apparent activation energy of decomposition of glyphosate (E) is 201.10 and 251.11 kJ mol^{-1} in the first and second stages, respectively, and the pre-exponential factor (A) is 1.15×10^{19} and 1.48×10^{21} s^{-1}, respectively. The apparent activation energy of glyphosate (E) is so large that the decomposition of glyphosate possesses higher thermal stability. Moreover, according to equations of 7–9 and E and A calculated, the thermodynamic parameters of glyphosate at the peak temperature were calculated and listed in Table 6. It can be seen that enthalpy ($\Delta H^{\neq}$), entropy change ($\Delta S^{\neq}$), and Gibbs free energy ($\Delta G^{\neq}$) are 196.80 kJ mol^{-1}, 107.03 J mol^{-1} K^{-1}, and 141.77 kJ mol^{-1} in the first stage, respectively, and 246.26 kJ mol^{-1},146.43 J mol^{-1} K^{-1}, and 160.82 kJ mol^{-1} in the second stage.

Conclusions

Using the thermal analysis of the Differential thermal analysis (DTA) and Thermogravimetric Analysis (TGA), the decomposition process was divided into three stages: the zero stage is the decomposition of impurities, and the mass loss in the first and second stage may be the groups of methylene and carbonyl, respectively, and the mechanism of thermal decomposition in the first stage was determined to be the Valensi equation, two-dimensional diffusion, 2D; in the second stage, it was determined to be an Avrami–Erofeev equation of which is nucleation and growth, and whose reaction order (*n*) is 4. The apparent activation energy and the pre-exponential factor of glyphosate were calculated to be 201.10 kJ mol^{-1} and 1.15×10^{19} s^{-1} in the first stage, respectively; and 251.11 kJ mol^{-1} and 1.48×10^{21} s^{-1} in the second stage. For thermodynamics properties of enthalpy ($\Delta H^{\neq}$), entropy change ($\Delta S^{\neq}$), and Gibbs free energy ($\Delta G^{\neq}$) are orderly 196.80 kJ mol^{-1}, 107.03 J $(\mathrm{mol\ K})^{-1}$, and 141.77 kJ mol^{-1} in the first stage; and 246.26 kJ mol^{-1},146.43 J mol^{-1} K^{-1}, and 160.82 kJ mol^{-1} in the second stage, in turn.

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