

Thermal Degradation Kinetics of *N,N'*-Di(diethoxythiophosphoryl)-1,4-phenylenediamine

REN Yuan-lin^{1,2*}, CHENG Bo-wen², ZHANG Jin-shu², JIANG Ai-bing² and FU Wen-li²

1. School of Textile, 2. Tianjin Municipal Key Laboratory of Fiber Modification and Functional Fiber, Tianjin Polytechnic University, Tianjin 300160, P. R. China

Abstract The non-isothermal degradation kinetics of *N,N'*-di(diethoxythiophosphoryl)-1,4-phenylenediamine in N_2 was studied by TG-DTG techniques. The kinetic parameters, including the activation energy and pre-exponential factor of the degradation process for the title compound were calculated by means of the Kissinger and Flynn-Wall-Ozawa(FWO) method and the thermal degradation mechanism of the title compound was also studied with the Satava-Sestak methods. The results indicate that the activation energy and pre-exponential factor are 152.61 kJ/mol and $9.06 \times 10^{14} \text{ s}^{-1}$ with the Kissinger method and 154.08 kJ/mol with the Flynn-Wall-Ozawa method, respectively. It has been shown that the degradation of the title compound follows a kinetic model of one-dimensional diffusion or parabolic law, the kinetic function is $G(\alpha)=\alpha^2$ and the reaction order is $n=2$.

Keywords *N,N'*-Di(diethoxythiophosphoryl)-1,4-phenylenediamine; Thermal degradation kinetics; Activation energy; Mechanism

1 Introduction

In recent studies, phosphorus-, nitrogen-, and silicon-containing compounds are considered as environment-friendly fire-retardants(FRs), because their generations bring no or less harm to ecology when they are burning in a fire^[1–9], so there is a rapid development of this type of FRs. Sulfur-containing compounds are another type of effective FRs^[10–14], although few researches have been directed to them. However, many applications of new FRs are limited, because of the synthesis method, the cost and the flame retardant elements coming from various compounds. There are less studies on the FR, which contains phosphorus, nitrogen and sulfur simultaneously in recent years' reports^[10,11,15–17]. *N,N'*-Di(diethoxythiophosphoryl)-1,4-phenylenediamine contains phosphorus, nitrogen and sulfur fire-resistant elements. Its synthesis, characterization^[18], crystal structure^[11] have been reported. Compared to the usual FRs, *N,N'*-Di(diethoxythiophosphoryl)-1,4-phenylenediamine has rich acid and carbon sources; it can perform its flame retardancy in the condensed phase and gas phase and increase the amount of carbonaceous residue or char

rather than the formation of poisonous halides, CO, CO₂ or other compounds during the process of decomposition, which can hinder the transfer of mass and heat during a fire and can provide materials with flame retardancy. In this article, its thermal decomposition is explored, because it can, in many cases, be used to determine the upper temperature limit of a material used. The kinetics of the decomposition of the title compound was examined in detail with TG-DTG methods. It is quite useful for the evaluation of the thermal stability of the title compound under a non-isothermal condition in the study of its thermal changes at high temperatures. Thermal decomposition of the title compound undergoes intrinsic chemical reaction steps for the preparation of the products, the investigation into the kinetics is important for optimizing the process and achieving good material properties; it is also necessary for numerical simulation of the decomposition process. To improve the understanding in stabilization or degradation control of the product, it is essential to reveal reactivity of the components, and thermal decomposition kinetics of the product. The data from the thermogravimetric expe-

*Corresponding author. E-mail: yuanlinr@163.com

Received October 25, 2007; accepted January 15, 2008.

Supported by the China Petroleum & Chemical Science and Technology Foundation(No.205026) and the Tianjin Science and Technology Plan Foundation, China(No.06TJTJC14400).

riments provide an important information about the stability of the product and the calculated values of the activation energy can be used as an alternative to the accelerated stability test results in predicting the life of the product, on the basis of which thermal stability and thermal decomposition mechanism of the title compound can thus be obtained.

2 Experimental

2.1 Material

N,N'-Di(diethoxythiophosphoryl)-1,4-phenylenediamine was synthesized according to the method reported in reference [11], and recrystallized from acetone.

2.2 Experimental Apparatuses and Conditions

The TG and DTG analyses for the title compound were conducted on a NETZSCH STA 409 PG/PC type thermal analyzer under the following conditions: atmosphere: pure nitrogen at a flow rate of 20 mL/min; sample mass: (11.5±0.1014) mg; heating rate: $\beta=5, 10, 15, 20$ K/min; temperature range: from room temperature to 900 °C; reference material: Al₂O₃.

2.3 Kinetic Methods

According to the reaction theory, kinetic equation for solid degradation, $B(s) \rightarrow D(s) + C(g)$ is usually expressed as

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (1)$$

where, α is the extent of conversion of B decomposed at time t , $f(\alpha)$ is the reacting mechanism function, k is the reaction rate constant, and obeys an Arrhenius equation:

$$k = A \exp(-E/RT) \quad (2)$$

where, A is the pre-exponential factor, E is the apparent activation energy, R is the gas constant, and T is the absolute temperature. Combining Eq.(1) with Eq.(2) gives the following relationship:

$$\frac{d\alpha}{dt} = A \exp(-E/RT) f(\alpha) \quad (3)$$

If the heating rate constant is $\beta = dT/dt$, then the reaction rate is defined as follows:

$$\frac{d\alpha}{dT} = (A/\beta) \exp(-E/RT) f(\alpha) \quad (4)$$

In this article, Kissinger method^[19], Flynn-Wall-Ozawa method^[20–22] and Satava-Sestak method^[23] were used to study the degradation kinetics of the title

compound.

The Kissinger equation and the Flynn-Wall-Ozawa equation are listed, respectively, as follows:

$$\ln \frac{\beta}{T_p^2} = \ln \frac{AR}{E} - \frac{E}{RT_p} \quad (5)$$

where, T_p is the temperature at the maximum weight loss.

$$\ln \beta = \lg \left[\frac{AE}{RG(\alpha)} \right] - 2.315 - 0.4567 \frac{E}{RT} \quad (6)$$

where, $G(\alpha)$ is the integral function of conversion.

Rearranging Eq.(6), the Satava-Sestak equation, is obtained

$$\ln G(\alpha) = \lg \left[\frac{A_s E_s}{R\beta} \right] - 2.315 - 0.4567 \frac{E_s}{RT} \quad (7)$$

When plotting $\lg \beta$ vs. $1/T$, E_o can be obtained. Thirty types of kinetic model functions^[24] were used in Satava-Sestak. The E_s and A_s and linear correlation coefficients r of different model functions were calculated from a plot of $\lg G(\alpha)$ vs. $1/T$.

3 Results and Discussion

3.1 Degradation Process of the Title Compound

The TG-DTG curves of the title compound are shown in Figs.1 and 2.

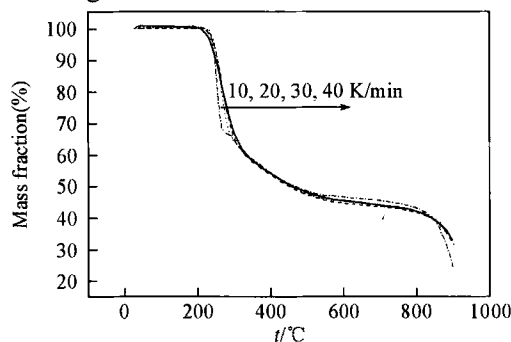


Fig.1 TG curves of the title compound in N₂ at different heating rates

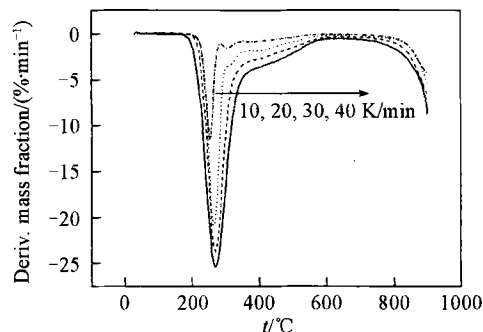


Fig.2 DTG curves of the title compound in N₂ atmosphere at different heating rates

From Fig.1, it can be seen that the original degradation temperatures are all over 280 °C at the dif-

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