Thermal Kinetics and Decomposition Mechanism of Methylphenylphosphinic Acid and Diphenylphosphinic Acid

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Abstract Thermal degradation and degradation kinetics of methylphenylphosphinic acid(MPPA) and diphenyl-phosphinic acid(DPPA) were investigated *via* thermogravimetric analysis(TGA) technique under non-isothermal conditions. The activation energies of the decomposition process for the two compounds were calculated through the Friedman and Kissinger-Akahira-Sunose(KAS) methods. The thermal decomposition mechanism was investigated by the Criado method based on a set of TGA data obtained at different heating rates. It was shown that the activation energies calculated from the decomposition reaction by different methods were consistent with each other. The results show that the probable model for the degradation of MPPA and DPPA agreed with the two-dimensional(D_2) and three-dimensional(D_4) diffusion models, respectively. Moreover, the thermodynamic functions($\Delta H^{\neq}$, $\Delta S^{\neq}$, $\Delta G^{\neq}$) of the two decomposition reactions were also calculated.

Keywords Organophosphinic acid; Thermogravimetric analysis; Thermal degradation; Kinetics

1 Introduction

Organophosphinic acid compounds include those containing direct P—C and P—OH linkages. They are extensively applied in medicinal chemistry, and used as agricultural chemicals, flame-retardants for fabrics and plastics, corrosion inhibitors, and selective extractants of metal salts from ores[1]. Methylphenylphosphinic acid(MPPA, CAS RN 4271-13-0, Fig.1) is usually used as polymer's additive. Compositions based on branched polyamides including MPPA exhibit good fire resistance, mechanical properties, and heat resistance[2]. Polyimides and polyquinoxalines were modified by MPPA and molded to give self-lubricating antifriction materials with good hardness, flexibility, and reduced wear at the elevated temperature[3]. Besides, they are also used as coatings and applied in bifunctional catalysis for organic reactions of arylamine[4,5]. Diphenylphosphinic acid(DPPA, CAS RN 1707-03-5, Fig.1) and its anhydride have been widely used as a reactive flame-retardant in epoxy resin based laminates for printed circuit boards[6,7]. Recently, DPPA has been utilized as an efficient promoter for the palladium catalytic systems[8—11]. Attention has also been paid to the chemistry of molecular

assemblies including host-guest complexes between the DPPA derivative and amine-containing hosts[12].

In view of the productions and applications of these materials, further studies should be focused on determining the thermal stability as well as the better understanding of the mechanism and kinetics involved in the thermal degradation of them. Thermogravimetric analysis(TGA) is one of the most commonly used methods to estimate the kinetic parameters of degradation processes, such as activation energies(E), Arrhenius pre-exponential factor(A), and the kinetic model $f(\alpha)$, which can be calculated *via* various kinetic methods[13,14]. Kinetic data obtained from TGA are very useful to help us understand the thermal degradation processes and mechanisms, which may also be utilized as parameters to input into a model of thermal degradation reaction. Nguyen *et al.*[15] investigated the relationship between the structure and stability of some phosphorus compounds by TGA under N_2 atmosphere. However, they did not study the thermal properties and decomposition kinetics of MPPA and DPPA.

In this work, the thermal degradation of MPPA and DPPA was studied under nitrogen atmosphere at different heating rates. The kinetic parameters for their thermal degradation were evaluated with the data processing performed by using well-known methods, *i.e.*, Friedman's isoconversional method[16] and Kissinger-Akahira-Sunose method(KAS method)[17,18]. The kinetic model for the degradation process was investigated by Criado method based on different solid state mechanisms. The thermodynamic parameters($\Delta H^{\neq}$, $\Delta S^{\neq}$, $\Delta G^{\neq}$) of the thermal decomposition reaction of MPPA and DPPA were also derived.
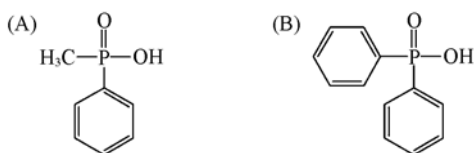
Fig.1 Chemical structures of MPPA(A) and DPPA(B)

2 Experimental

2.1 Materials and Measurement

MPPA(98%, mass fraction) and DPPA(99%, mass fraction) were purchased from Aldrich, which are all white crystallines. Thermogravimetric analyses of all the materials were carried out on an SDT Q600 analyser(TA Instruments, USA). The thermal analysis apparatus was calibrated by measuring the TG and DTG curves of a standard specimen, such as indium (99.99%) or zinc(99.99%) before the sample was analysed. Al_2O_3 was used as a reference material in the process of the analysis. Samples(3—5 mg) were heated from ambient temperature to 600 °C at various heating rates of 5, 10, 20 and 40 °C/min. A high purity nitrogen stream was continuously passed into the furnace at a flow rate of 100 mL/min. Based on the original mass loss dependence on the temperature the first derivative data, *i.e.*, DTG were accordingly obtained.

2.2 Theoretical Approach for Kinetic Study

According to non-isothermal kinetic theory, the kinetic equation of thermal analysis[19] can be expressed as follows:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) f(\alpha) \qquad (1)$$

where α is the extent of conversion; β(°C/min) is the heating rate; $A(s^{-1})$ is the pre-exponential factor; E(kJ/mol) is the apparent activation energy; T(K) is the absolute temperature; R(8.314 J·mol^{-1}·K^{-1}) is the gas constant.

2.2.1 Friedman's Isoconversional Method

This method[16] is a differential isoconversional method, which is based on the following natural logarithmic equation:

$$\ln\left(\beta \frac{d\alpha}{dT}\right) = \ln\left[Af(\alpha)\right] - \frac{E}{RT} \qquad (2)$$

Hence, a plot of $\ln(\beta d\alpha/dT)$ *vs.* $1/T$ at each α gives E from the slope of the plot.

2.2.2 Kissinger-Akahira-Sunose Method

KAS method[17,18] is an integral isoconversional linear method, the equation is expressed as

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\frac{AE}{g(\alpha)R} - \frac{E}{RT} \qquad (3)$$

where $g(\alpha)$ is the integral form of the reciprocal of $f(\alpha)$, which is the reaction model and depends on the reaction mechanism, $g(\alpha) = \int_0^\alpha d\alpha/f(\alpha)$. From Eq.(3), the plot of $\ln(\beta/T^2)$ *vs.* $1/T$ can be made and activation energy is calculated from the slope of the plot at different conversion.

2.2.3 Mechanism Model

In order to find the reaction kinetic model of the thermal degradation, the Criado method was chosen as it involves degradation mechanisms. The used model and expressions of associated functions $f(\alpha)$ and $g(\alpha)$ were obtained from the literatures[19,20]. The $z(\alpha)$ master plots were derived by combining the differential and integral forms of the reaction models[19]. The kinetic model of the process can be determined by the introduced $z(\alpha)$ function:

$$z(\alpha) = f(\alpha)g(\alpha) = \left(\frac{d\alpha}{dt}\right)_\alpha T_\alpha^2 \left[\frac{\pi(x)}{\beta T_\alpha}\right] \qquad (4)$$

where $x=E/RT$, $\pi(x)$ is the functions of temperature integral formula, T_α(K) is the temperature at a given extent of conversion. It has been established[21] that the term in the brackets of Eq.(4) has a negligible effect on the shape of the $z(\alpha)$ function. The theoretical $z(\alpha)$ plots are obtained by plotting the product $f(\alpha)g(\alpha)$ against α for different reaction models. By comparing experimental $z(\alpha)$-α curves with theoretical ones, the wanted $f(\alpha)$ would be determined if experimental $[\alpha, z(\alpha)]$ values were all fallen on the theoretical master plots. Once the reaction model has been identified, the pre-exponential factor is determined from the following equation[19]:

$$A = \frac{-\beta E_0}{RT_{max}^2 f'(\alpha_{max})} \exp\left(\frac{E_0}{RT_{max}}\right) \qquad (5)$$

where subscript max denotes the value related to the maximum of the differential kinetic curve obtained at a given heating rate.

2.2.4 Estimation of the Thermodynamic Functions

After the values of E and A have been obtained, thermodynamic parameters($\Delta H^{\neq}$, $\Delta S^{\neq}$, $\Delta G^{\neq}$) of the reaction can be calculated by Eqs.(6), (7) and (8)[22—24]:

$$Ae^{(-E/RT)} = ve^{(-G^{\neq}/RT)} = \frac{kT}{h}e^{(-G^{\neq}/RT)} \qquad (6)$$

$$\Delta H^{\neq} = E^{\neq} - RT_p \qquad (7)$$

$$\Delta G^{\neq} = \Delta H^{\neq} - T_p\Delta S^{\neq} \qquad (8)$$

where A is the pre-exponential factor; e=2.7183 is the Neper number; k is the Boltzmann constant; h is the Plank constant and v is the Einstein vibration frequency. The thermodynamic paremeters including the enthalpy of activation($\Delta H^{\neq}$), the entropy of activation($\Delta S^{\neq}$), the Gibbs free energy of activation decomposition($\Delta G^{\neq}$) were calculated at $T=T_p$(T_p is the DTG peak temperature at the corresponding stage), since this temperature characterizes the highest rate of the degradation, and therefore, is an important parameter.

3 Results and Discussion

3.1 Thermal Degradation

Fig.2 shows the TG and DTG curves of MPPA and DPPA, corresponding to dynamic experiments carried out at different heating rates(5, 10, 20 and 40 °C/min). All the curves are approximately the same shape and indicate the mass loss independent of the heating rate. All the TG curves show that a single step degradation with well-defined initial degradation temperatures(T_{onset}), final degradation temperatures(T_{endset}) and maximum degradation temperature(T_{max}). The data obtained from TG and DTG curves at different heating rates are listed in Table 1. Additionally, the decomposition stage is shifted toward higher temperature when the heating rate increase. The mass loss of the sample during thermal degradation is a function of degradation rate and time. Comparing MPPA with DPPA, one can notice that although they both are phosphinic acids, DPPA with phenyl group attached to phosphorus element exhibits higher thermal degradation temperature than MPPA combined with methyl group. This can be explained by considering the

bond strength of the pendant attached to P atom. Note that the bond strengths of different pendants are in the order of P—C$_6$H$_5$>P—CH$_3$[25,26]. Thus, it is postulated that P—CH$_3$ whose bond strength is weaker has the greater tendency to generate small phosphorus-containing species. In conclusion, the thermal degradation temperature of the compound having phenyl group is higher than that of the compound having methyl group if the other structures are identical.
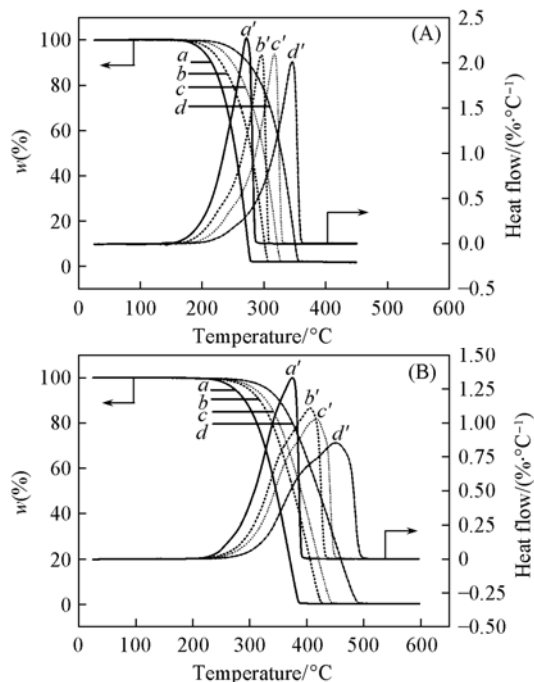

Fig.2　TG(*a*—*d*) and DTG(*a'*—*d'*) curves of MPPA(A) and DPPA(B) at different heating rates under N$_2$ atmosphere

Heating rate/(°C·min^{-1}): *a*, *a'*. 5; *b*, *b'*. 10; *c*, *c'*. 20; *d*, *d'*. 40.

Table 1　*T*$_{onset}$, *T*$_{endset}$ and *T*$_{max}$ of MPPA and DPPA at different heating rates

Sample	*β*/(°C·min^{-1})	*T*$_{onset}$/°C	*T*$_{endset}$/°C	*T*$_{max}$/°C
MPPA	5	191.1	280.9	271.7
	10	199.4	303.0	296.1
	20	214.5	324.3	316.9
	40	248.2	351.1	345.9
DPPA	5	267.1	380.9	370.5
	10	281.3	424.1	405.9
	20	289.8	439.2	417.1
	40	319.7	483.2	450.6

3.2　Kinetic Studies

The model-free methods(*e.g.*, isoconversional, KAS and Friedman) allow one to evaluate the activation energy without determining the reaction model. According to Eqs.(2) and (3), the plots of ln(*β*d*α*/d*T*) *vs*. 1000/*T*(Friedman), and ln(*β*/*T*^{2}) *vs*. 1000/*T*(KAS) corresponding to different conversions degrees *α* can be obtained by a linear regression of least-square method, respectively. The activation energies and the correlation coefficients of MPPA and DPPA are presented in Table 2, respectively. From Table 2, it can be seen that the activation energies of MPPA and DPPA do not vary significantly with the change of conversion. The mean activation energies *via* the Friedman

method are 69.3 and 83.8 kJ/mol for MPPA and DPPA, respectively. The average activation energies obtained *via* KAS method for MPPA and DPPA are 66.6 and 89.0 kJ/mol, respectively. The mean activation energies obtained by Friedman and KAS are very close to each other. DPPA sample, however, showed a higher activation energy of thermal degradation than MPPA. It can be attributed to the bond strength of P—C$_6$H$_5$ greater than that of P—CH$_3$. This result is consistent with that of thermal analysis. The activation energy and the dependence of *E*$_α$ on *α* by Friedman are greater than those by KAS, which is attributed to the application of the Friedman method to the TGA data requiring to use numerical differentiation that introduces imprecision into the rate data[19].

Table 2　Activation energies(*E*$_α$) and correlation coefficients(*R*^{2}) calculated by Friedman and KAS methods for the thermal degradation of MPPA and DPPA

Compd.	*α*	Friedman method		KAS method	
		E$_α$/(kJ·mol^{-1})	*R*^{2}	*E*$_α$/(kJ·mol^{-1})	*R*^{2}
MPPA	0.1	64.4	0.981	70.3	0.998
	0.2	63.7	0.986	63.9	0.995
	0.3	65.2	0.982	63.7	0.995
	0.4	67.7	0.986	64.2	0.988
	0.5	70.1	0.989	66.4	0.999
	0.6	72.3	0.993	66.9	0.989
	0.7	73.9	0.993	66.9	0.990
	0.8	74.3	0.989	70.2	0.994
	0.9	72.5	0.926	66.7	0.990
DPPA	0.1	97.8	0.994	93.9	0.950
	0.2	99.7	0.967	93.5	0.949
	0.3	93.5	0.961	93.3	0.982
	0.4	87.1	0.949	93.0	0.982
	0.5	81.9	0.939	93.5	0.960
	0.6	78.1	0.933	87.2	0.980
	0.7	74.2	0.930	87.3	0.951
	0.8	69.7	0.931	82.0	0.948
	0.9	72.3	0.958	77.1	0.940

According to Criado method[27], we substituted parameters in Eq.(4) with both each of the 41 kinds of mechanism functions and one of tested data. The master plots of *z*(*α*)/*z*(0.5) *vs*. *α* for MPPA and DPPA are shown in Fig.3. The comparison of the experimental master plots with theoretical ones reveals that
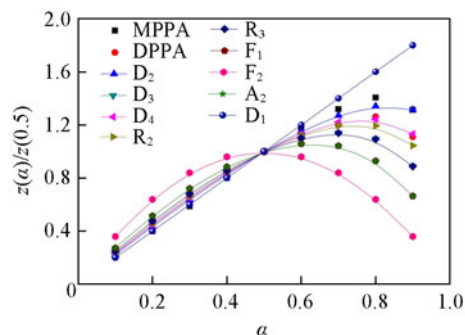

Fig.3　Master plots of different kinetic models and experimental data at 5 °C/min for MPPA and DPPA

D: Diffusion models; R: contracting geometry models; F: reaction-order models; A: Avrami-Erofeev models. More explanations with notes see ref.[19].

the reaction kinetic model of the thermal degradation of MPPA and DPPA is most probably described by two-dimension(D_2) and three-dimension(D_4) diffusion models respectively. Therefore, the degradation functions $f(\alpha)$ of MPPA and DPPA might be modeled by Eqs.(9) and (10), respectively:

$$f_{MPPA}(\alpha) = [-\ln(1-\alpha)]^{-1} \tag{9}$$

$$f_{DPPA}(\alpha) = \frac{3}{2}\left[(1-\alpha)^{-\frac{1}{3}}-1\right]^{-1} \tag{10}$$

The relative predominance of the different mechanisms actually operating in a particular system depends on the chemical environment of the phosphorus[28]. Generally, chain cleavage and radical reactions are considered as the principal mechanism of MPPA and DPPA pyrolysis. In this case, thermal transport plays an important role in the degradation. So, the diffusion model is responsible for the degradation. Additionally, during the decomposition of the DPPA, phenyl has a barrier effect on slowing down product volatilization and thermal transport, which assists DPPA with high thermal stability.

The pre-exponential factors of MPPA and DPPA were calculated with the average activation energies obtained by KAS method and the T_{max} from Table 1 *via* Eq.(5). The kinetic parameters of MPPA and DPPA at a heating rate of 5 °C/min are 1.76×10^5 and 2.56×10^5 s^{-1}, respectively.

The calculated values of $\Delta H^{\neq}$, $\Delta S^{\neq}$ and $\Delta G^{\neq}$ for the decomposition step of MPPA are 63.1 kJ/mol, -149.9 J·K^{-1}·mol^{-1}, 155.0 kJ/mol, and those for DPPA are 80.7 kJ/mol, -148.9 J·K^{-1}·mol^{-1}, 188.3 kJ/mol, respectively. Both the entropies of activation($\Delta S^{\neq}$) for the two decomposition steps are negative. In terms of the activated complex theory(transition theory)[29,30], a negative value of $\Delta S^{\neq}$ indicates a highly ordered activated complex. The result may be interpreted as a ''slow'' stage. The positive values of $\Delta H^{\neq}$ and $\Delta G^{\neq}$ for the decomposition show that it is connected with the introduction of heat and it is a non-spontaneous process. DPPA sample, however, showed higher $\Delta H^{\neq}$ and $\Delta G^{\neq}$ for thermal degradation than that of MPPA. It well explains why the thermal stability of DPPA is greater than MPPA. These thermodynamic functions are in consistent with kinetic parameters.

4 Conclusions

In order to investigate the thermal stability of organophosphinic acid, the thermal degradations of MPPA and DPPA were studied in a nitrogen atmosphere. The kinetics of the thermal decompositions of MPPA and DPPA was studied with non-isothermal TG and model-fitting method. The activation energies of MPPA and DPPA were calculated *via* Friedman and KAS kinetic methods and were found to be close to each other, which indicate the independent process and the nature of non-isothermal methods as well as TGA. The results calculated with the kinetic models show that the most probable model for the degradation of MPPA and DPPA agree with two-dimension(D_2) and three-dimension(D_4) diffusion models respectively. Thermodynamic properties, $\Delta H^{\neq}$, $\Delta S^{\neq}$ and $\Delta G^{\neq}$ for the two thermal decomposition reactions were also derived.

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