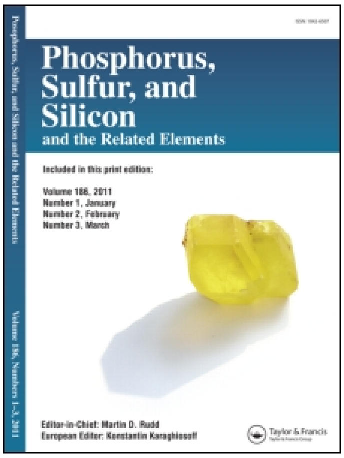

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Chang, T. C. , Wu, K. H. , Wu, T. R. and Chiu, Y. S.(1998) 'THERMOGRAVIMETRIC ANALYSIS STUDY OF A CYCLIC ORGANO-PHOSPHORUS COMPOUND', Phosphorus, Sulfur, and Silicon and the Related Elements, 139: 1, 45 — 55

To link to this Article: DOI: 10.1080/10426509808035676

URL: http://dx.doi.org/10.1080/10426509808035676

Phosphorus, Sulfur and Silicon, 1998, Vol. 139, pp. 45-55
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THERMOGRAVIMETRIC ANALYSIS STUDY OF A CYCLIC ORGANO-PHOSPHORUS COMPOUND

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(Received 29 July, 1997 ; In final form 16 September, 1997)

Four methods were used to study the thermal cyclisation of 2-(2-hydroxyphenyl)-phenylphosphonous acid **3**, and the results were compared with the thermal decomposition of 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO). The decomposition of DOPO was found to be a simple process composed of at least one stage for which apparent activation energies can be calculated. These investigated methods were those of van Krevelen, Horowitz-Metzger, Coats-Redfern, and MacCallum-Tanner. These methodologies evaluated the similar apparent activation energies E_a for cyclisation of **3** and for decomposition of DOPO. Moreover, these apparent activation energies for decomposition of DOPO were compared with that calculated by the isothermal method.

Keywords: Methodology; Degradation; Activation Energy; 9,10 – Dihydro-9-osea-10- phosphaphenanthrene – 10 – oxide

INTRODUCTION

9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) is an organo-phosphorus compound of great interest. This class of materials was prepared first by Saito,[1] and was investigated by several groups.[2–5] DOPO has many applications, such as an anti-discoloring agent for ABS resins, thermostabilizers of polypropylene, color paling agent for phenolic resins and epoxy resins, and flame-retardants. However, the value of the activa-

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tion energy for thermal decomposition of DOPO is not found in the literature.

Various kinds of phosphorus-containing polymers have been studied by thermogravimetric analysis (TGA),[6–9] in which is recorded the weight-change of a sample heated at a constant rate of heating. Ozawa methods[10] are interesting because they do not use the reaction order in the calculation of the activation energy but if the reaction deviates from the first order, the other methods give quite different values. Therefore, a thermal decomposition study of DOPO is analyzed by TGA in this paper. The values of kinetic parameters have been obtained employing the methods of van Krevelen,[11] Horowitz-Metzger,[12] Coats-Redfern,[13] and MacCallum-Tanner,[14] These values of apparent activation energy for decomposition of DOPO are approximately constant. Furthermore, the activation energy evaluated by isothermal measurements is conducted for comparison.

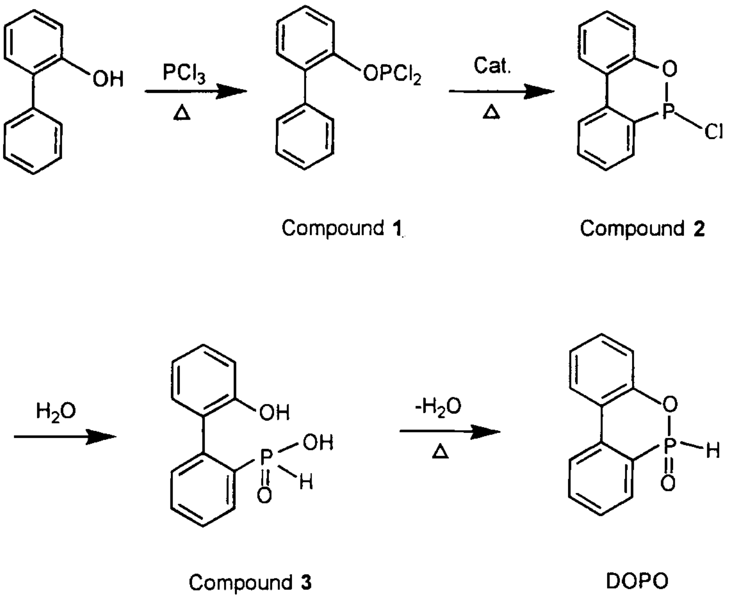
EXPERIMENTAL

Synthesis of DOPO

White crystals of 2-(2-hydroxyphenyl)-phenylphosphonous acid **3** were prepared by the Saito method (Scheme 1). [1] When compound **3** was heated at 160°C (30 mm Hg) for 2 h, the compound lost one molecule of water and changed into DOPO. **3** : mp (105°C); IR (KBr) 3359, 1592, 1448, 1363, 1076, 988, 903, 757, 531, 470 cm^{-1}. DOPO : mp(122°C); IR (KBr) 3061, 2437, 1594, 1479, 1428, 1235, 904, 757, 597, 517, 423 cm^{-1} ; MS (rel intensity) m/z 216 (M^+, 100), 199 (M^+-17, 60), 168 (M^+-17–31, 30).

Characterization

Infrared spectra were recorded (Bomem DA 3.002) using KBr-pellet technique. The ^{31}P-NMR spectra were determined on a JEOL FX-90Q spectrometer, and these were referenced to 85 % H_3PO_4 as an external standard. Mass spectra were measured on a JEOL JMS-D-100 mass spectrometer; the relative intensities are given in parentheses.



SCHEME 1

Decomposition

The kinetics of decomposition of compound **3** and DOPO were measured by Seiko SSC 5000 TG/DTA instrument. The sample weight was about 10 mg. The degraded gaseous products, as soon as they were produced, were bled into a quadruple mass spectrometer (VG Quadruples Micromass) under continuous vacuum (10^{-6} bar) and attached directly to the TGA with linear heating rate (10°C /min) under helium (100 mL/min). This method gave information on the temperatures at which components were formed. Isothermal TG analyses under nitrogen was carried out at temperatures 180, 190, 200, and 210°C, respectively.

RESULTS AND DISCUSSION

Thermograms obtained for compound **3** and DOPO are given in Figure 1 for the heating rate of 10°C/min. The TGA curve of compound **3** under nitrogen indicates two main reaction stages, which are reflected in two peak in the DTG curve. Compound 3 is stable up to approximately 100°C and then looses roughly about 8 % of its weight. This indicates that compound **3** lost one molecule of water and then changed into DOPO. Therefore, the weight loss in the second stage is due to the decomposition of DOPO. The thermogram of DOPO (Fig. 1) shows one stage of weight loss that starts at around 200°C.

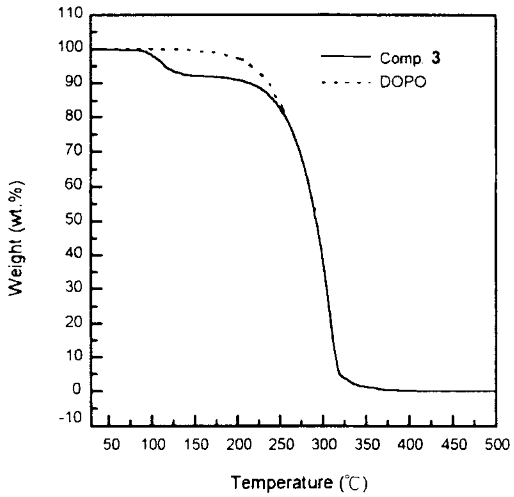


FIGURE 1 The TGA curves of compound 3 and DOPO under nitrogen in 10 K/min

The mass spectra for decomposition of the DOPO are measured from 190 to 500°C. Figure 2 shows the mass spectrum at decomposition (192°C), in which the major peaks of 14, 16, 18, 28, 32 and 40 amu (atomic mass unit) are attributable to CH_2, O, H_2O, CH_2CH_2, O_2 and C_3H_4, respectively. As the temperature is raised from 200 to 266°C, the decomposition rate is slightly pronounced, but the intensities of amu peaks of 14, 16, 18, 28, 32 and 40 are independent on temperature (Fig. 3). The results may be rationalized on the basis of the homogeneous decomposition in DOPO. In addition, the lack of a dependence of the gaseous products concentrations on temperature indicates that further reactions among the products do not take place under these conditions.

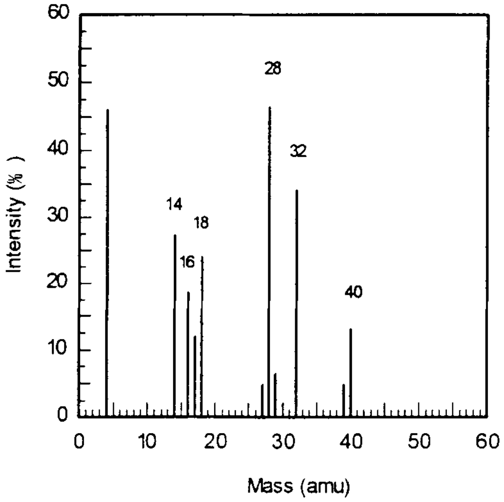


FIGURE 2 Products from the thermal decomposition of DOPO at 192°C

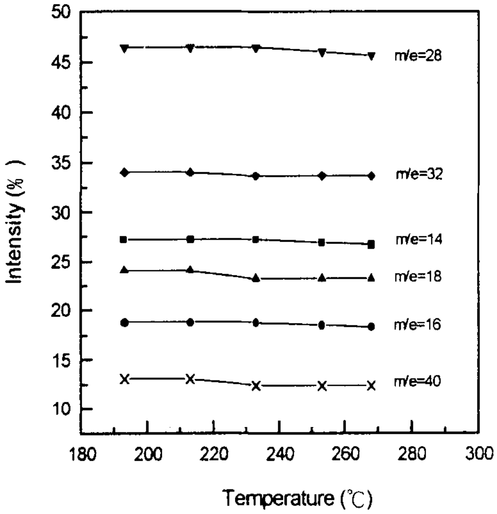


FIGURE 3 Changes of intensity for products of the thermal decomposition versus duration of thermal decomposition for DOPO

Reactions of solid decomposition may take place by one of a number of elementary mechanism, as well as combinations of these mechanisms. Thus, it is difficult to find a meaning of the reaction order *n* of a DOPO thermal decomposition. In this paper, the reaction order of thermal decomposition is determined by the Kissingers' equation :[15]

$$n = 1.26\sqrt{S}$$

where S is the shape index of the differential thermal analysis. The shape index is defined as the absolute value of the ratio of the slopes of tangents to the curve at the inflection points. The values of *n* in dehydrolysis is 1.0 ($0.005 < a < 0.10$) for compound **3**, and that in thermal decomposition is 0.68 ($0.15 < a < 0.95$) for DOPO, respectively. The degree of conversion *a* is defined as the ratio of actual weight loss to total weight loss.

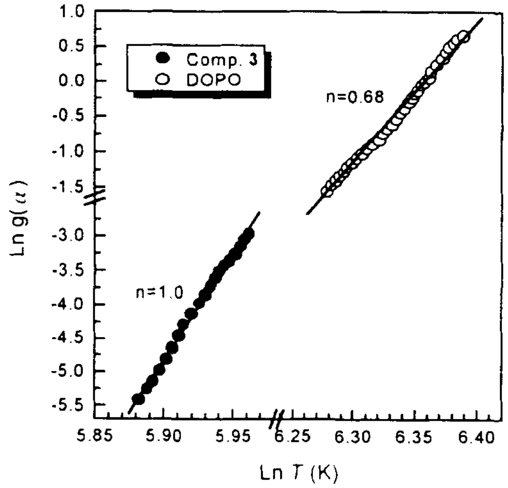


FIGURE 4 The plot of ln g(α) versus ln T for dehydrolysis of compound **3** and thermal decomposition of DOPO at 10 K/min

Several techniques using different approaches have been developed for solving the activation energies. The four methods are applied in this work investigated by the van Krevelen[11], Horowitz-Metzger,[12] Coats-Redfern[13] and MacCallum-Tanner[14], respectively. Figure 4 shows the activation energy determined by the method of van Krevelen in nitrogen for a weight loss thermogram of 10°C/min. The slopes of the ln *g(a)* versus ln *T* plot give activation energies which are 92 and 93 kJ/mol for cyclisation and decomposition, respectively. According to Horowitz-Metzger method in

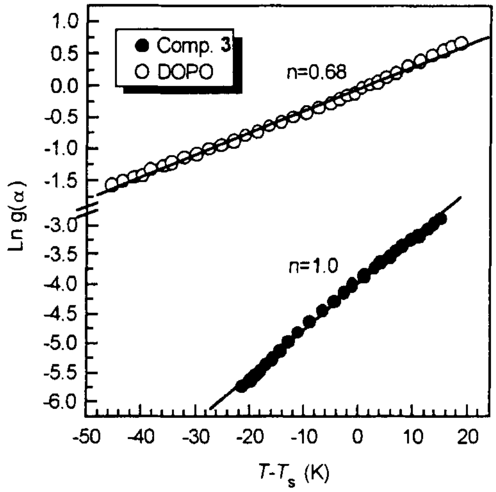


FIGURE 5 The plot of ln g(α) versus $T\text{-}T_S$ for dehydrolysis of compound **3** and thermal decomposition of DOPO at 10 K/min

the same conditions, a relation between ln $g(a)$ and $T\text{-}T_s$ is show in Fig. 5. T_S is the temperature at which $(1- a) = 1/e = 0.368$. The activation energies for the cyclisation and decomposition are 95 and 97 kJ/mol, respectively. These data agree with those from van Krevelen method. The plot of ln $[g(a)/T^2]$ versus $1/T$ gives a straight line with a slope equal to $-E_a/R$.[13] The activation energies obtained by this approach are 98 and 101 kJ/mol for cyclisation of compound **3** and decomposition of DOPO, respectively. On the other hand, Figure 7 represents a plot of log $g(a)$ against $1/T$ obtained using the MacCallum-Tanner method. This plot is possible to identify the individual stages of the decomposition and to calculate the activation energies from the slope of the appreciate segments. The activation energies are 90 and 91 kJ/mol for cyclisation of compound **3** and decomposition of DOPO, respectively.

Table I summarizesthe reaction reaction energy, preexponential factor and correlation coefficient of cyclisation for compound **3** and thermal decomposition for DOPO. It is found that the values of cyclisation E_a for compound **3** estimated by the (Krevelen, Herowitz-Metzger, Coats-Redfern and MacCallum-Tanner methods, are approximately 94 kJ/mol, while the values of decomposition E_a for DOPO are about 96 kJ/mol. Moreover, the values of correlation coefficient listed in Table I show a good agreement among the four methods.

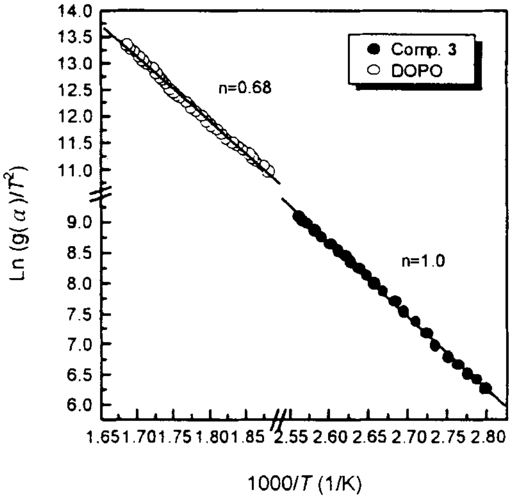


FIGURE 6 The plot of ln $[g(\alpha)/T^2]$ versus $1/T$ for dehydrolysis of compound **3** and thermal decomposition of DOPO at 10 K/min

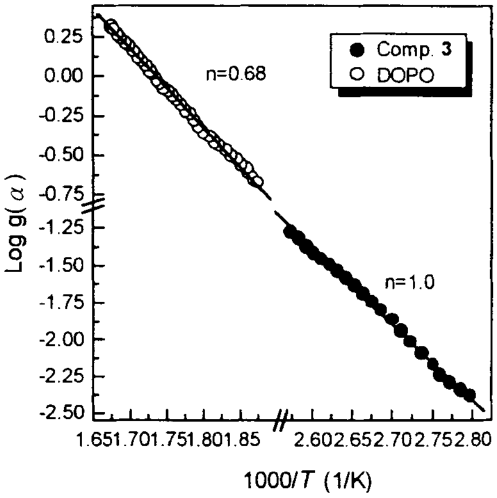


FIGURE 7 The plot of log $g(\alpha)$ versus $1/T$ for dehydrolysis of compound **3** and thermal decomposition of DOPO at 10 KJmi

TABLE I The characteristic parameter[a] of cyclisation for compound **3** and thermal decomposition for DOPO at a heating rate of °C/min

Method	*$0.005 < a < 0.10$*				*$0,15 < a < 0.95$*			
	n	*E_a (kJ/mol)*	*A (min^{-1})*	*Regression*	*n*	*E_a (kJ/mol)*	*A (min^{-1})*	*Regression*
Van Krevellen	1.0	92	4.71×10^{11}	0.9973	0.68	93	1.54×10^{8}	0.9970
Horowitz	1.0	95	2.54×10^{11}	0.9987	0.68	97	1.47×10^{8}	0.9984
Coats	1.0	98	2.63×10^{13}	0.9982	0.68	101	4.32×10^{8}	0.9981
MacCallum	1.0	90	1.79×10^{12}	0.9986	0.68	91	$3{,}12 \times 10^{8}$	0.9987

[a] *n*: reaction order; E_a: activation energy; *A*: preexponential factor.

We will consider isothermal measurements to evaluate the true activation energy. The rate of decomposition of DOPO can be solved by derivative method to yield

$$\ln(d\alpha/dt) = \ln A + \ln f(\alpha) - E_a/RT$$

Where f(*a*) is the conversion functional relationship. According to this equation, a straight line should be obtained when the logarithm of the rate is plotted against the reciprocal of the absolutetemperature (Fig. 8). An *Ea* of 98 kJ/mol if decomposition for DOPO is calculated from the slope of Figure 8, and this agrees with the values evaluated by the Krevelen, Herowitz-Metzger, Coats-Redfern and MacCallum-Tanner methods.

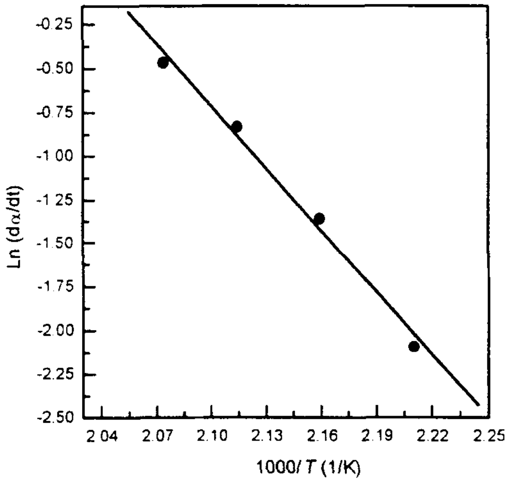


FIGURE 8 The plot of ln (dα/dt) versus 1/*T* for the decomposition of DOPO

Acknowledgements

We thank if the National Science Council and the Ministry of Economic Affairs of the Republic of China for finacial support.

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