



Kinetics of thermal degradation of intumescent flame-retardant spiroposphates

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Abstract. The thermal degradation behaviour of various spiroposphates synthesized using SDP (phenol), SDOC (*o*-cresol), SDMC (*m*-cresol), SDPC (*p*-cresol), SDDMP (2,4-dimethylphenol) and SDTMP (2,4,6-trimethylphenol) with 3,9-dichloro-2,4,8,10-tetraoxa-3,9-diphosphaspiro-[5,5]-undecane-3,9-dioxide (SDCDP) are investigated using thermogravimetric analyzer. The spiroposphates show multistage degradations in the temperature range 180–550°C. The second stage of degradation is more prominent and the substituent effect is clearly reflected at this stage of degradation. The compound SDP showed superior performance since it has the greatest char yield value (44%) and LOI value (27%). The model free kinetic methods of Flynn-Wall-Ozawa and Vyazovkin methods are used to calculate the apparent energy of activation for the thermal degradation (E_a -D) of these spiroposphates. The material SDTMP showed the highest E_a -D values.

Keywords. Spiroposphates; intumescence; thermogravimetric analysis; degradation kinetics; flame retardants.

1. Introduction

Polymeric materials (due to light weight, durability, mechanical performance and resistance towards chemicals, etc.) are advantageously used in many fields (household products, defence materials, aerospace parts and marine parts, etc.). However, the use of polymeric materials is restricted due to its fire risk properties [1,2]. Usually the incorporation of flame-retardant additives or the development of flame-retardant coatings for polymer is the convenient method to impart polymer flame retardancy [3,4]. At present, research has been focused on to develop environmental friendly flame-retardant systems. The patents and literature on environmental friendly flame retardants illustrated the importance of phosphorus-based flame retardants and indicated as very good alternate for halogenated flame retardants. The research on phosphorus-based flame retardants is originated with ammonium polyphosphate (APP) [5].

Phosphorus-based intumescent systems are attracted by many researchers, since it forms nonoxidizable multi-cellular charred layer in the fire condition. The formed char insulate and protect the materials of interest. The acid source, carbonific and spumific agents required to formulate

the intumescent system has more than one functional group. Thus the mechanism of intumescence is complex in nature [6–9].

Previously, the authors synthesized a series of spiroposphates by reacting spirodichlorodiphosphate with phenol, *o*-cresol, *m*-cresol, *p*-cresol, 2,6-dimethylphenol and 2,4,6-trimethylphenol [10,11]. The materials were pyrolysed at 500°C for a constant period (5 s) and the volatile products evolved were analysed using GC-MS. From these results attempts were made to elucidate the degradation mechanism of spiroposphates, which will add to the present understanding of the intumescent behaviour of phosphorus-based compounds. The research carried out on various spiroposphates has been reviewed [12].

It is well known that the flame retardancy of the materials also depends on the thermal stability, degradation rate, char forming rate and char yield. Thermogravimetric (TG) analysis is one among the standard procedures to investigate the thermal stability and the degradation of a material. Getting appropriate data and calculations will provide the kinetic triplets, the apparent activation energy for thermal degradation (E_a -D), the frequency factor (A) and the reaction model $f(\alpha)$. As per the recommendations of Flynn-Wall-Ozawa (FWO) [13,14] and Vyazovkin (VYZ) [15], multiple heating

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rate data were acquired to calculate the E_a -D values. There is no previous reported work concerning the thermal stability and the degradation kinetics of the spirophosphates having phenolic and substituted phenolic units. Detailed thermal studies of spirophosphates have been carried out by the authors and the results of the degradation kinetics of these materials are presented and discussed.

2. Experimental

2.1 Materials

Pentaerythritol was supplied by Alfa-Aaser, Johnson Matthey GmbH, Karlsruhe, Germany. Phosphoryl chloride and the solvent chlorobenzene were purchased from Merck Specialities Private Ltd., Mumbai, India. Phenol, *o*-cresol, *m*-cresol, *p*-cresol and pyridine were purchased from SD-Fine Chem. Limited, India. The materials were used as received without further purification.

2.2 Synthesis of 3,9-diphenoxy-2,4,8,10-tetroxa-3,9-diphosphaspiro-5,5-undecane-3,9-dioxide (SDP)

The procedure given by David Mathan *et al* [10,11] was used to synthesize the compound SDP using phenol. Similar procedure was adopted to synthesize other compounds SDOC, SDMC, SDPC, SDDMP and SDTMP using spirodichlorodiphosphate with *o*-cresol, *m*-cresol, *p*-cresol and 2,6-dimethylphenol and 2,4,6-trimethylphenol, respectively. The synthetic procedure is presented in supplementary information and the general equation is given in supplementary figure SF1.

2.3 Methods

TA Instruments Q50 thermogravimetric analyzer was used to conduct the TG analysis. The sample (3–5 mg) was weighed into platinum crucible and was heated from ambient to 800°C using different heating rates (10, 20, 30 and 40°C min⁻¹). The nitrogen flow was maintained at 60 ml min⁻¹ to avoid the secondary reaction of evolved gases in TG analysis. The universal analysis 2000 software provided by TA instruments was used for the data analysis. The programme Microsoft office-Excel was used for the calculation of E_a -D values from the TG data.

2.3a FWO method: Following Doyle's approximation, FWO [13,14] derived the following expression that relates β , A and E_a .

$$\log \beta = \log(AE_a/Rg(\alpha)) - 2.315 - (0.4567E_a/RT) \quad (1)$$

The plot between $\log \beta$ and $-1/T$ results in a straight line. The apparent α -dependent activation energy can be calculated from the slope ($0.4567E_a/R$) of the straight line.

2.3b Vyazovkin method: The integrated [15] form of Arrhenius equation is given below:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = A \int_0^\alpha \exp\left(\frac{-E_a(\alpha)}{RT}\right) dt = AJ[E_a(\alpha), T] \quad (2)$$

where $g(\alpha)$ is the integral form of the reaction model, $f(\alpha)$ and $T(t)$ is the heating program and A the Arrhenius constant. With a linear heating rate of $\beta = dT/dt$, $T(t)$ is linear, and in equation (2), dt can be substituted by dT/β .

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^t \exp\left(\frac{-E_a(\alpha)}{RT}\right) dT = \frac{AI}{\beta[E_a(\alpha), T]} \quad (3)$$

To avoid this dependence on the numerical approximation, Vyazovkin and Dollimore used the fact that for any heating rate β , $g(\alpha)$ is constant. Thus, with heating rates β_1 , β_2 and β_3 three integrals are obtained [$g(\alpha)_{\beta_1} = g(\alpha)_{\beta_2} = g(\alpha)_{\beta_3}$].

$$\frac{A}{\beta_1} I[E_a(\alpha), T]_1 = \frac{A}{\beta_2} I[E_a(\alpha), T]_2 = \frac{A}{\beta_3} I[E_a(\alpha), T]_3 \quad (4)$$

Consequently, A can be truncated and six equations can be formulated and their summarized equation is as follows:

$$\sum_{i=1}^n \sum_{j \neq i}^n \frac{I[E_a(\alpha), T]_i \beta_j}{I[E_a(\alpha), T]_j \beta_i} = 6 \quad \text{for } n = 3 \quad (5)$$

From the above equation, activation energy for the systems can be calculated.

3. Results

The complete synthetic aspects and structural characterization of the compounds SDP, SDOC, SDMC, SDPC, SDDMP and SDTMP by both Fourier transform infrared and proton nuclear magnetic resonance methods were presented and discussed by the author in a previous paper [10,11].

3.1 TG studies

The recorded thermograms of SDP, SDOC, SDMC, SDPC, SDDMP and SDTMP in nitrogen atmosphere at the heating rate of 10°C min⁻¹ are depicted in figure 1A. The first derivative curves are shown in figure 1B. The reproducibility of the TG curves was verified by running the analysis three times and the accuracy was within $\pm 1\%$. The materials were found to be hygroscopic and hence all the materials showed a slight mass loss (<1.0%) in the temperature range 150–170°C. The TG curves obtained for all the materials by heating at 10°C min⁻¹ showed multi-stage degradations. Using the TG thermograms and first

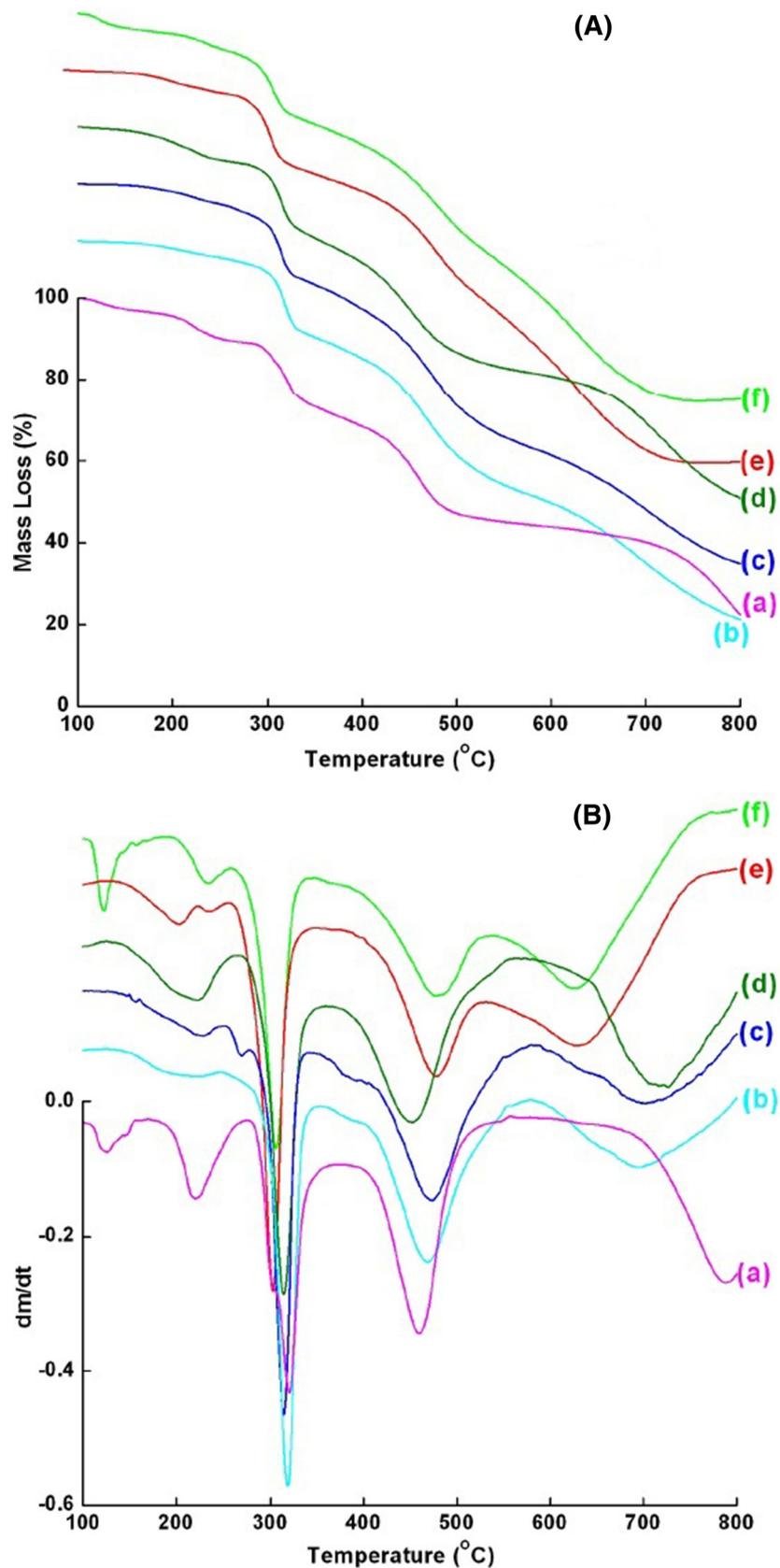


Figure 1. (A) TG and (B) DTG curves for the compounds (a) SDP, (b) SDOC, (c) SDMC, (d) SDPC, (e) SDDMP and (f) SDTMP (heating rate: $10^{\circ}\text{C min}^{-1}$).

Table 1. Details of the degradation stages noted for the thermal degradation of SDP, SDOC, SDMC, SDPC, SDDMP and SDTMP.

Samples	Stage I					Stage II				Stage III			
	$T_{5\%}$ (°C)	T_S (°C)	T_M (°C)	T_E (°C)	Mass loss (%)	T_S (°C)	T_M (°C)	T_E (°C)	Mass loss (%)	T_S (°C)	T_M (°C)	T_E (°C)	Mass loss (%)
SDP	211	178	221	272	7	278	320	366	17	388	459	541	24
SDOC	272	139	213	246	4	251	318	350	20	357	468	554	35
SDMC	255	165	232	255	5	284	319	344	16	357	477	555	37
SDPC	193	140	224	264	8	273	317	358	18	374	454	512	26
SDDMP	237	148	206	227	5	258	304	344	19	386	480	528	34
SDTMP	186	195	238	262	4	267	308	341	17	380	483	540	30

Table 2. Details of the char yield (%) and the LOI value of SDP, SDOC, SDMC, SDPC, SDDMP and SDTMP.

Samples	Char yield (%) (600°C)	LOI value at 800°C
SDP	44	27
SDOC	36	20
SDMC	34	20
SDPC	39	22
SDDMP	28	19
SDTMP	28	19

derivative curves, useful parameters are derived and compiled in tables 1 and 2.

Regarding the first degradation stage, the compounds both SDP and SDPC show much broader degradation temperature range when compared to other materials, SDOC, SDMC, SDDMP and SDTMP. The mass loss noted for this stage of degradation is slightly higher for the compounds SDP (7%) and SDPC (8%), whereas the compounds SDOC, SDMC, SDDMP and SDTMP undergo nearly 4% mass loss. The starting temperature (T_S) for the first stage of degradation of the compounds SDOC, SDPC and SDDMP is comparatively low and is nearly around 140°C. The temperatures corresponding to 5% mass loss for the materials fall within the temperature range of 180–270°C.

All the materials showed a sharp mass loss and are the second stage of degradation. This particular degradation stage is associated with the eruptive release of volatile products from the thermally degrading matrices. During the second stage of degradation, the mass loss varied between 16 and 20%. The effect of the structure of the phenolic moiety in the spirophosphate is manifested prominently at this stage of degradation. The total amount of mass lost at this degradation stage is found to be in the order SDOC > SDMC > SDDMP > SDPC > SDTMP > SDP. In this stage, only the amounts of degradation of the investigated spirophosphates are varied. However, the amount of mass

loss is practically same for the compounds SDP, SDOC, SDMC, SDPC, SDTMP and SDDMP. The T_S for the compounds SDOC and SDDMP is comparatively lower than the compounds SDP, SDMC, SDPC and SDTMP, which indicate the superior performance of the compounds SDP, SDMC, SDPC and SDTMP. Compared to the first and second stages of degradation, the third stage of degradation involves higher mass loss. About 35% mass loss was noted in this degradation stage of the compounds SDOC, SDMC, SDDMP and SDTMP. However, the compounds SDP and SDPC showed 25% mass loss. Following these degradation stages, the investigated materials proceed with degradations in multistage. After the third stage of degradation, the rate of degradation of SDP and SDPC are found to be slower, whereas the rate of degradation of the compounds SDP, SDOC, SDMC, SDDMP and SDTMP becomes faster. The maximum char yield (44%) was observed in the compound SDP.

The LOI values of the polymer systems should be above the threshold value of 26, to render self-extinguishing value and for their qualification in many applications requiring good flame resistance. The LOI value calculated according to the Van Kreevian equation [16] $LOI = 17.5 + 0.4\sigma$, where σ is the percentage of char yield.

The calculated LOI value of the investigated compounds is compiled in table 2. The LOI value is found to be in the range of 19–27%. The unsubstituted phenol ring in the phosphate unit of the compound SDP has the greater LOI value than the compounds having mono-, di- and tri-methyl substituted phenol ring in the phosphate unit of the compounds SDOC, SDMC, SDPC, SDDMP, and SDTMP.

3.2 Kinetics of degradation using multiple heating rates

Single heating kinetic methods assume that the kinetic parameters are constant with increase in temperature. This assumption is valid for simple chemical reaction, whereas this assumption is not valid for complicated chemical reactions. Because the kinetic parameter α depends on the temperature and E_a depends on α [17]. In this study, kinetics of degradation of spirophosphates are discussed using FWO

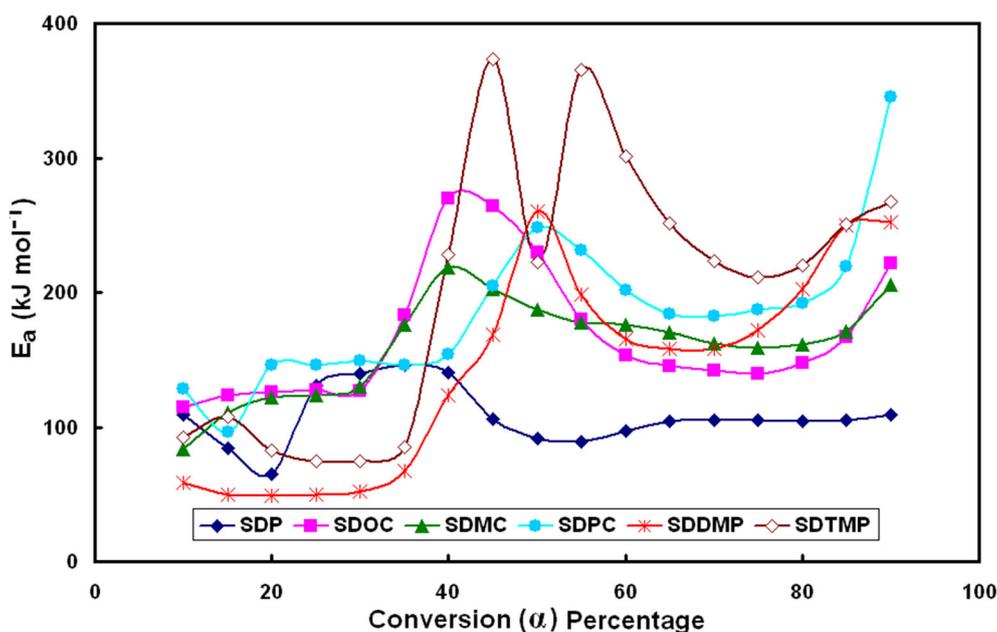


Figure 2. FWO method: plots of E_a vs. α for various spiroposphates.

and VYZ methods, which employ TG curves obtained from multiple heating rate measurements.

In figure 1, the TG (1A) and DTG (1B) curves recorded at the heating rate of $10^\circ\text{C min}^{-1}$ for different spiroposphates are presented. In this study, the author used four different heating rates ($\beta = 10, 20, 30$ and $40^\circ\text{C min}^{-1}$) and the results are shown in supplementary figure SF2. The following recommendations have been developed by the Kinetics Committee of the International Confederation for Thermal Analysis and Calorimetry (ICTAC) that the relative experimental errors in the kinetic data are larger at lowest and highest conversions; it might be advisable to limit analysis to the certain ranges [18]. Linear plots for conversion percentage ($\alpha = 10$ – 90) were obtained in steps of 5% conversion. If the calculated apparent activation energy values from the above multiple heating rate methods are the same for the various conversion percentages, it indicates a single reaction mechanism, whereas if the activation energy values change with conversion percentage, it reveals a complex reaction mechanism.

The TG curves for the investigated spiroposphates SDP, SDOC, SDMC, SDPC, SDDMP and SDTMP at different heating rates illustrated that at lower heating rate ($10^\circ\text{C min}^{-1}$) equilibrium state is reached readily with increase in temperature, whereas at faster heating rates ($20, 30$ and $40^\circ\text{C min}^{-1}$), the equilibrium state is reached slowly due to the slow diffusion of heat. Consequently, the degradation temperature shifts to higher temperature region.

FWO and VYZ methods are chosen for the present investigation, since the relative activation energy can be calculated

without prior knowledge of the reaction mechanisms and the reaction order. By the application of the FWO method, the activation energy for the degradation reactions can be determined and the plots of $\log \beta$ against $-1/T$ for the compounds SDP, SDOC, SDMC, SDPC, SDDMP and SDTMP are depicted in supplementary figure SF3. Generally, the multistage degradation reactions of a material are analysed with the help of the nonlinear regression of the straight lines obtained in the graph by plotting $\log \beta$ against $-1/T$ [19]. For the compound SDP nearly parallel straight lines (greater R^2 value) are obtained in the 10 to 90% conversion levels. However, parallel straight lines are obtained at the conversion levels of 20 and 50–60%, but with a lesser degree of correlation (lesser R^2 value). Fundamentally, the parallel straight lines point out a single reaction mechanism or the unification of multidegradation reactions of the material [20]. Since the material SDP is an intumescent material, there is no chance for a single degradation mechanism and hence one can assume that nearly parallel lines at the conversion levels of the degrading SDP may be ascribed to the unification of the multidegradations.

The parallel straight lines with lesser degree of correlation obtained at 20 and 50–60% conversion levels indicate the change in the degradation mechanism or degradation process of SDP. Similarly, for the compound SDMC, 40 and 75–90% conversion levels showed the lesser R^2 value. Lesser R^2 values are noted at 45% conversion for the compound SDDMP and 10 and 45–55% conversions for the compound SDTMP. The explanation given for the compound SDP is valid for the compounds SDOC, SDMC, SDPC, SDDMP and SDTMP also.

Variations of iso-conversional activation energy with conversions for all the materials examined are illustrated in figure 2. Depending upon the degradation reactions and the rate of such reactions, tremendous change in the activation energies was noted (figure 2).

The VYZ method was also applied for the TG curves obtained by heating the samples of SDP, SDOC, SDMC, SDPC, SDDMP and SDTMP with different heating rates. The estimated apparent activation energy values (VYZ method) for the different spiroposphates are presented in supplementary table ST1. It is observed that the activation energy values calculated using FWO and VYZ methods vary by ± 7 kJ mol⁻¹. The discrepancies in the values of activation energy may be explained as due to the systematic error caused owing to the initial approximation employed in the development of FWO and VYZ methods. The discrepancies noted for the compound SDP is presented in supplementary figure SF4.

For an intumescent material, the acid formation, melting, acid attack and release of blowing gas must occur almost simultaneously and successively. In the conversion percentage 20–50%, higher values of activation energy are noted for the compound SDP. The conversion percentage ranges pertinent to higher values of activation energy are different for different compounds under study. Depending upon the number and position of the methyl group attached to the phenolic part of the phosphate unit of the spiroposphates, the higher values of activation energies calculated against conversion percentage of the compounds are found to vary. Depending on the substituent attached to the phenolic part, the temperatures at which the process of acid formation, melting, acid attack and release of blowing gas take place vary and hence variation in the E_a values with conversion percentage.

4. Conclusion

The TG studies revealed that the compound SDCDP gave 29% char at 600°C. This amount was increased with respect to phenolic substituents attached in the phosphate unit and the maximum of char yield (43%) was observed for the compound SDP. The effect of phenolic substituents present in the phosphate unit is clearly seen in the second degradation stage. The intensities of second degradations of investigated compounds are in the order of SDOC > SDMC > SDPC > SDCDP > SDP. The calculated LOI value of the investigated spiroposphates

using Van Krevelan equation is found to be in the range of 18–26%.

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