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# Synthesis and thermal properties of spiro phosphorus compounds

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**Abstract** Intumescent materials, 3,9-dichloro-2,4,8,10-tetraoxa-3,9-diphosphaspiro-[5,5]-undecane-3,9-dioxide and 3,9-dichloro-2,4,8,10-tetraoxa-3,9-diphosphaspiro-[5,5]-undecane having the capacity to produce dehydrating agent, blowing agent, and undergo carbonization during burning have been synthesized. The thermal behavior of the synthesized materials was investigated using differential thermal analysis, thermal volatilization analysis, programmed vacuum pyrolysis–mass spectrometry, flash pyrolysis–mass spectrometry and off-line pyrolysis–gas chromatography–mass spectrometry. The materials show exothermic degradation after 250 °C. Monitoring the release of hydrogen chloride and water, the blowing agents for the production of carbon foam, clearly indicated the superior performance of the pentavalent phosphorus compound over the trivalent phosphorus compound. The major gaseous degradation products released during pyrolysis showed the presence of sufficient quantities of several alkyl-substituted benzenes and fused aromatics. Suitable degradation mechanism has been proposed and discussed to explain the formation of various organics during thermal degradation.

**Keywords** Spiro phosphorus compounds · Intumescence · Thermal analysis · Flash pyrolysis–mass spectrometry · Off-line pyrolysis–GC–MS

## Introduction

In the modern world, we the people live with flammable products such as chemicals, textile, upholstery, computers, mobile phones, etc. Flammability depends on the chemical composition of the materials which generate huge amount of heat, subsequently release toxic corrosive gases on combustion/pyrolysis [1]. Hence, it is necessary to develop thermally stable products by modifying the chemical structure or to make the material thermally stable by compounding it with flame retardants [2]. Usually, the incorporation of flame retardant additives or the development of flame retardant coating for flammable materials is a cost effective and easiest method for improved thermal stability.

Flame retardant is a chemical substance, which inhibits or retards physically or chemically the combustion process by releasing non-flammable products or altering the degradation path and allows more time for people to escape from the fire hazard [3, 4]. Halogenated flame retardants remove reactive H and OH radicals, which are produced during combustion. According to environment concerns the use of halogenated flame retardant systems are restricted [5–7]. Inorganic metal hydroxides such as aluminum hydroxide, magnesium hydroxide, etc., are used to retard the flammability, for effective achievement relatively high loadings are used and hence it alters the existing property [8]. Compounds having phosphorus can be effectively used to impart flame retardancy. It traps the radicals formed in

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the combustion process by releasing the $P_2$, PO, $PO_2$, and HPO radicals and induces the formation of carbon foam [5, 9]. Nitrogen containing flame retardants are the environment friendly flame retardant, which on heating, releases non-flammable free nitrogen, ammonia, and weak HCN which dilute the flammable gases. Nitrogen compounds itself not act as flame retardant, commonly nitrogen compounds are used as synergist [3, 10]. Boron (borax, boric acid, and borates) and silicon (silicones, organosilanes, silsesquioxanes, and silicates) containing compounds are used to impart thermal stability to the flammable materials. Both boron and silicon containing compounds form their oxides during pyrolysis, which prevents the access of atmospheric air to the substrate and there by diminishing the formation of combustible gases [11–13]. Intumescent means mixture of components on heating various chemical reactions taking place between them and produce multicellular voluminous char, which insulates and protects the underlying materials from heat, oxygen, and fuel essential for combustion of the materials [10, 14, 15]. Intumescent flame retardant system can be used in several materials such as polymers, metallic materials, textiles, wood, etc. [16, 17]. Intumescent activity is maximized by using carbon rich compounds along with phosphorus compounds as acid sources which catalyze the carbonization and spumific agents like urea, urea–formaldehyde resin, dicyandiamide, melamine, polyamides, etc. On heating, carbonifics, polyhydric compounds loss water and give char in the presence of acid sources; simultaneously nitrogen containing blowing/spumific agents release non-flammable gases which help to swell char [12]. The intumescent materials can act as more than one way in imparting flame retardancy because all the materials used are having more than one functional group [18].

Phosphorus-based intumescent materials are degrading at relatively low temperature, due to their weak bonds; hence it can act as flame retardant by modifying the decomposition temperature of the substance. During the decomposition process they form carbon layer which insulates the transfer of mass, oxygen, and heat during fire [19, 20]. Phosphorus-based intumescent flame retardant system can be used either by incorporating as additive to the materials to be flame retarded or incorporating into the polymer main chain covalently as one of the monomer or precursor. Additive types are predominantly used since reactive flame retardants are expensive due to their special manufacturing technique [2, 3, 11].

Spiro phosphorous compounds, 3,9-dichloro-2,4,8,10-tetraoxa-3,9-diphospha-spiro-[5,5]-undecane-3,9-dioxide (PSPDPC) and 3,9-dichloro-2,4,8,10-tetraoxa-3,9-diphosphaspiro-[5,5]-undecane (TSPDPC) are potent intumescent flame retardant materials. Since the conversion of these compounds to several structurally diverse materials exists, a detailed study of the thermal properties is essential. In this work, both PSPDPC and TSPDPC were synthesized and their thermal properties are investigated in detail and presented.

## Experimental

### Materials

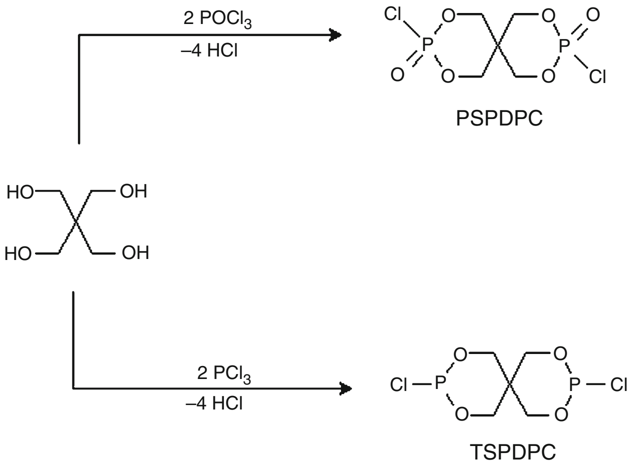
The synthetic routes of 3,9-dichloro-2,4,8,10-tetraoxa-3,9-diphosphaspiro-[5,5]-undecane-3,9-dioxide (PSPDPC) and 3,9-dichloro-2,4,8,10-tetraoxa-3,9-diphosphaspiro-[5,5]-undecane (TSPDPC) are shown in Scheme 1.

### Synthesis of 3,9-dichloro-2,4,8,10-tetraoxa-3,9-diphosphaspiro-[5,5]-undecane-3,9-dioxide

Exactly 2 mol of phosphoryl chloride was added drop wise for 2 h under nitrogen atmosphere to 1 mol of pentaerythritol kept at 90 °C in a round bottom flask fitted with water condenser. The reaction mixture was refluxed at 100 °C for 20 h. The resultant hard cake was crushed and refluxed with excess phosphoryl chloride for an additional 2 h. The excess phosphoryl chloride was removed by decantation followed by distillation under vacuum. The obtained product was washed with carbon tetrachloride followed by ethanol and finally with ether. The resultant white colored PSPDPC was dried under vacuum [21, 22].

### Synthesis of 3,9-dichloro-2,4,8,10-tetraoxa-3,9-diphosphaspiro-[5,5]-undecane

The mixture of pentaerythritol and phosphorus trichloride in the mole ratio of 1:2 was refluxed in sufficient quantity of dichloro methane. Refluxing was continued for 1 h after



**Scheme 1** Synthetic routes of PSPDPC and TSPDPC

the last crystal of pentaerythritol had disappeared. Finally, the solvent was removed by vacuum distillation. The colorless crystalline solid obtained was TSPDPC [23].

### Analysis

Differential thermal analysis (DTA) of the synthesized materials was performed in nitrogen atmosphere at a heating rate of 10 °C min$^{-1}$ from ambient to 450 °C using Mettler TA 2000 model DTA instrument. The glass apparatus used for thermal volatilization analysis (TVA) was described elsewhere [24]. TVA analysis was carried out with 50 mg of the powdered sample in high vacuum. TVA curves were recorded by heating the material linearly from ambient to 450 °C at a rate of 10 °C min$^{-1}$. The total ion current (TIC) of the volatile products formed during the programmed heating (10 °C min$^{-1}$) of the material in a Perkin Elmer Sigma 3B oven was recorded using a Balzers Quadrupole Mass Spectrometer QMG 511.

Flash pyrolysis of the materials at different temperatures (100–400 °C in 50 °C steps) were carried out for 5 s by inserting the samples, deposited on a platinum ribbon, directly into the mass spectrometer (QMG 511). The off-line pyrolysis of the materials at 400 °C for 10 min in nitrogen atmosphere was done by using an all glass apparatus described in detail by Vijayakumar [25]. The volatile low molecular weight products formed during degradation were collected over a frozen matrix of tetrahydrofuran [26, 27]. Separation and identification of the products were performed using Hewlett Packard Gas Chromatograph (HP 5890) containing a 12 m column HP-1 (cross-linked methyl silicone gum) coupled to a Hewlett Packard Mass Selective Detector (HP 5970). The data analysis was performed using Hewlett Packard Work Station, HP 59970.

## Results and discussion

### Differential thermal analysis

DTA curves of PSPDPC and TSPDPC were recorded in nitrogen atmosphere are illustrated in Fig. 1. The broad endotherm of PSPDPC at around 240 °C is responsible for the phase transformation such as melting of the compound and the broad exotherm having the maximum at 340 °C is attributed to the release of degradation products. However, TSPDPC shows a broad exotherm at 327 °C. No endotherm is observed for this material. From Fig. 1, it is clear that the spiro compound TSPDPC starts to degrade at a lower temperature than the compound PSPDPC. PSPDPC shows intumescence behavior with melting, but the compound TSPDPC undergoes intumescence without melting. The unsymmetrical nature of the DTA curve indicates the complexity of the degradation that is proceeding at this temperature region and definitely the degradation is not a single step process.

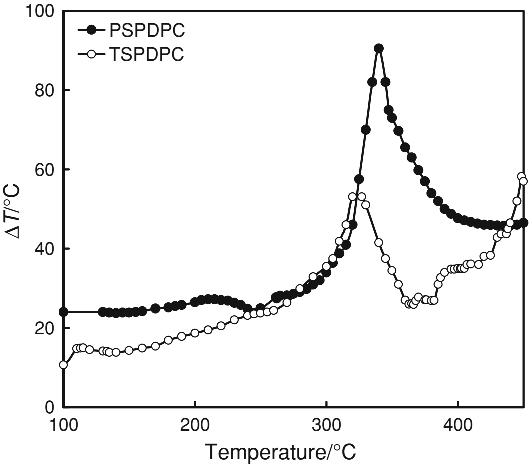


**Fig. 1** DTA traces of PSPDPC and TSPDPC (heating rate: 10 °C min$^{-1}$)

### Thermal volatilization analysis

Pressure sensitive TVA traces of PSPDPC and TSPDPC recorded from 100 to 450 °C under vacuum condition are shown in Fig. 2.

In the TVA trace of PSPDPC, the gradual increase of pressure is noted from 150 up to 200 °C, where as for TSPDPC the pressure increase is seen after 180 °C and leveled around 230 °C. This pressure increase may be attributed to the softening of the material followed by degassing of the material and/or to the release of the absorbed water molecules from the material. The possibility of condensation of the material in high vacuum is

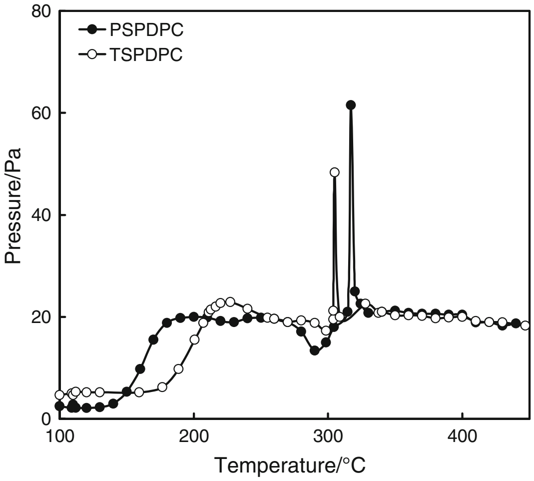


**Fig. 2** TVA traces of PSPDPC and TSPDPC (heating rate: 10 °C min$^{-1}$)

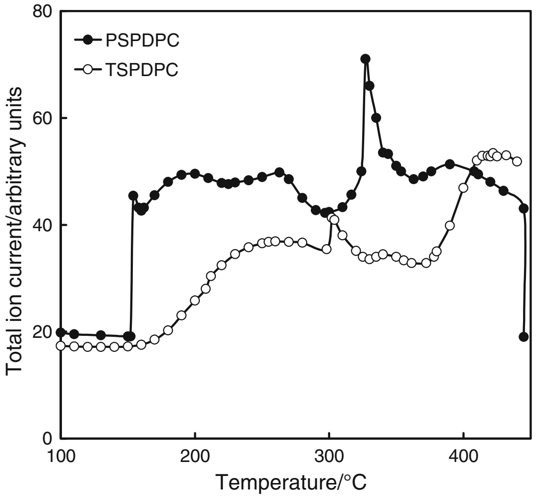


**Fig. 3** Programmed pyrolysis–total ion current measurements for PSPDPC and TSPDPC (heating rate: 10 °C $\mathrm{min}^{-1}$)

also another factor for this pressure change. After 300 °C, pressure increases gradually and reaches maximum at 317 °C for PSPDPC and 305 °C for TSPDPC. Above 325 °C in PSPDPC and 340 °C in TSPDPC, no change in pressure was observed. The sudden increase in pressure after 300 °C within a short time span indicates eruptive release of gases from both the materials and this may be an important factor which contributes to the intumescent behavior of these materials.

## Total ion current measurement during pyrolysis

The results of programmed pyrolysis of the materials followed by the monitoring of the TIC in a mass spectrometer are shown in Fig. 3. Here, also sudden increase of TIC was noted above 300 °C for both the materials investigated. PSPDPC shows the highest ion current value at around 327 °C, whereas TSPDPC shows a considerable increase in the ion current value at around 305 °C. Both the TVA and TIC measurements clearly indicate that the material TSPDPC is showing sudden release of degradation products at a lower temperature than the compound PSPDPC. From Fig. 3, one can safely state that the total amount of volatiles released from the compound PSPDPC is comparatively higher than from the compound TSPDPC.

## Evolution profile of $H_2O$ and HCl: flash pyrolysis–mass spectrometry

The normalized mass spectra recorded for the products obtained by the flash pyrolysis of PSPDPC and TSPDPC at

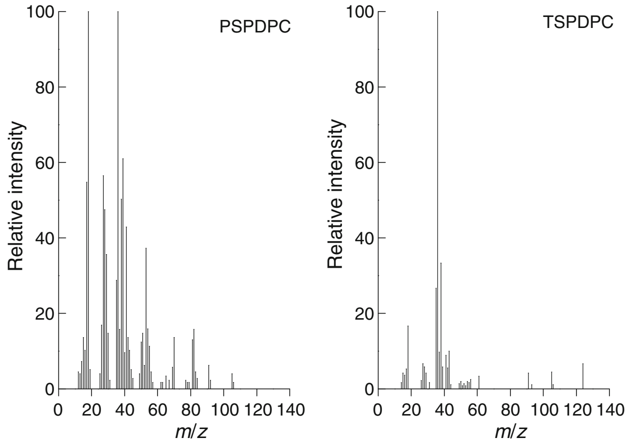


**Fig. 4** Mass spectra of volatiles produced from PSPDPC and TSPDPC by flash pyrolyzing at 500 °C for 5 s

**Table 1** Flash pyrolysis studies: possible structures for the various *m/z* values

| *m/z* value | Possible structure of the ion |
|---|---|
| 18 | $\overline{\mathrm{H_2O}}\rceil^{\bullet+}$ |
| 26 | $\overline{\mathrm{C_2H_2}}\rceil^{\bullet+}$ |
| 27 | $\overline{\mathrm{C_2H_3}}\rceil^{\bullet+}$ |
| 28 | $\overline{\mathrm{CO}}\rceil^{\bullet+}$, $\overline{\mathrm{C_2H_4}}\rceil^{\bullet+}$ |
| 29 | $\overline{\mathrm{CHO}}\rceil^{+}$, $\overline{\mathrm{C_2H_5}}\rceil^{+}$ |
| 31 | $\overline{\mathrm{CH_2OH}}\rceil^{+}$ |
| 35 | $\overline{\mathrm{Cl}}\rceil^{+}$ |
| 36 | $\overline{\mathrm{HCl}}\rceil^{\bullet+}$ |
| 37 | $\overline{\mathrm{Cl}}\rceil^{+}$ |
| 38 | $\overline{\mathrm{HCl}}\rceil^{\bullet+}$ |
| 39 | $\overline{\mathrm{C_3H_3}}\rceil^{+}$ |
| 41 | $\overline{\mathrm{C_3H_5}}\rceil^{+}$ |
| 42 | $\overline{\mathrm{C_3H_6}}\rceil^{\bullet+}$ |
| 43 | $\overline{\mathrm{C_3H_7}}\rceil^{+}$ |
| 51 | $\overline{\mathrm{C_4H_3}}\rceil^{+}$ |
| 53 | $\overline{\mathrm{C_4H_5}}\rceil^{+}$ |
| 54 | $\overline{\mathrm{C_4H_6}}\rceil^{\bullet+}$ |
| 69 | $\overline{\mathrm{C_4H_5O}}\rceil^{+}$ |
| 70 | $\overline{\mathrm{C_4H_6O}}\rceil^{\bullet+}$ |
| 81 | $\overline{\mathrm{C_5H_5O}}\rceil^{\bullet+}$ |
| 82 | $\overline{\mathrm{C_5H_6O}}\rceil^{\bullet+}$ |
| 91 | $\overline{\mathrm{C_4H_8Cl}}\rceil^{+}$ |
| 105 | $\overline{\mathrm{C_6H_5CO}}\rceil^{+}$ |
| 124 | $\overline{\mathrm{C_8H_{12}O}}\rceil^{\bullet+}$, $\overline{\mathrm{C_7H_8O_2}}\rceil^{\bullet+}$ |

500 °C for 5 s is shown in Fig. 4. Compound PSPDPC showed intense $m/z = 18$ and 36 indicating the formation of water and hydrogen chloride, respectively. The material TSPDPC showed the presence of intense $m/z = 36$ (HCl) peak but the peak responsible for water ($m/z = 18$) is not very prominent as is noted for the compound PSPDPC. In Table 1, the $m/z$ values and the probable structure for the ions are presented.

The evolution profile of the major degradation products (water and hydrogen chloride) was monitored by flash pyrolyzing the materials (PSPDPC and TSPDPC) for 5 s at a specified temperature and then recording the mass spectrum from $m/z = 10$ to 140. Intensity of the $m/z = 18$ and 36 are found out and recorded against the pyrolysis temperature (Figs. 5, 6).

Sufficient quantities of gases must be released from the material under consideration so that it can act as an intumescent material. The carbonaceous foam formation during degradation is essential for an intumescent material. From Figs. 5 and 6, it is clear that both the materials investigated are able to produce large quantities of water and hydrogen chloride after 300 °C. The amount of gases released from PSPDPC is considerably higher than from TSPDPC, as evidenced by the intensity values. All the above investigations strongly support the fact that the two spiro phosphorus compounds are having sufficient intumescent activity and the activity is noted above 300 °C.

## Off-line pyrolysis–GC–MS studies

The total ion chromatograms for the volatile products obtained by degrading PSPDPC and TSPDPC isothermally for a specified period (400 °C for 10 min) are shown in Fig. 7. The compounds identified on the basis of the fragmentation pattern noted in their mass spectra are shown in Table 2.

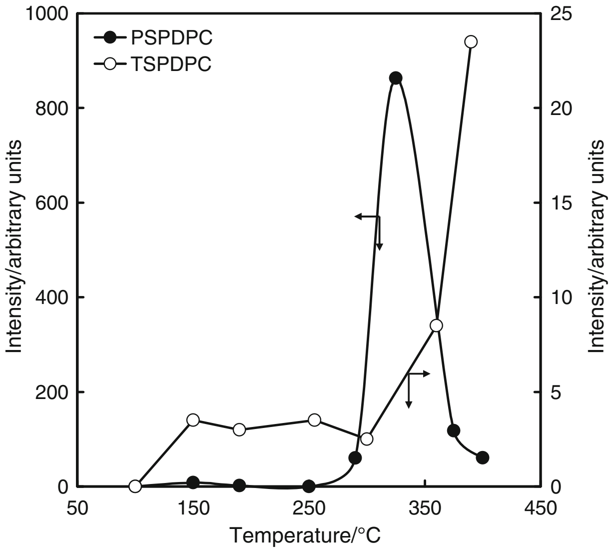


**Fig. 5** Evolution profile of $H_2O$ obtained by flash pyrolyzing the spiro compounds at different temperatures for 5 s

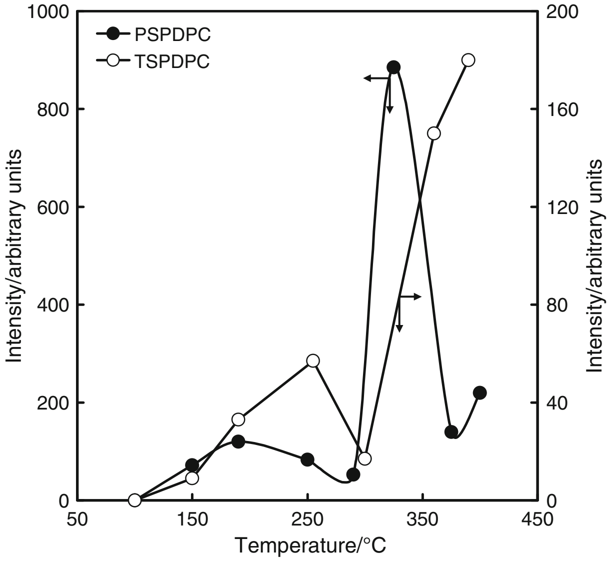


**Fig. 6** Evolution profile of HCl obtained by flash pyrolyzing the spiro compounds at different temperatures for 5 s

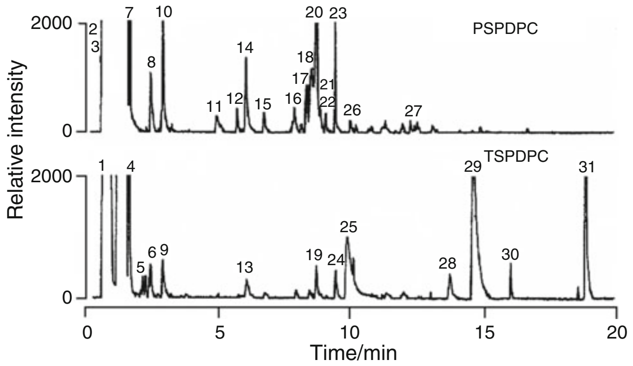


**Fig. 7** Off-line pyrolysis–GC–MS studies: total ion chromatogram for the volatiles obtained by isothermally (400 °C) degrading PSPDPC and TSPDPC for 10 min

From Table 2, it is obvious that apart from hydrogen chloride, several aliphatic and alicyclic chloro compounds are identified in the volatile products. In spite of benzene and toluene, various isomeric aromatic hydrocarbons are also noted among the degradation products. It is interesting to note spiro compounds containing five carbons atoms on degradation liberate different isomeric aromatic hydrocarbons. From this it is clear that compound or compounds capable of undergoing isomerization, cyclization, and polymerization are produced during the degradation of the spiro compounds. The formation of spiro-[2,2]-pent-1,

**Table 2** Isothermal pyrolysis of PSPDPC and TSPDPC: products identified in the volatile fraction

| S. no. | Retention time/min | Name of the products |
|---|---|---|
| 1 | 0.58 | HCl |
| 2 | 0.66 | $C_2H_5Cl$—ethyl chloride |
| 3 | 1.45 | $C_3$ or $C_4$ compound containing chloro group |
| 4 | 1.56 | $C_6H_6$—benzene |
| 5 | 1.60 | $C_5H_{11}Cl$—2-chloro-2-methyl butane |
| 6 | 1.64 | $C_3$ or $C_4$ compound containing chloro group |
| 7 | 2.42 | $C_5$ compound containing $CH_3$ group |
| 8 | 2.84 | $C_6H_5CH_3$—toluene |
| 9 | 4.91 | $C_4H_5Cl$—chloromethylcyclopropene or isomer |
| 10 | 5.67 | $C_8H_{10}$—Isomer I (dimethyl benzene isomer/ethyl benzene) |
| 11 | 6.01 | Unknown |
| 12 | 6.02 | $C_8H_{10}$—Isomer II (dimethylbenzene isomer/ethyl benzene) |
| 13 | 6.69 | $C_8H_{10}$—Isomer III (dimethylbenzene isomer/ethyl benzene) |
| 14 | 7.83 | $C_5H_6Cl_2$—1,1-dichloro-2-ethenylcyclopropane or isomer |
| 15 | 8.28 | $C_5H_6Cl_2$—1,1-dichloro-2-ethenylcyclopropane or isomer |
| 16 | 8.47 | Compound containing cyclopropene unit |
| 17 | 8.64 | $C_9H_{12}$—Isomer I (ethylmethyl benzene, trimethyl benzene) |
| 18 | 8.68 | $C_9H_{12}$—Isomer II (ethylmethyl benzene/trimethyl benzene) |
| 19 | 8.83 | $C_9H_{12}$—Isomer III (ethylmethylbenzene/trimethyl benzene) |
| 20 | 9.02 | $C_9H_{12}$—Isomer IV (ethylmethylbenzene/trimethyl benzene) |
| 21 | 9.27 | $C_9H_{12}$—Isomer V(ethylmethylbenzene/trimethyl benzene) |
| 22 | 9.36 | $C_9H_{12}$—Isomer VI (ethylmethylbenzene/trimethyl benzene) |
| 23 | 9.82 | $C_9H_{12}$—Isomer VII (ethylmethylbenzene/trimethyl benzene) |
| 24 | 9.95 | $C_9H_{12}$—Isomer-VIII (ethylmethylbenzene/trimethyl benzene) |
| 25 | 12.20 | Compound containing indane nucleus |
| 26 | 13.70 | $m/z$ = 271, 272, 273 |
| 27 | 14.60 | $m/z$ = 182 |
| 28 | 16.00 | $m/z$ = 345, 346, 347 |
| 29 | 18.80 | $m/z$ = 133 ($C_4H_6O_3P$) |

3-diene from PSPDPC is detailed by Vijayakumar et al. [28]. The formation of such a sterically much constrained compound is restricted in TSPDPC due to the no availability of the oxygen in the phosphorus atom. Hence, the formation of several di- or tri- alkylated benzene is restricted from the compound TSPDPC. The formed hydrogen chloride acts as a strong proton donor in the degrading matrix and induces several ionic rearrangements and condensations leading to the formation of several isomeric alkyl-substituted aromatic hydrocarbons.

Compared to various aromatic compounds, the number of organophosphorus compounds registered among the volatile degradation products is very minimum (Table 2). One possible explanation for this particular observation is that, the phosphoric and poly phosphoric acids formed during the thermal degradation may react with carbonization source and form thermally stable P–C and P–O–C bonded char (phospho-carbonaceous char) [22]. Similar behavior was noted by Camino et al. [29] in their detailed study of the thermal degradation of 3,9-dihydroxy-2,4,8,10-tetraoxa-3,9-diphosphaspiro-[5,5]-undecane-3,9-dioxide and proposed the mechanism of formation of phospho-carbonaceous structure through carbocation route. The formed phospho-carbonaceous char serves as an excellent heat resistant barrier.

## Conclusions

From the foregoing findings one can state that, PSPDPC shows intumescence at relatively lower temperature with melting as compared to TSPDPC. The complexity of the degradation of both PSPDPC and TSPDPC is clearly seen in the DTA curve and the degradation is multistep process. The sudden increase in pressure in the TVA traces of the two spiro compounds indicate the eruptive release of gaseous products during thermal degradation and this phenomenon is responsible for the intumescence behavior and also for the production of voluminous foamed char. Compared to TSPDPC, PSPDPC generates more amounts of volatiles at a faster rate as evidenced by TIC measurements. The evolution profile of water and hydrogen chloride from PSPDPC and TSPDPC by flash pyrolysis showed PSPDPC is able to liberate these compounds comparatively in high quantities than TSPDPC. Off-line pyrolysis studies indicate the structure of PSPDPC facilitates the formation of sterically much constrained spiro pentadiene, which is responsible for the formation of several isomeric alkylated aromatic hydrocarbons. The major amount of phosphorus in both PSPDPC and TSPDPC are involved in the formation of phospho-carbonaceous char via phosphoric and poly phosphoric acids formed during the thermal degradation.

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