Intumescent flame retardant spirophosphates: pyrolysis-GC-MS studies

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Abstract

Different spirophosphates containing phenol and substituted phenols are synthesized and their structures are characterized using FT-IR and ^{1}H-NMR. Pyrolysis - Gas Chromatography - Mass Spectrometry (Py-GC-MS) studies are made at two different temperatures (500 and 700°C) for constant time interval (5s) and the isothermal pyrolysis products are identified so as to understand the effect of the substituents present in the phenolic part on the thermal degradation of the spirophosphates. The main volatile products identified are methacrolein, phenol, o-cresol, m-cresol and p-cresol. The amount of formation of phenol and substituted phenols from degrading spirophosphates are low, where as the amount of volatile aromatic hydrocarbons increase considerably when the samples are pyrolysed at higher temperature (700°C). The reactive spiro-[2,2]-pent-1,3-diene (spirodiene) and benzyne formed during the pyrolysis process may account for the formation of different volatile aromatic hydrocarbons. Based on these factors, the mechanism of intumescence of spirophosphates is presented and discussed.

Keywords: Degradation mechanism, flame retardancy, intumescence, isothermal degradation, Py-GC-MS.

Introduction

World moves on polymers due to their excellent properties such as light weight, durability, mechanical performance and resistant towards chemicals etc. However, the main drawback of the polymeric materials is fire risk, since all the synthetic polymers are derived from petroleum products[1]. With increasing consumption of polymeric materials in house hold products, aerospace parts and marine parts, etc., it has to be remarkably flame retardant depending on their applications[2]. In 1980s halogenated flame retardants are highlighted extensively to polymer flame retardancy. Latter many researchers recognized that halogenated flame retardants produced noxious and corrosive halogenated dibenzodioxins and dibenzofurans on fire condition[3]. So research has been focused on to develop environmental friendly flame retardant systems having efficiency similar to halogenated flame retardant materials. The search for alternate of halogen flame retardants results the hydroxides of metal, phosphorus, boron, silicon, nitrogen as well as inorganic nanopaticles containing compounds as flame retardants. The growing patent and literature on halogen free flame retardants points out the significance of phosphorus based compounds as flame retardants. The function of phosphorus compounds for imparting polymer flame retardancy originated with ammonium polyphosphate (APP)[4].

In recent years researchers paid much attention to phosphorus based intumescent system due to the evolution of a lesser amount of smoke, less toxic and corrosive gases and small amounts are enough to impart sufficient flame retardancy. Moreover the heat of combustion of the system by about 70 kcal mol^{-1} were reduced by phosphorus based flame retardants and is depend on the nature of polymers[5]. Intumescent system produces multi-cellular charred layer on degradation which prevents the underlying materials by restricting the oxygen diffusion to the underneath materials. Typically intumescent system comprises three main ingredients which includes acid source (phosphoric acid, polyphosphoric acid, etc.), carbon rich compound (sorbitol, pentaerythritol, etc.) and blowing agent (urea, urea-formaldehyde resin, dicyandiamide, melamine, polyamides, etc.). The multifaceted intumescent flame retardant mechanism is noted, since intumescent system is a combination of compounds having different functional groups[6].

Rudi Ratz et al. synthesised and studied the compound spirodichlorodiphosphate (SDDP)[7]. Halpern et al. prepared intumescent material by treating SDDP with melamine and established its effectiveness towards polypropylene[8]. In the year 2002, Vijayakumar et al. elucidated the chemical mechanism of intumescence of SDDP and spiro acids by investigating pyrolysis and pyrolysis products of the same[9]. Sivasamy et al. synthesised a series of polymer of aromatic spirophosphates by treating SDDP with different dihydric phenols and studied their thermal behaviour[10,11].

The authors have extended this study by synthesizing series of spirophosphates by reacting spirodichloro-diphosphate with phenol and substituted phenols.

The volatile gaseous products generated in fire scenario are gaining much attention, since it is responsible for the combustibility, corrosiveness and toxicity[12]. Therefore study on the detailed mechanism of thermal degradation of intumescent materials is significant and/or necessary for polymer flame retardancy. The application of Py-GC-MS to elucidate the thermal degradation mechanism of intumescent materials has become wide spread. In the present study, a series of spirophosphates are synthesized and characterized. The materials were pyrolysed at two different temperatures (500 and 700°C) for a constant period (5s) and the volatile products evolved were analyzed using GC-MS. From these results attempts have been made to elucidate the degradation mechanism of spirophosphates, which will add to the present understanding of the intumescent behavior of phosphorus based compounds.

Materials and methods

Pentaerythritol was received from Alfa-Aaser, Johnson Matthey GmbH, Karlsruhe, Germany. Phosphoryl chloride and the solvent chlorobenzene were purchased from Merck Specialities Private Ltd., Mumbai, India. Phenol, isomers of methyl phenols and pyridine were purchased from sd-Fine Chem. Limited, India. The purchased materials were subjected to the chemical reaction as received.

Synthesis of 3,9-diphenoxy-2,4,8,10-teroxa-3,9-diphosphas piro-5,5-undecane-3,9-dioxide(SDP): The intermediate, 3,9-dichloro-2,4,8,10-teroxa-3,9-diphosphaspiro-5,5-undecane-3,9-dioxide (SDDP) was synthesized as per the procedure reported previously[7,13] and was used without purification for the preparation of SDP, SDOC, SDMC and SDPC. The compound SDDP (29.7g, 0.1mol), pyridine (0.3mL) and chlorobenzene (40 mL) were charged to a 100mL round bottomed flask equipped with mechanical stirrer, dropping funnel, condenser which vented to the sink and protected from atmospheric air. Phenol (20.98g) was added drop wise and was allowed to reflux until the evolution of HCl ceased. After that, the obtained product was washed several times with ice cold diethylether and filtered. The vacuum dried material was a pale brown solid (26g, 70%)[12].

A similar procedure was adopted for the synthesis of SDOC, SDMC and SDPC using *o*-cresol, *m*-cresol and *p*-cresol respectively.

Techniques: The elemental analyses were performed using a Perkin-Elmer 2400 CHN/O analyzer and the molecular formulae of the spirocompounds were confirmed. The FT-IR spectra of the synthesized materials were recorded on Fourier Transform Infrared-8400S spectrophotometer, Shimadzu, Japan using KBr pellet technique. Proton NMR spectra of all the samples were recorded in a Bruker-300MHz NMR spectrometer using DMSO-d_6 as solvent and tetramethylsilane as internal standard.

To elucidate the thermal degradation mechanism of the different spirophosphates, Py-GC-MS studies were performed at 500°C and 700°C under helium atmosphere. A SGE pyrojector attached to a Thermo TR-5 MS SQC gas chromatograph having a general purpose 15m quartz capillary column coated with hexamethylsiloxane which is coupled to a Thermoscientific DSQII MS quardrapoule mass spectrometer is used for the present investigations.

About 0.1mg of the sample was weighed in to the capillary tube of the SGE pyrojector. The materials were pyrolysed at 500°C for 5s. The volatiles were separated in a GC. In GC, the oven was maintained isothermally for 5 min at 50°C. The temperature was lifted from 50 to 250°C at a heating rate of 10°Cmin[-1] and set aside at the final temperature for 5min. The total ion chromatogram was obtained by using DSQII MS quardrapoule mass spectrometer (ion source, EI=70eV, mass range scanned=10 to 500amu, scanning rate=2s per scan and detector temperature=230°C). The identification of degradation products was done by NIST library provided by Thermo Fischer, the fragmentation pattern of the compound under consideration and by injecting authentic samples.

Results and discussion

Characterization: The intumescent materials synthesized for the present investigations are illustrated in Figure- 1 and their structural characterizations are done by FT-IR and ^{1}H-NMR spectral studies.

The elemental analyses values are consistent with the structure of the spirophosphates (Table-1). The FT-IR and ^{1}H-NMR spectra of the compound SDP are presented in Figure-2a and 2b respectively. Characteristic absorption bands in the FT-IR spectra and its assignments to the particular groups present in the synthesized spiro compounds (SDDP, SDP, SDOC, SDMC, and SDPC) are compiled in Table-2. The peak just about 1150 cm^{-1} was responsible to the quartnery carbon atom ($C(CH_2)_4$) in the spiro unit. The presence of characteristic vibration bands at 913, 853, 778 and 691cm^{-1} in all compounds ascertained the presence of spiro structural unit in these materials. The absence of the band responsible for P-Cl unit (550cm^{-1}) in SDP, SDOC, SDMC and SDPC indicated the completion of the reaction between SDDP and phenols[14,15]. Moreover the new bands at around 1642 cm^{-1} (benzene) and 1466cm^{-1} (-CH_3) in all the spirophosphates further confirmed the chemical structures of the intumescent materials SDP, SDOC, SDMC and SDPC.

In Table-3, the ^{1}H-NMR results for the investigated compounds are presented. The interactions of three kinds of spatial arrangements of two types of methylene protons in spiro unit result in multiplets[10]. The peaks noted at 3.50-4.65 and 7.20-7.50 ppm is due to the –CH_2 protons in spiro structural unit and aromatic ring protons respectively. The appearance of a peak noted at 2.3ppm in the ^{1}H-NMR of SDP, SDOC, SDMC and SDPC, peak responsible for the protons present in the methyl

group attached in the aromatic nucleus, confirmed the proposed chemical structures for the materials under consideration.

Py-GC-MS study: Total ion chromatograms of the pyrolysis products from the spirophosphates, SDP, SDOC, SDMC and SDPC isothermally at 500°C and 700°C are illustrated in Figure-3. The major volatile products are methacrolein, phenol and substituted phenols. Among the volatile degradation products, aromatic hydrocarbons like alkyl substituted benzenes, indenes and naphthalenes are formed in minor amounts. The different volatile products formed are listed in Table-4. From Figure-3, it is clear that the distribution of phenolic compounds and the alkyl substituted aromatic hydrocarbons is very much dependent on the pyrolysis temperature and as the pyrolysis temperature increases compared to the phenolic compounds, the alkyl substituted aromatic hydrocarbons are formed in considerable amounts.
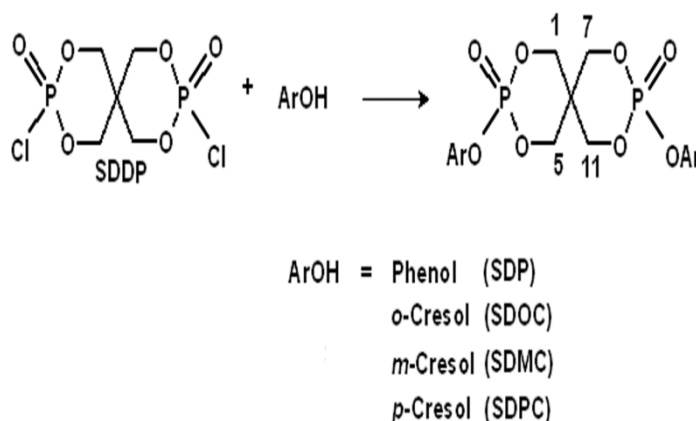

AroH = Phenol (SDP)
 o-Cresol (SDOC)
 m-Cresol (SDMC)
 p-Cresol (SDPC)

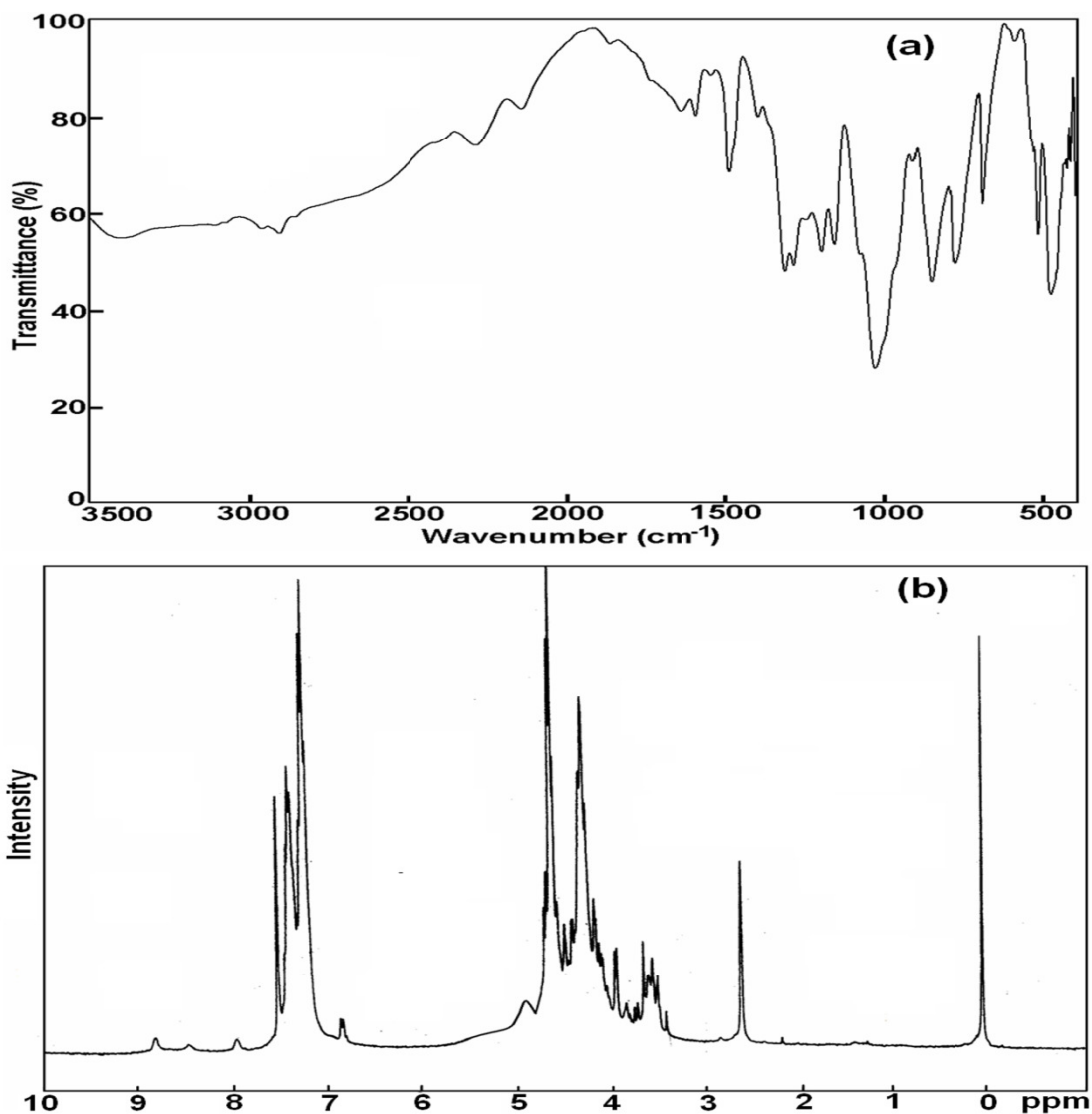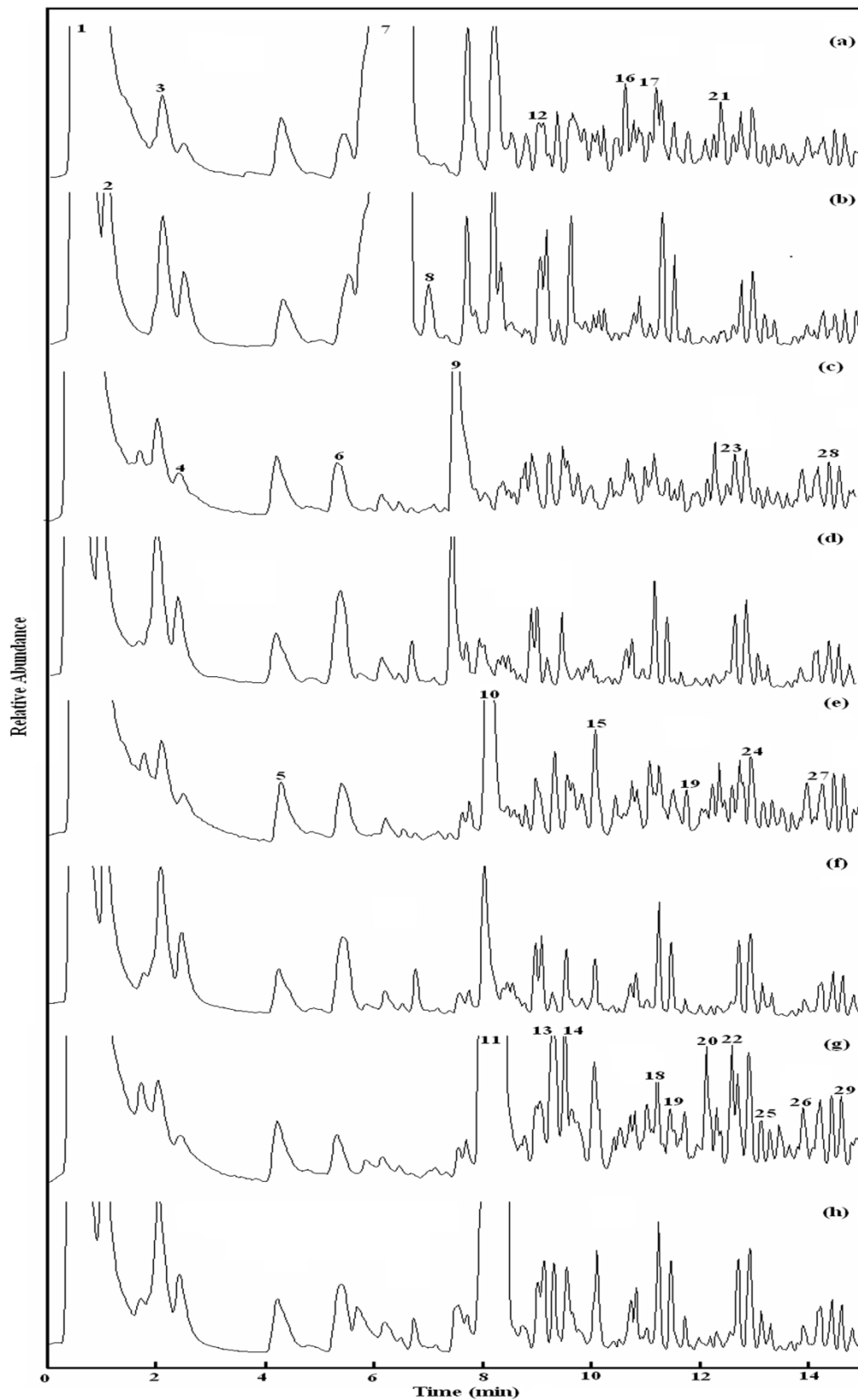**Figure-1:** Synthetic routes of SDP, SDOC, SDMC and SDPC.

Figure-2: The IR (a) and ^{1}H-NMR (b) spectra of SDP.

Figure-3: Total ion chromatogram of volatile products formed from SDP, SDOC, SDMC and SDPC on isothermal pyrolysis at 500°C (a:SDP, c:SDOC, e:SDMC, g:SDPC) and 700°C (b:SDP, d:SDOC, f:SDMC, h:SDPC) for 5 min.

Table-1: Elemental analysis of the different spiro compounds.

Compounds	C %		H %		O %		P %		Cl %	
	Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found
SDDP	20.23	20.45	2.72	2.80	32.34	32.13	20.87	20.71	23.88	23.17
SDP	49.56	48.97	4.40	4.12	31.07	31.21	15.03	15.17	-	-
SDOC	51.87	52.05	5.04	4.95	29.09	28.91	14.07	14.21	-	-
SDMC	51.87	51.58	5.04	5.17	29.09	29.21	14.07	13.93	-	-
SDPC	51.87	51.63	5.04	5.11	29.09	29.17	14.07	14.18	-	-

Table-2: IR Studies - Characteristic absorption bands noted for different spiro compounds.

Structural entity	Band Position (cm^{-1})				
	SDDP	SDP	SDOC	SDMC	SDPC
P=O	1277	1285	1283	1285	1286
C-O-P	1017	1028	1012	1014	1013
Typical of spiro structure	910, 853, 780, 691	913, 853, 778, 691	909, 856, 783, 692	909, 857, 784, 692	910, 859, 783, 692
$C(CH_2)_4$	1150	1156	1148	1152	1153
P-Cl	549	-	-	-	-
Benzene ring	-	1642	1644	1615	1641
CH_3 deformation	-	-	1466	1467	1465

Table-3: Proton NMR Studies - Chemical shift values for various protons present in different spiro compounds.

Type of proton	Chemical Shift (δ, ppm)				
	SDDP	SDP	SDOP	SDMP	SDPC
$-CH_2$ protons in spiro unit	3.5-4.7	3.5-4.65	3.6-4.3	3.6-4.66	3.5-4.68
Aromatic ring protons	-	7.1-7.5	7.2-7.5	7.0-7.5	7.2-7.6
$-CH_3$ protons	-	-	2.3	2.4	2.36

Table-4: Volatile products identified in the isothermal (500°C and 700°C) pyrolysis of SDP, SDOC, SDMC and SDPC.

Retention Time (min)	Compound Structure / Name	Molecular formula / Molecular weight	SDP	SDOC	SDMC	SDPC
0.59	Methylacrolein	C_4H_6O / 70	**	**	**	**
1.08	Toluene	C_7H_8 / 92	**	**	**	**
2.11	Xylene	C_8H_{10} / 106	**	**	**	**
2.53	Xylene Isomer	C_8H_{10} / 106	**	**	**	**
4.33	Ethylmethylbenzene	C_9H_{12} / 120	*	*	*	*
5.31	Isomer of ethylmethyl-benzene, May be Trimethylbenzene	C_9H_{12} / 120	*	*	*	*
5.74	Phenol	C_6H_5OH / 94	**	-	-	-
7.01	Indene	C_9H_8 / 116	**	-	-	-
7.66	*o*-Cresol	C_7H_8OH / 108	-	**	-	-
8.04	*m*-Cresol	C_7H_8OH / 108	-	-	**	-
7.99	*p*-Cresol	C_7H_8OH / 108	-	-	-	**
9.20	1,2-Dihydronaphthalene	$C_{10}H_{10}$ / 130	*	*	*	*
9.40	Dimethylphenol	$C_8H_{10}O$ / 122	*	*	*	*
9.60	*p*-Acetoxytoluene	$C_9H_{10}O_2$ / 150	*	*	*	*
10.13	Trimethylphenol	$C_9H_{12}O$ / 136	*(trace)	*(trace)	*	*
10.65	Dimethylbenzofuran	$C_{10}H_{10}O$ / 146	*	*(trace)	*(trace)	*(trace)
11.20	Isomer of Dimethyl-benzofuran, May be Ethylbenzofuran	$C_{10}H_{10}O$ / 146	*	*	*	*
11.32	Benzocycloheptatriene	$C_{11}H_{10}$ / 142	*	*	*	*
11.53	Isomer of # 18, May be Methylnaphthalene	$C_{11}H_{10}$ / 142	*	*	*	*
12.22	7-Methoxy-1,2-dihydronaphthalene	$C_{11}H_{12}O$ / 160	-	-	-	*
12.40	Trimethylindene isomer	$C_{12}H_{14}$ / 158	*	-	-	-
12.67	Isomer of # 20, May be Dimethyl-1-indanone	$C_{11}H_{12}O$ / 160	*	*	*	*
12.83	Isomer of 7-Methoxy-1,2-dihydronaphthalene	$C_{11}H_{12}O$ / 160	*	*	*	*
12.99	Dimethylnaphthalene	$C_{12}H_{12}$ / 156	*	*	*	*
13.20	Isomer of Dimethylnaphthalene	$C_{12}H_{12}$ / 156	*	*	*	*
13.99	Trimethylnaphthalene	$C_{13}H_{14}$ / 170	*	*	*	*
14.29	Isomer of Trimethylnaphthalene	$C_{13}H_{14}$ / 170	*	*	*	*
14.49	Isomer of Trimethylnaphthalene	$C_{13}H_{14}$ / 170	*	*	*	*
14.67	Isomer of Trimethylnaphthalene	$C_{13}H_{14}$ / 170	*	*	*	*

*Products identified among the pyrolysis products and the structure proposed on the basis of fragmentation pattern, **Products identified by injecting authentic samples

In order to explicate the formation of volatile products from degrading spirophosphates it is necessary to know the weak bonds present in the spirophosphates. The absence of *β*-hydrogens in spirophosphates limits the occurrence of cyclic

cis-elimination reactions whereas these materials are more prone for thermal degradation via either degradation initiated by free radical and/or carbocation mechanism. Since the free radical mechanism is more favoured for the degradations occurring at higher temperatures, the degradation initiated by the formation of carbocations is the most preferred type of initiation of degradation in the spirophosphates[15].

Camino et al. studied the intumescence of 3,9-dihydroxy derivative of SDDP and reported the formation of carbocation to produce phosphocarbonaceous char[15,16]. Vijayakumar et al. demonstrated the conformational aspects of SDDP which permits the migration of hydrogen from $C_1(H)$ and $C_7(H)$ to $P_9(O)$ and $P_3(O)$ respectively[9]. Balabinovich, pointed out that the heterolysis scission of a C-O bond present in the spiro unit leads to the formation of ionic intermediates followed by the subsequent rearrangement via stabilization of carbocation and

breaking of P-O bonds. The foregoing discussion reveals that the spirophosphate compounds undergo easy thermal degradation through the cleavage of CH_2-OP and CH_2O-P bonds present in a spiro unit and P-OAr bond in the phosphate unit (Scheme-1).

In the previous work, the authors synthesized four different spirophosphates from SDDP with phenol, *p*-Cresol, dimethyl and trimethyl phenol and studied their thermal degradation behaviour by Py-GC-MS method. From the analysis of the volatile degradation products formed, the degradations are supposed to start with either intra or intermolecular migration of hydrogen atom from 1, 5, 7 and 11th position, to the oxygen attached to the phosphorous atom in the spiro unit, leading to the formation of phosphonium ion intermediates followed by successive rearrangements and breaking of C-O bond in spiro unit and P-O bond in phosphate unit[12].
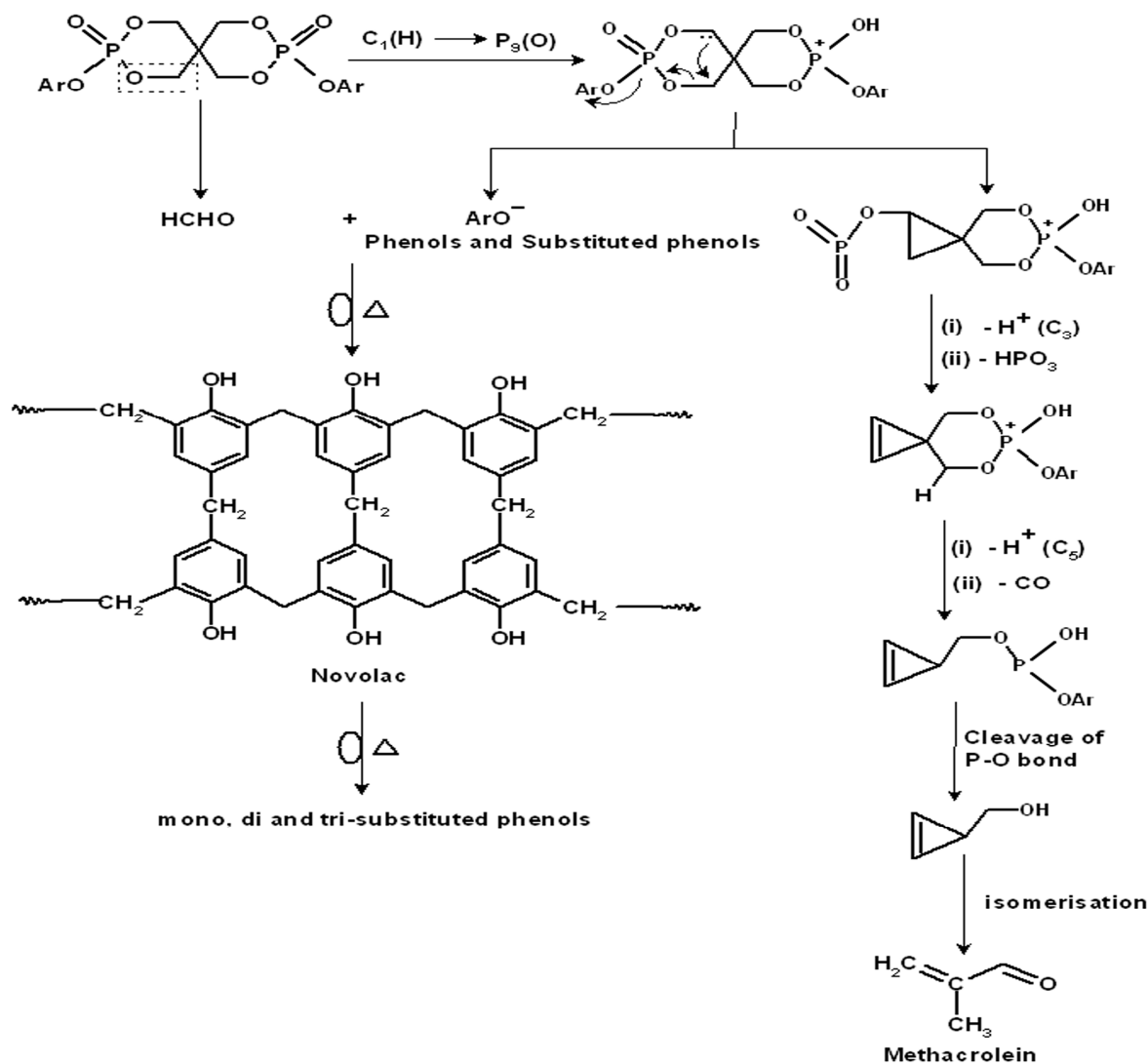
Scheme-1: Mechanism of formation of methacrolein and substituted phenols from spirophosphates.

In the present investigations, the examination of distribution of volatile compounds acquired by pyrolyzing the spirophosphates at 500°C and 700°C, allow one to categorize all the products into four main groups: (a) isomers of compounds containing C_4H_6O, particularly methacrolein, (b) phenolic products such as phenol, *o*-cresol, *m*-cresol, *p*-cresol, dimethyl phenol and trimethyl phenol, (c) hydrocarbons like toluene, xylenes, naphthalenes, etc. and (d) furan ring containing compounds. The formation of these groups of compounds can be easily accounted by the already proposed mechanism i.e., the formation of phosphonium ion followed by the several rearrangements and subsequent cleavage of C-O and P-O bonds.

Methacrolein was found to be one of the major degradation products of spirophosphates and is the isomerization product of cyclopropenylmethanol. The possible mechanism of formation of methacrolein from spiro unit of spirophosphates is clearly shown in Scheme-1. Under the pyrolysis conditions employed, spirophosphates undergoes number of ionic rearrangements and condensation reactions direct the formation of cyclopropenylmethanol, which comes out after isomerization as methacrolein from the degrading spirophosphates.

The evolution of phenol, *o*-cresol, *m*-cresol, *p*-cresol from SDP, SDOC, SDMC and SDPC respectively indicates the cleavage of P-OAr bond. The concerted mechanism of P-OAr bond cleavage is presented in Scheme-1. As seen from Figure-3, the amount of formation of respective phenols from SDP, SDOC, SDMC, and SDPC is in the order phenol (SDP) > *o*-cresol (SDOC) > *m*-cresol (SDMC) > *p*-cresol (SDPC). The possible explanation for the above order is as follows: when an electron-withdrawing substituent is present in the benzene ring, the cleavage of P-OAr bond is favoured. Since methyl group present in the benzene nucleus is electron-releasing, it restricts the P-OAr bond cleavage present in phosphate unit and hence depending upon the orientation of methyl group, the amount of formation of *o*-cresol, *m*-cresol, *p*-cresol from SDOC, SDMC and SDPC varies. Along with phenol, mono-, di- and tri-substituted phenols are also formed from the degrading SDP and the plausible mechanism for their formation has been presented in Scheme-1. The low molecular weight pyrolysis products from the spirophosphates are H_2O, HCHO, CO_2 and CO and the modes by which these materials are liberated from the degrading spirophosphates are presented in Scheme-1 and 2.

The evolution of H_2O from spirophosphorous compounds was supported by the study of Vijayakumar et al[10]. Since formaldehyde is a very reactive compound, it easily undergoes reaction with nucleophilic compounds, for example phenols to give the methylol substituted phenols. This reactive material undergoes condensation and produces the novolac type phenol-formaldehyde resin. The acidic environment created during the degradation of the spirophosphates catalyses the condensation of phenol and formaldehyde, both being liberated during the thermal degradation of the different spirophosphates investigated in this study. Huggard et al. reported that, at high temperature novolac type phenol-formaldehyde resin develop highly crosslinked reinforcing char in the presence of acidic species created by red phosphorus[18]. In the present system it is well known that spirophosphates on degradation evolves variety of acidic species and thus there is a chance for the char forming dehydration reaction. Owing to the intermittent formation of novolac type phenol-formaldehyde resin from the thermally degrading spirophosphates, the formation of mono-, di- and tri-substituted phenols can be easily explained[19]. The thermally degrading spirophosphates limit the diffusion of formaldehyde to the vapour phase and reduces the concentration of the volatiles in the gas phase. The homogeneous fixation of this reactive material in the condensed phase in the form of novalac type phenol- formaldehyde resin favors the formation of multi alkyl susbstituted phenols during degradation and also enhances the production of the condensed phase thermal insulator, phosphocarbonaceous char.

It is interesting to note the presence of different methyl substituted aromatic hydrocarbons like toluene, xylene, etc. among the degradation products obtained from the spirophosphates. Apart from simple aromatics, condensed aromatics like naphthalenes and indanes were also noted among the volatile products. The formation of spirodiene and its isomers particularly ethylenecyclopropane and cumulenes from the degrading spirophosphates are responsible for the production of different aromatic hydrocarbons. The identification of cyclopropene containing compounds in the flash pyrolysis-mass spectrometry studies was reported eleswhere[13]. Vijayakumar et al. discussed the formation of spirodiene and its formation mechanism is illustrated in Scheme $2^{9,12}$. The highly strained, reactive and hydrogen deprived nature of this compound facilitate the isomerization, polymerization and crosslinking reactions and is responsible for the formation of several simple and condensed aromatics.

From Figure-3 it is obvious that while pyrolysing the samples at 500°C, the amount of phenolic compounds formed are higher than the hydrocarbons where as when the pyrolysis temperature was 700°C, the simple and condensed aromatic hydrocarbons are formed in higher amounts at the expense of the different phenols. The possible mechanism for this finding is depicted in Scheme-3.

Initially the thermal degradation of spirophosphates starts with the migration of hydrogen atom present in spiro unit to the oxygen atom present in the phosphate group. This facilitates the breaking of the P-OAr bond and the production of phenols. When the pyrolysis is carried at higher temperature (700°C), the chance for the migration of hydrogen present in the benzene ring of phenol unit through the six membered cyclic transition states helps the formation of the reactive reaction intermediate benzyne. This intermediate undergoes subsequent rearrangements, condensation reactions and Diels-Alder reactions at higher temperature in acidic environments and increases the probability for the formation of number of aromatics and condensed aromatic hydrocarbons.
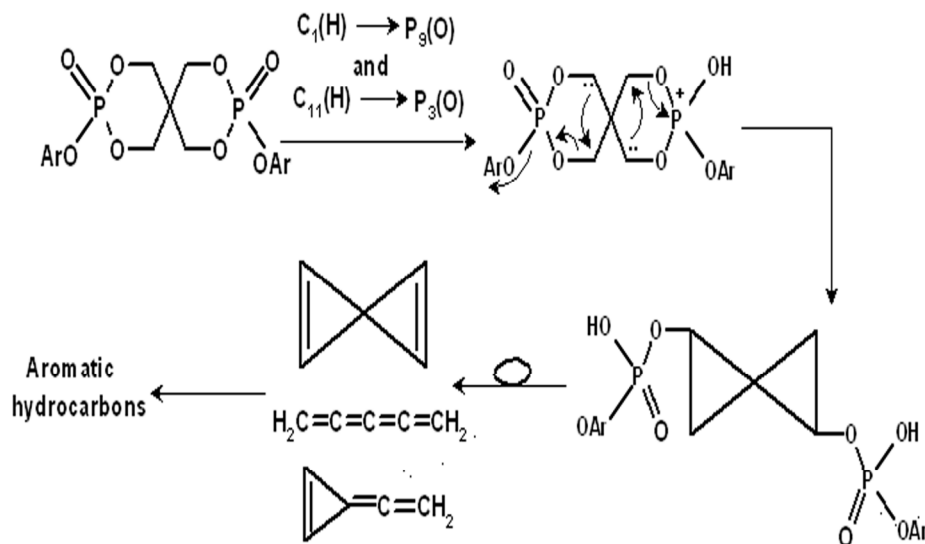
Scheme-2: Mechanism of formation of spiro-[2,2]-pent-1,3-diene and its isomers from spirophosphates.
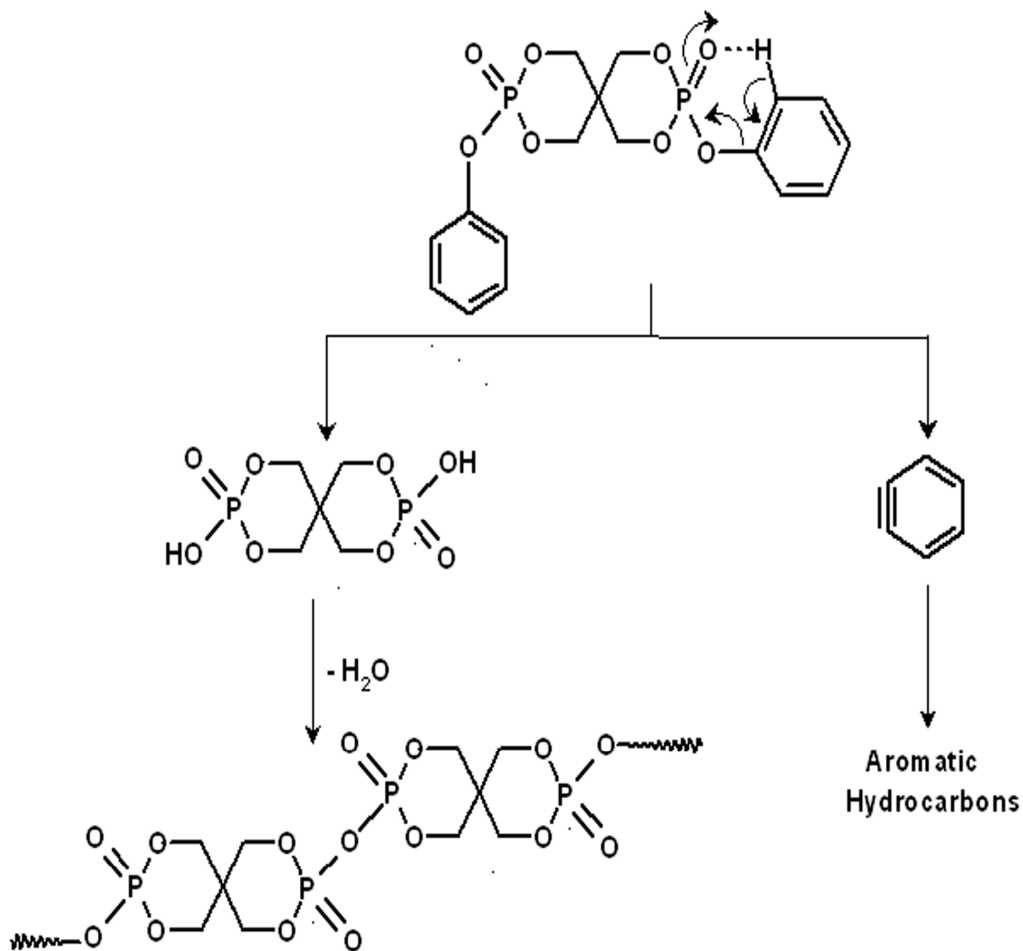
Scheme-3: Formation of benzyne intermediate from spirophosphates

Furan ring containing volatiles such as benzofuran and substituted benzofurans were seen in minor amounts in the degradation products of spirophosphates. Characteristically benzofurans can be synthesized from ortho alkyl substituted phenols and/or O-alkyl substituted phenols. It is well known that phenols undergo addition reactions with alkeneic compounds in the presence of acids. Phenols and hydrocarbons noted among the degradation products of spirophosphates may undergo addition reaction in the presence of acidic medium created by the degrading spirophosphates leading to the formation of phenolic ethers. The formed aromatic ethers may undergo Claisen rearrangement and subsequent reactions may yield the precursors of benzofurans such as ortho alkyl substituted phenols and/or O-alkyl substituted phenols.

Conclusion

In the present investigation, the proposed chemical structures of SDP, SDOC, SDMC and SDPC are confirmed by FT-IR and ^{1}H-NMR studies. The formations of respective phenols from SDP, SDOC, SDMC and SDPC respectively indicate the P-OAr bond cleavage in the phosphate unit. Pyrolysis of spirophosphates proceed via the formation of spirodiene and its isomers, cumulenes and cyclopropene derivatives. However pyrolysis of these compounds at higher temperature (700°C), favors the cleavage of P(O)-Ar bond resulting in the formation of benzyne intermediate, which facilitates the production of aromatics like toluene, xylene, etc and condensed aromatics like naphthalenes and indanes from the spirophosphates. The formation of formaldehyde during the degradation of spirophosphates and its subsequent reaction with the different phenols formed leads to the formation of novolac type phenol-formaldehyde resin. Hence the flammability of the material is reduced and thermal feed back in the condensed system is considerably arrested due to the formation of the rigid phosphocarbonaceous char.

Acknowledgements

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