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Structural Basis for Intumescence – Study of Model Compounds Containing Spiro Phosphorus Moiety and Polymers Containing Such Units

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Summary: Spiro phosphorus compounds play a vital role, in recent years, in imparting flame retardancy and intumescence to the polymers. To ascertain the mechanism of the intumescency, model spiro phosphorus compounds, *i.e.*, 3,9-disubstituted-2,4,8,10-tetraoxa-3,9-diphosphaspiro-[5.5]-undecan- 3,9-dioxide, were chosen (compound I : substitution is chloro group and compound II : substitution is hydroxo group). The model compounds were investigated using Differential Thermal Analysis (DTA) and Thermal Volatilization Analysis (TVA), Vacuum Pyrolysis-MS and Off-line Pyrolysis followed by degradation product analysis by GC-MS.

Dichlorospiro compound (I) showed an eruptive release of gases at 320 °C and dihydroxo spiro compound (II) at about 350 °C. The major components of the gas released were found to be HCl and H_2O in the case of compound I and H_2O in the case of compound II. The degradation product analysis showed the formation of wide varieties of substituted and condensed aromatic compounds in measurable quantities. From the acquired data, it is confirmed that the intumescence takes place within a narrow range of temperature (10°) and in this temperature limit extensive dehydrohalogenation and dehydration are taking place. Highly thermally reactive unsaturated hydrocarbons are produced which mainly undergo polymerization to aromatic compounds and finally to char.

Introduction

Extensive discussion of intumescent coating technology has been given by Vandersall.[1] The following types of ingredients are necessary to achieve proper intumescence: a) a catalyst that causes the decomposition of carbon containing compounds and helps in the gas formation reaction, b) a carbonaceous material which produces enough carbon like masses to permit an adequate density and thickness of carbonaceous foam, c) a flowing agent which decomposes to produce abundant quantities of non-combustible gases and d)

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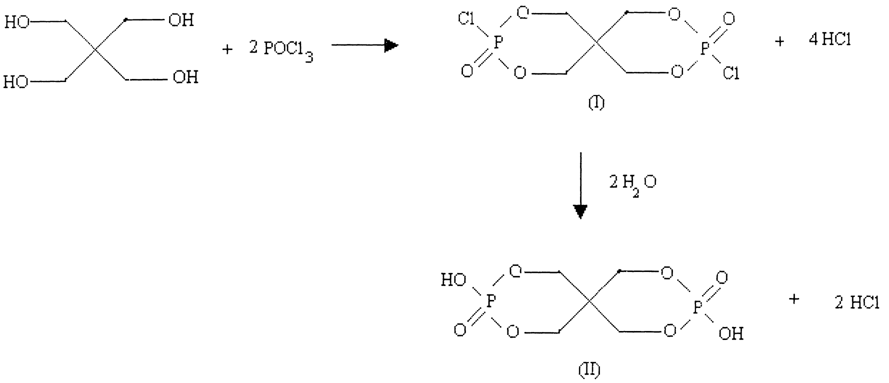
an additive which aids the flame retardation. During the act of intumescence, it is most important that the liquefication of the medium, the gas generation and the cross-linking reactions to form the foam char must occur almost simultaneously in the sequence given above. 3,9-Disubstituted-2,4,6,8-tetraoxo-3,9-diphosphaspiro-[5.5]-undecane-3,9-dioxide (spiro) containing compounds show intumescent flame-retardant behaviour since this structural moiety is having both acid and carbon source in single entity.[2,3] The objective of this investigation is to elucidate the chemical mechanism of the intumescent behaviour of the spiro by thermal analyses and by the analysis of the pyrolysis products.

Experimental

Pentaerythritol was allowed to react with phosphorus oxychloride (in 1:2 mole ratio) to form dichloro substituted spiro compound (I) [4] according to Scheme 1. The two chlorine atoms were replaced with hydroxy groups by simple hydrolysis to form dihydroxy substituted spiro compound (II). Compound (I) was condensed with resorcinol, hydroquinone, bisphenol A and fluorene dicarbinol using melt condensation technique. In all the cases the reaction vessel was completely flushed with nitrogen continuously until the evolution of HCl ceases. Then vacuum was applied to complete the condensation. The spiro compounds I and II were spectrally characterized by IR studies. The spectra of the samples were recorded on a Perkin Elmer 283 IR Spectrophotometer using KBr pellet technique.



Scheme 1.

The differential Thermal Analysis (DTA) of I and II was carried out in a Mettler TA 2000 system. The Thermal Volatilization Analysis (TVA) was performed in an all-glass apparatus detailed elsewhere.[5] Pyrolysis of I in vacuum was run and the degradtion products were directly fed into Balzer Quadrapule Mass spectrometer QMG 511 for the identification of gaseous products evolved. Flash pyrolysis of I (500 °C for 5 sec) was done by inserting the sample, deposited on a platinum ribbon, directly into the mass spectrometer. The Off- line pyrolysis was carried and the technique for collecting the volatile and cold ring fraction of the pyrolusates is detailed elsewhere.[6,7] The products were separated and identified using a Hewlett Packard Gas Chromatograph (HP 5890) containing a 12 m capillary 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

Studies on Model Compounds.

The molecular structures of the synthesized I and II have been ascertained by IR studies. In both the compounds, the four absorption peaks (921, 851, 775 and 685 cm^{-1} characteristic of 2,4,8,10-tetraoxo-3,9-diphosphaspiro-[5.5]-undecane unit[4] are noted. The C-O-P stretching vibrations are observed at 1020 cm^{-1} in I and at 1031 and 1010 cm^{-1} in II. In the latter compound, the broad and shallow P-OH absorption is noted at 2700-2500 cm^{-1} . The DTA, TVA and the pyrolysis mass spectrometry on-line total ion current (TIC) traces for I are depicted in Figure 1. The DTA trace shows an endotherm peak around 240 °C which is attributed to the melting of the compound. An exothermic peak with maximum at 340 °C is also noted. The TVA trace which is sensitive to pressure increase shows evolution of gases from 150 °C onwards and levelled around 200 °C . But, in DTA trace no corresponding exo / endo-thermic peaks are observed in this temperature range. As would be explained later, the mass spectrum, recorded under similar conditions of pyrolysis with TIC technique, reveals that the increase of pressure is due to the release of HCl gas. This evolution is explained as due to the hydrolysis of the compound initiated by the absorbed water molecule owing to the hygroscopic properties of the compound. After the melting of the compound, an eruptive release of gases is noted at 315 °C . This pressure shock is over within the temperature range of 5-10 °C . After 325 °C no pressure change is observed. This behaviour seems to be characteristic for the intumescent property of these kind of materials. Because of the slight difference in the response of the detector, the peaks and valleys in the TIC trace are slightly shifted towards high temperature. The mass spectrum obtained during the flash pyrolysis of I at 500 °C is presented in Figure 2. The most intense peaks are grouped in the m/z region 35-40 apart from water peak at m/z 18. The possible ionic species representing m/z 35-40 are given below:

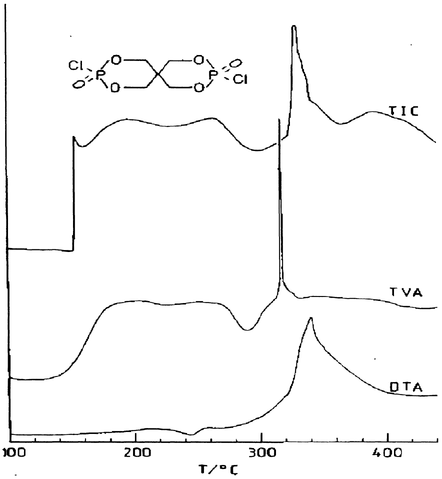


Figure 1. The DTA, TVA and TIC traces of dichlorospiro compound (I) (heating rate : 10 °C min^{-1}).

m/z	35	36	37	38	39	40
possible species	Cl^+	HCl^+	Cl^+	HCl^+	$C_3H_3^+$	$C_3H_4^+$

The flash pyrolysis results reveal that the major amount of volatile products released from I is due to HCl and H_2O . These two volatile products are monitored by heating I from 100 ° to 400 °C at a heating rate of 10 °C min^{-1}. The evolved gaseous products are fed into the mass spectrometer and the mass spectra are recorded at the following temperatures 100, 150, 190, 250, 290, 325, 375 and 400 °C. From the recorded mass spectra, the intensities of m/z 18 and 36 are extracted and plotted (Figure 3). In the intumescent temperature region (~325 °C), it is observed a sudden release of H_2O and HCl.

These two gases are acting as the the flowing agents. The possible mechanism for the evolution of these two gases is exemplified below (Schemes 2 and 3).

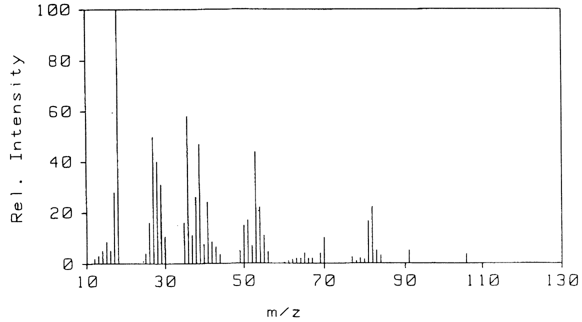


Figure 2. Mass spectrum obtained during the flash pyrolysis of compound I at 500 °C.

In Scheme 2, the possible conformations of the spiro compound I are presented. Depending upon the disposition of the P=O and P-Cl groups, the transfer of hydrogens from C_1 to oxygen / chlorine at P_9 and C_7 to oxygen / chlorine at P_3 is possible. This transfer is possible only if the molecule exists in boat conformation. In Scheme 3, the transfer of hydrogens from C_1 and C_7 to oxygens at P_9 and P_3 respectively with concomittant rearrangements leading to the formation of the compound-containing spiro-

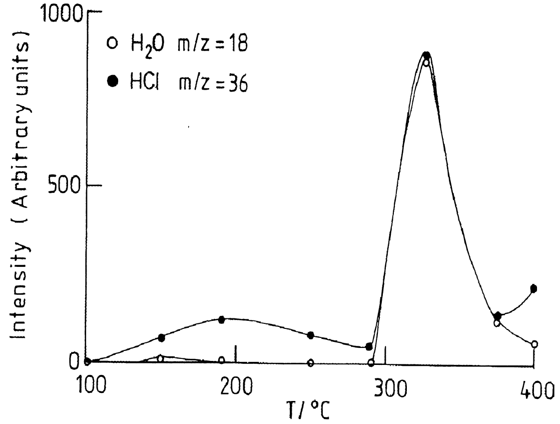
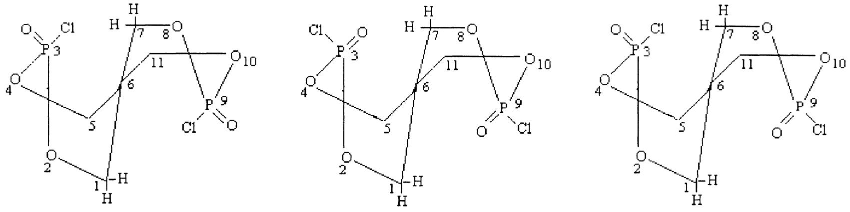
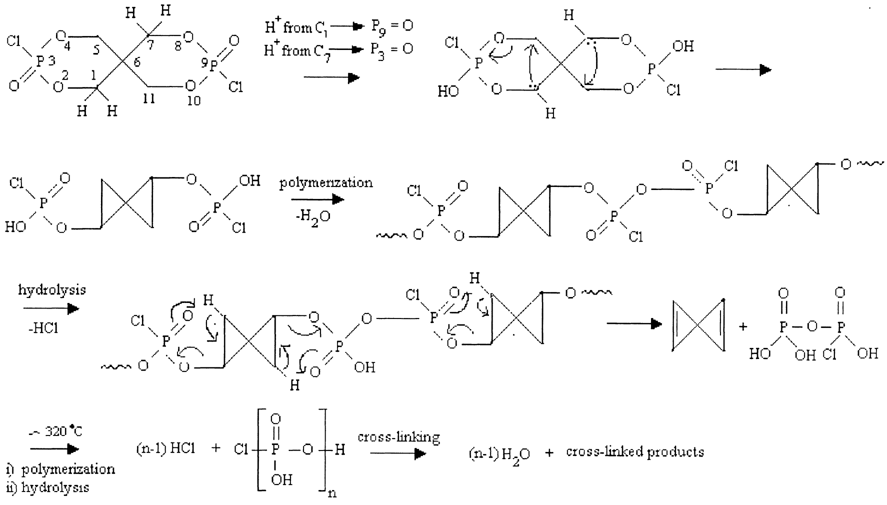


Figure 3. Variation of the intensities of the ionic species with m/z 18 and 36 during heating of the compound (I) from 100 ° to 400 °C at the heating rate of 10 °C min^{-1}.

[2.2]-pent-1,3- dienyl unit is shown. This molecule undergoes a series of reactions involving polymerization, hydrolysis and subsequent decomposition with the liberation of H_2O and HCl. The compound spiro-[2.2]-pent-1,3-diene[8] is highly strained and extremely reactive and is the precursor for the carbonaceous foam formed due to intumescence. Formation of the compound spiro-[2.2]-pent-1,3-diene is supported from the analyses of the volatile and cold ring fractions obtained during the pyrolysis of I. In the volatile fractions, compounds containing cyclopropene rings have been identified (1-chloromethylcyclopropene, 1,1-dichloro-2-ethenylcyclopropane, *etc.*). At high temperature spiro-[2.2]-pent-1,3-diene isomerizes to 3-ethynyl-1-cyclopropene, $HC{\equiv}C\text{-}CH_2\text{-}C{\equiv}CH$, $H_2C{=}C{=}C{=}C{=}CH_2$, $HC{\equiv}C\text{-}CH{=}C{=}CH_2$, *etc.* Owing to the polymerization of the compounds, formation of substituted benzenes, condensed aromatics, like naphthalenes, azulenes,



Scheme 2.



Scheme 3.

fluorenes and anthracenes is expected. As to the expectation, ethylbenzene, 1,2 -dimethylbenzene, 1-ethyl-2-methylbenzene, 1,2,3-trimethylbenzene, 2,3-dihydro-4-methylindene, isomeric dimethylnaphthalenes, 1,4,6-trimethylnaphthalene, 7-ethyl-1,4-dimethylazulene, mono- and di-methyl substituted fluorenes, substituted anthracences and phenanthrenes are noted in the pyrolysis products of I. Compund II on heating shows an eruptive release of water at 350 °C. The compounds identified in the pyrolysis products of II are more or less the same as identified in I. This ascertains a similar type of degradation path (as given in scheme 3) taking place in compound II during pyrolysis. Using the compound I as one of the reactive monomers, a family of aromatic spirophosphates has been synthesized taking dihydric phenols viz., resorcinol, hydroquinone, bisphenol A and flourene dicarbinol as the other monomer. A detailed structural charecterization using FT-IR and ^{1}H-, ^{13}C-, and ^{31}P- NMR techniques has been undertaken. The results along with the thermal characterization and pyrolysis studies will be communicated later.

Conclusion

From the detailed on-line and off-line degradation studies of 3,9-disubstituted-2,4,8,10-tetraoxo-3,9-diphosphaspiro-[5.5]-undecane-3,9-dioxide, its intumescent behaviour is believed due to the simultaneous elimination of H_2O and HCl with concomittant foam char formation. It is further concluded that a compound should have a hydrogen-deprived carbon system and hydrogen-pluging moiety in it to show intumescent behaviour.

[1] H. L. Vandersall, *Paper presented at the Wayne State Univ. Polymers Conf. Series, Program 5,* Detroit, Mich., June 13-17, 1996.

[2] Y. Halpern, D. M. Molt, R. H. Niswander, *Ind. Eng. Chem. Prod. Res. Dev.* **1984**, *23*, 233.

[3] Z. L. Ma, W. G. Zhao, Y. F. Liu, J. R. Shi, *J. Appl. Polym. Sci.* **1997**, *66*, 471.

[4] R. Ratz, O. J. Sweeting, *J. Org. Chem.* **1963**, *28*, 1608.

[5] C. T. Vijayakumar, J. K. Fink, *J. Appl. Polym. Sci.* **1982**, *27*, 1629.

[6] C. T. Vijayakumar, K. Lederer, A. Kramer, *J. Polym. Sci. Part A : Polym. Chem.* **1989**, *27*, 2723.

[7] P. Sivasamy, *Ph.D. Thesis*, Madurai Kamaraj University, Madurai, India, 1989.

[8] M. S. Baird, *Topics in Current Chemistry, Compt. Org. Synth.* **1988**, *3*, 144.