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Thermal decomposition study of 2-methyl-1,2-oxaphospholan-5-one 2-oxide

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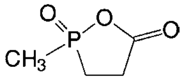
Abstract

2-Methyl-1,2-oxaphospholan-5-one 2-oxide (OP) is useful in a wide range of flame-retarded compositions. It is a thermally stable substance which, in inert atmosphere, looses weight at 200 °C on dynamic heating, leaving a solid residue, the amount of which is sensitive to the presence of moisture. Due to the reactive P–O bond, the thermal stability of OP can be increased by reaction with amines or alcohols and it can be introduced into a variety of plastics. Upon pyrolysis at 450 °C, OP volatilizes and decomposes, producing CO_2, low-chain hydrogencarbons, aliphatic and aliphatic–aromatic phosphine oxides and a black deposit, where polymeric phosphine oxides and phosphorus acid anhydrides were detected. Mechanism to explain the occurrence of the different products is proposed. Based on these data the condensed- and vapor-phase fire retardant mode of action of OP appear to be feasible.

Keywords: Pyrolysis; Flame retardance; Thermogravimetry; GC/MS; FT-IR; Oxaphospholanes

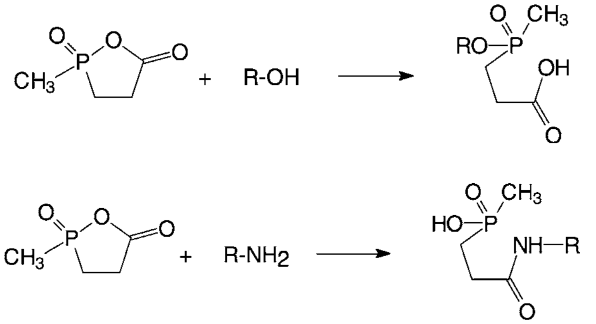
1. Introduction

Oxaphospholanes are heterocyclic saturated compounds containing three carbons, one phosphorus and one oxygen in the ring. 2-Methyl-1,2-oxaphospholan-5-one 2-oxide (OP, **I**) also known as 2-methyl-2,5-dioxo-1,2-oxaphospholane, a cyclic anhydride of 2-carboxyethylmethylphosphinic acid, is a commercial product of Fa Clariant (Germany), which is used to produce a flame retardant poly(ethylene terephthalate) sold under the trade name Trevira® CS.



(I)

The material made via reaction of CH_3PCl_2 with acrylic acid in the presence of acetic anhydride contains 23% phosphorus and is of great interest as a perspective additive and reactive fire retardant. In the later case chemical reactivity of OP towards alcohols and amines could be used [1]:



In combination with melamine, OP pre-reacted with 1,3-phenylenediamine is described as giving non-flammable poly(butylene terephthalate) [2]. Flame-retarded polyester fabrics [3], moldings [4], films [5], resins [6] are prepared using OP introduced into polymeric materials by copolymerization. As an additive fire retardant, OP was found to be effective in combination with poly(sulfonyldiphenylene phenylphosphonate) and poly(2,6-dimethylphenylene oxide) in poly(butylene terephthalate) [7] and in combination with poly(2,6-dimethylphenylene oxide) in high impact polystyrene [8].

These examples show the importance of OP as a fire retardant additive for plastics. However, at present no data on

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OP thermal decomposition are available which could illustrate its flame retardant action.

2. Experimental

OP (Exolit® PE 110, registered trademark of Clariant, Germany) was used as received.

Thermal analysis was carried out by thermogravimetry and differential scanning calorimetry (DSC) using a Mettler TA 3000 thermal analyzer at a heating rate 10 °C/min in argon and air (gas flow 60 ml/min).

High boiling degradation products (HBPs) and gaseous degradation products (low boiling degradation products, LBPs) were collected in isothermal experiments at 450 °C (e.g. at the temperature of the surface of burning polymeric materials). For these experiments, OP (about 100 mg) was put in the bottom of an ampoule which was vertically placed in an preheated oven and inert gas flow was constantly applied in the ampoule. The middle part of the ampoule was cooled by running water and its output was connected with a U-tube which was placed in liquid nitrogen. The HBPs condensed in the middle part of the ampoule were washed out by acetone and subsequently analyzed by GC/MS, whereas the insoluble HBPs were analyzed by FT-IR. Volatile products collected in the U-tube were also investigated by GC/MS. The solid residue from the ampoule was investigated by IR spectrometry on a Perkin-Elmer set-up (“Spectrum-1000” FT-IR) using KBr pellets.

GC/MS experiments were performed using Hewlett-Packard equipment (HP6890/5972A) and HP-5 30 m column employing the electron impact method. After injection of the HBPs sample (injector temperature 250 °C) the oven was kept constant for 2 min at 40 °C. Subsequently, it was increased at a rate of 10 °C/min to 280 °C and kept at this level for 5 min. For the analysis of the LBPs, the 30 m HP-1 capillary column was also found to be an appropriate column. The column was temperature programmed from −10 °C (2 min) to 250 °C at 10 °C/min. The mass spectra were obtained by electron ionization at 70 eV keeping the source at about 180 °C. A mass spectrometric identification was carried out using WILEY and NBS libraries. When compounds were not included in the libraries, they were identified on the basis of both the highest molecular ion *m*/*z* value and of the ion decomposition pattern constructed for the best fit with the mass spectrum.

3. Results

3.1. Thermal analysis

In inert atmosphere OP exhibits a one-step weight loss process starting at about 200 °C and leaving 3% solid residue that is stable to 600 °C (Fig. 1, curve a). The amount of the residue increases in the moisture-containing gas flow (curve b), and the observed weight increase at 80–190 °C is likely to be due to the strong absorption of moisture. From the TGA curve recorded under air (curve c), it is seen that the residue is resistant to oxidation, as it does not burn out on heating to 600 °C.

The DSC curve of OP is presented in Fig. 2. In inert gas flow, it shows one endotherm at 97 °C due to melting and one endotherm at 269 °C, which corresponds to the weight loss in TG.

3.2. FT-IR study

OP pyrolyzed in the degradation apparatus leaved a black solid residue in the bottom part of the ampoule and formed HBPs condensed in the upper part of the tube and LBPs trapped in the U-tube. The residue was analyzed by means of FT-IR, whereas the HBPs and LBPs were subjected to the GC/MS analysis.

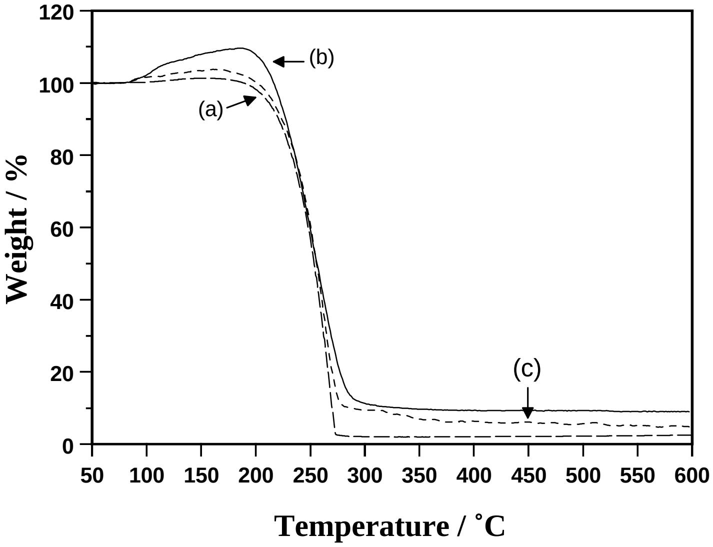


Fig. 1. Thermogravimetry of OP in inert gas (a), in inert gas containing moisture (b), in air (c) flow (60 ml/min). Heating rate 10 °C/min.

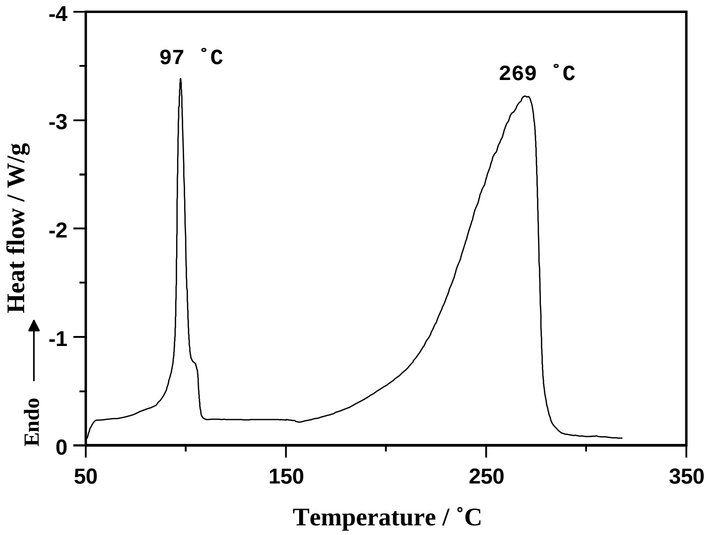


Fig. 2. DSC analysis of OP in inert gas flow (60 ml/min). Heating rate 10 °C/min.

The infrared spectrum of the virgin OP is shown in Fig. 3 (spectrum a). The two intense absorption bands at 1134 and 996 cm^{-1} are associated with P=O and P–O stretching. The bands at 1736 and 1233 cm^{-1} are characteristic of the C=O and (O=)C–O bonds. The absorptions at 1318 and 897 cm^{-1} are typical of CH_3–(P), whereas the band at 1412 cm^{-1} is attributed to the absorption of CH_2.

The spectrum of the solid residue left in the degradation ampoule (spectrum b) shows a new broad strong absorption band at 1120 cm^{-1} which is attributed to the P=O bond and its position is characteristic of phosphine oxides like $O = PR_3$, R = alkyl or phenyl [9]. The absorptions of alkyl C–H stretching are found at 1466 cm^{-1}. A shoulder at 1313 cm^{-1} is assigned to the CH_3–(P) vibration. New absorption bands at 1595 cm^{-1} (aromatic C=C) and 785 cm^{-1} (aromatic C–H) indicate polycyclic aromatic character of the solid residue [10]. The aromatisation processes also result in the formation of dimethylbenzene and aliphatic–aromatic phosphine oxides, as will be described latter.

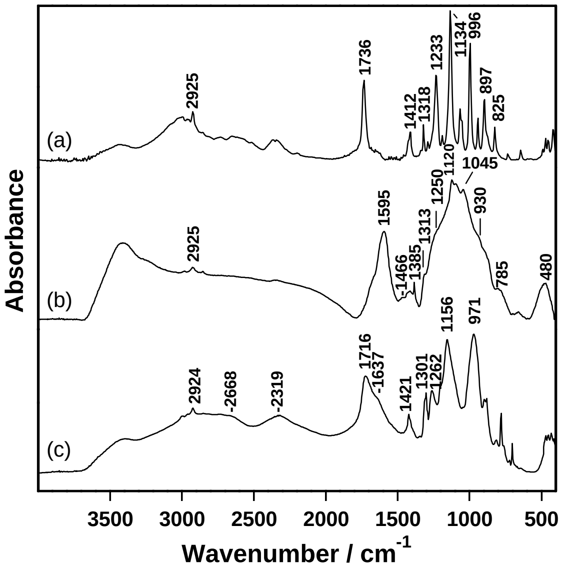


Fig. 3. Infrared spectra of initial OP (a), solid product (residue) collected in the degradation tube under nitrogen at 450 °C for 30 min (b) and an insoluble in acetone HBP (c). Pellets in KBr.

No C=O absorption is present in the spectrum (b) anymore. Therefore, a shoulder at 1250 cm^{-1} is attributed to the phosphoryl absorption in phosphorus acid anhydride R–P(=O)–O–(O=)P–R [9]. The P–O–P group gives raise a shoulder at 930 cm^{-1} and an absorption band at 480 cm^{-1} [9]. These data show an appearance most likely of phosphocarbonaceous residue containing linked methylphosphoryl group which can be formed by elimination of CO or CO_2 upon heating of OP.

In Fig. 3 (spectrum c), IR spectrum of the insoluble HBP formed upon pyrolysis at 450 °C is shown. The spectrum exhibits absorptions bands of O=P at 1156 cm^{-1} and P–O–H at 2668, 2319, 1637 and 971 cm^{-1} [9]. The P–CH_3 can be recognized on 1301 cm^{-1}. The absorption bands at 2668, 1716, 1421 and 1262 cm^{-1} can be attributed the carbon acid moieties. The spectrum is assumed to be that of 2-carboxyethylmethylphosphinic acid formed by reaction of OP with moisture.

3.3. GC/MS study

The typical gas chromatogram of the HBPs is presented in Fig. 4. The peaks, their area and the peaks assignment are listed in Table 1. The typical mass spectra of the HBPs are presented in Figs. 5–9. The corresponding ion decomposition pattern of compounds 5 and 6 (Table 1) are shown in Figs. 10 and 11. The major HBPs are OP and various aliphatic and aliphatic–aromatic phosphine oxides. As described above, aromatic structures were also detected in the solid pyrolysis residue.

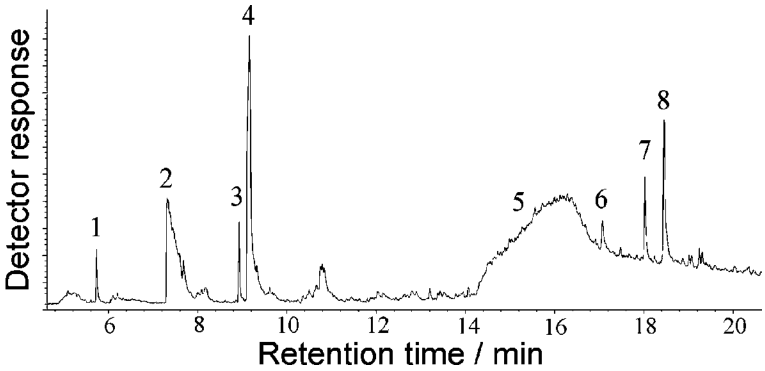


Fig. 4. Gas chromatogram of the HBPs formed upon pyrolysis of OP at 450 °C for 30 min. Peaks assignment in Table 1.

Table 1
HBPs of the pyrolysis of OP

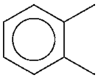
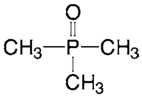
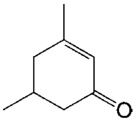
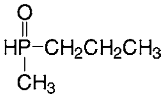
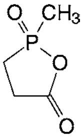
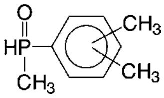
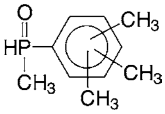
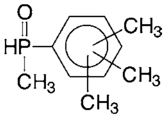
Peak code	Molecular mass (*m*/*z*)	Relative area (%)	Compound
1	106	1	
2	92	14	
3	124	1.5	
4	106	14	
5	134	62	
6	168	1	
7	182	2	
8	182	4.5	

Fig. 12 presents the typical gas chromatogram of the LBPs. The main products are CO_2, C_2H_4, C_3H_7 and other hydrogen carbons formed in the course of secondary reactions of alkyl radicals.

In conclusion, the fact that OP was identified in the HBPs is taken as evidence for the volatilization of the parent compound on heating. In this way, the GC/MS study of the HBPs

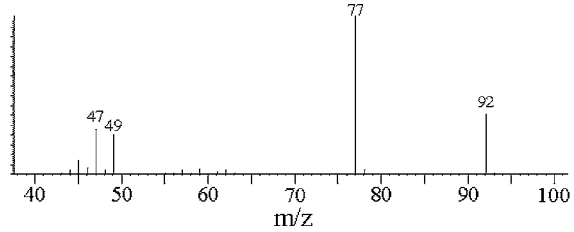


Fig. 5. Mass spectrum of the product 2 (Table 1) generated by pyrolysis of OP.

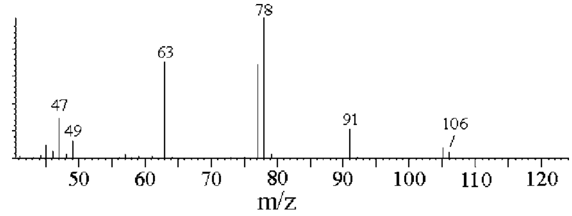


Fig. 6. Mass spectrum of the product 4 (Table 1) generated by pyrolysis of OP.

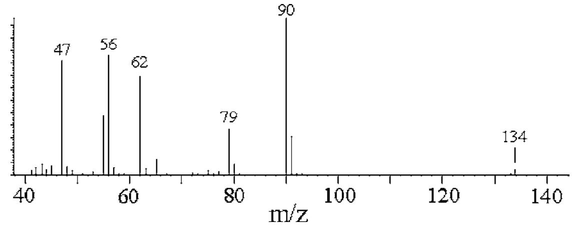


Fig. 7. Mass spectrum of OP (product 5, Table 1).

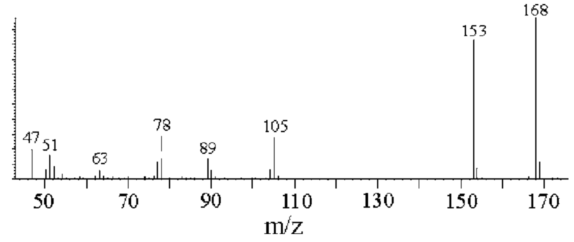


Fig. 8. Mass spectrum of the product 6 (Table 1) generated by pyrolysis of OP.

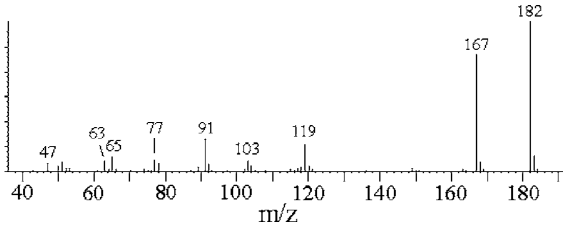


Fig. 9. Mass spectrum of the product 7 (Table 1) generated by pyrolysis of OP (the product 8 also exhibits the same spectrum).

indicates that the decomposition of OP occurs together with the volatilization.

4. Discussion

From the results described above, the pyrolysis of OP results in two competing processes: volatilization and decomposition. The latter originates from a reaction involving an elimination of CO_2 from the oxaphospholane ring. The CO_2 elimination is also the main process occurring under electron impact (Figs. 7 and 10). In connection with this,

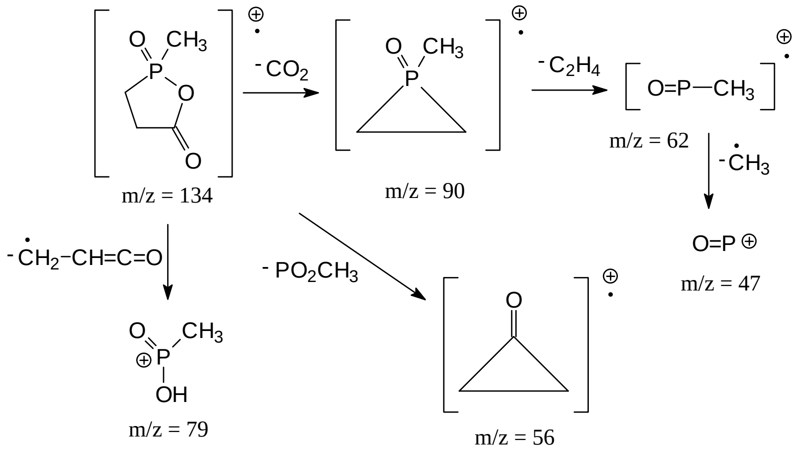


Fig. 10. Mass spectral fragmentation pattern of the molecular ion of OP.

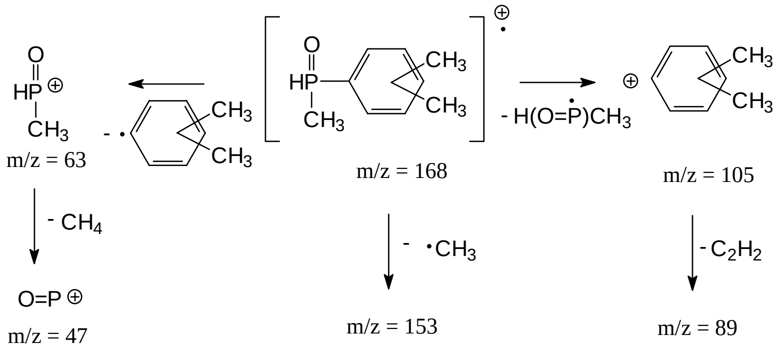


Fig. 11. Mass spectral fragmentation pattern of the molecular ion of compound 6 (Table 1).

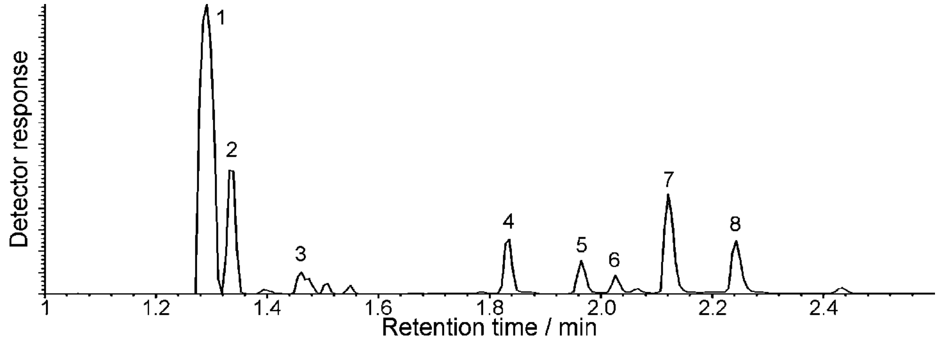


Fig. 12. Gas chromatogram of the LBPs formed by pyrolysis of OP at 450 °C for 30 min. 1: CO_2 (major) + C_2H_4, 2: propene, 3: 2-butene, 4: ethylcyclopropane, 5: 1,2-dimethylcyclopropane, 6: 2-methyl-1-butene, 7: 1,4-pentadiene, 8: 1,3-pentadiene.

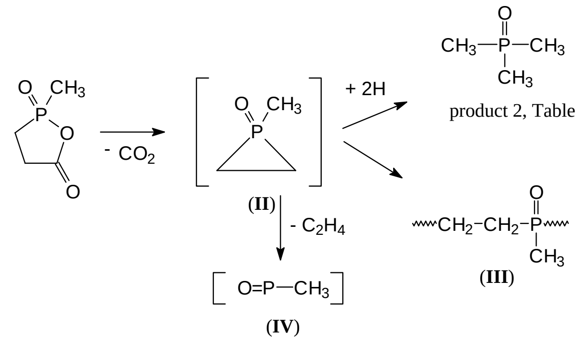


Fig. 13. Possible mechanism of formation of product 2 (Table 1) and polymeric phosphine oxides.

the simplest way for the formation of product 2 (Table 1) is likely to be a reaction route through a cyclic transition state **II** followed by hydrogen abstraction as depicted in Fig. 13. It should be noted that the possible polymerization of **II** results in the formation of polymeric phosphine oxides **III**, i.e. substances which was identified in the solid residue by FT-IR (Fig. 3, spectrum b).

As reported in [11], pyrolysis of cyclic phosphine oxides produces phosphinidene oxides, which result from scission of two P–C bonds. The corresponding process for **II** will involve the elimination of ethylene. The possible reactions that have been attributed to phosphinidene oxides like **IV** include addition to a double bond, a carbonyl group, but also to water and alcohols [11].

A possibility for scission of the P–C bond in **III** cannot be excluded too. In this case, a formation of the vinyl group (**V**, Fig. 14) is expected. Cyclisation of the vinyl bonds leads to a cross-linked structure **VI**, which, followed by aromatisation, gives an aromatic ring **VII**. Further condensation of the aromatic rings can result in formation of polyaromatic structures (Fig. 3, absorption band at 1595 cm^{-1}). The structures **VI** are likely to undergo not only aromatisation but also decomposition by scission of the C–C bonds. This process might result in the formation of different hydrogen carbons (Fig. 12). The structure **VI** can be considered as a source for the formation of aliphatic–aromatic phosphine oxides 6–8 (Table 1).

The formation of phosphorus acid anhydrides in the solid residue can be rationalized in terms of loss of the –CH_2–CH_2–CO– moiety from the OP ring, as shown in Fig. 15. The –CH_2–CH_2–CO– fragment is likely to become a part of a pyrolysis product (Table 1).

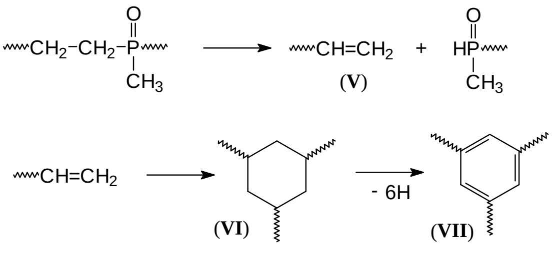


Fig. 14. Possible mechanism of formation of aromatic structures in the solid pyrolysis residue of OP.

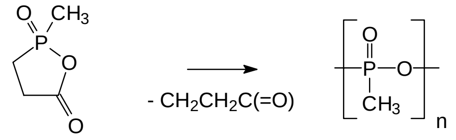


Fig. 15. Possible mechanism of formation of phosphorus acid anhydrides upon the pyrolysis of OP.

5. Conclusion: fire retardant effect

The important aspect of OP decomposition is that it forms thermally stable polymeric products consisting of a phosphine oxide and phosphorus acid anhydride structures. Upon burning of the polymer formulations, even in low amounts, this difficult combustible material may add to fire retardancy by producing a char barrier, such protecting the underlying polymer from a heat- and mass-transfer [12,13].

GC/MS analysis of the HBPs provides that OP volatiles under heating. Therefore, the vapor-phase fire retardant mode of action might be effective. In the flame phase, OP is likely to undergo dissociation producing radicals due to the CO_2 elimination. These radicals are expected to be capable of scavenging hydrogen atoms. In this way, the branching rate-controlling step in the flame chemistry will be inhibited [12,13].

Furthermore, the pyrolysis of OP yields phosphine oxides (Table 1). As reported in [12], these chemical substances can act as flame retardants that are able to show vapor-phase action.

Based on these data the condensed- and vapor-phase fire retardant mode of action of OP appear to be feasible.

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