

Thermal decomposition study of 1,4-diisobutyl-2,3,5,6-tetrahydroxy-1,4-diphosphorinane 1,4-dioxide

A.I. Balabanovich*

Research Institute for Physical Chemical Problems of the Belarussian State University, ul. Leningradskaya 14, 220050 Minsk, Belarus

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Abstract

The thermal decomposition behavior of 1,4-diisobutyl-2,3,5,6-tetrahydroxy-1,4-diphosphorinane 1,4-dioxide (Cyagard), a fire retardant additive, was studied by thermogravimetry, differential scanning calorimetry, FT-IR and GC/MS. Cyagard decomposes vigorously exhibiting a strong sharp-exothermic effect. This effect is caused by a phosphine oxide \rightarrow phosphinate \rightarrow phosphonate rearrangement. The created P–OC ester bonds further degrade to form acidic P–OH and ketone P–COCH₃ bonds. The scission of the P–C bond yields acetaldehyde which evolves in the gas phase. In high boiling decomposition products, diphosphine dioxides, as well as species containing acidic P–OH and ester P–OC bonds are detected.

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1. Introduction

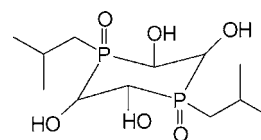
1,4-Diisobutyl-2,3,5,6-tetrahydroxy-1,4-diphosphorinane 1,4-dioxide (Cyagard) is a cyclic diphosphine dioxide. It contains about 20% phosphorus and is an efficient fire retardant additive. Reportedly [1], it is active in polypropylene. In poly(butylene terephthalate), the addition of Cyagard moderately increases the limiting oxygen index and provides a marginal V-2/V-0 rating in the UL94 test with a very short average combustion time [2]. Furthermore, it was tested in high-impact polystyrene [3], widely used as injection molding material. Cyagard affects the limiting oxygen index values of HIPS which steady increase from 18.0 to 22.9 upon addition of 10–40 wt.% of the additive. The addition of 15 wt.% Cyagard, 25 wt.% PPO and 1 wt.% polytetrafluoroethylene results in a nondripping self-extinguishing formulation (a UL94 V-1 rating).

The importance of Cyagard as a fire retardant additive for plastics is shown by these examples. However, there is still lack of data on its thermal decomposition behavior, which could illustrate its flame retardant mode of action.

This paper continues the thermal decomposition study of phosphorus-containing flame retardant additives [4].

2. Experimental

Cyagard(I) was a commercial product of Cytec Industries Corp. available under the trade name Cyagard RF-1204. This is a white powder, insoluble in water, made from mono-isobutyl phosphine and glyoxal followed by oxidizing of the end product.



(I)

Thermal analysis was carried out using a Mettler TA 3000 thermal analyzer provided with a thermogravimetry module and a differential scanning calorimetry (DSC) cell. The temperature precision of the thermobalance and of the DSC cell was ± 2 and ± 0.2 °C correspondingly. The weight data precision was ± 1 μ g under constant conditions. Standard

* Tel.: +375-172-224509; fax: +375-172-264696.

E-mail address: balabanovich@bsu.by (A.I. Balabanovich).

measurements were performed at a heating rate of 10 °C/min in an argon flow of 60 cm³/min.

Solid residues collected at different steps of thermal decomposition in thermogravimetry were investigated by IR spectroscopy on a Perkin-Elmer “Spectrum 1000” FT-IR spectrometer using KBr pellets.

Products of thermal degradation were collected with the aid of a glass setup consisting of a tube that contained the sample (about 100 mg) at the bottom and a cold water condenser at the upper part. While an argon or helium stream passed through, the bottom part was heated up to a rate of 10 °C/min. The gas flow from the tube was directed into a cell where volatile products were trapped at liquid nitrogen temperature and successively analyzed by GC/MS (GC/MS model HP 6890/5972) using a HP-5 30 m column which was temperature programmed from –10 °C (2 min) to 250 °C at a heating rate of 10 °C/min. High boiling products, HBPs, formed distinguished rings at the inner wall of the condenser were analyzed by FT-IR using KBr pellets. In addition, they were washed out by acetone. The acetone solution was subsequently analyzed by GC/MS. In this experiment, the column was temperature programmed from 40 °C (2 min) to 280 °C (10 min) at a heating rate of 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. In a few cases, when compounds were not included in the libraries, they were identified on the basis of both the 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

A typical DSC curve for Cyagard presented in Fig. 1 shows one strong sharp-exothermic phenomenon at 302 °C. This exothermal decomposition behavior is unusual because the breakdown of a P–C bond requires energy supply (a P–C bond is as thermally stable as a C–C one, therefore endothermal decomposition of phosphine oxides should be expected).

As the exotherm appears, Cyagard exhibits a rapid stage of weight loss (about 45%) followed by a more slowly stage of weight loss leaving $3 \pm 0.3\%$ solid residue (Fig. 2).

3.2. IR- and GC/MS study of the pyrolysis products

The infrared spectrum of the original Cyagard is presented in Fig. 3 (spectrum a). The P=O stretching vibration gives rise to a strong band at 1131 cm⁻¹, whereas two other strong bands at 3251 and 1048 cm⁻¹ are attributed to the OH and C–O(H) stretching, respectively. The bands involving isobutyl aliphatic vibrations are located at 2957–2870, 1466 (duplet) cm⁻¹ [5].

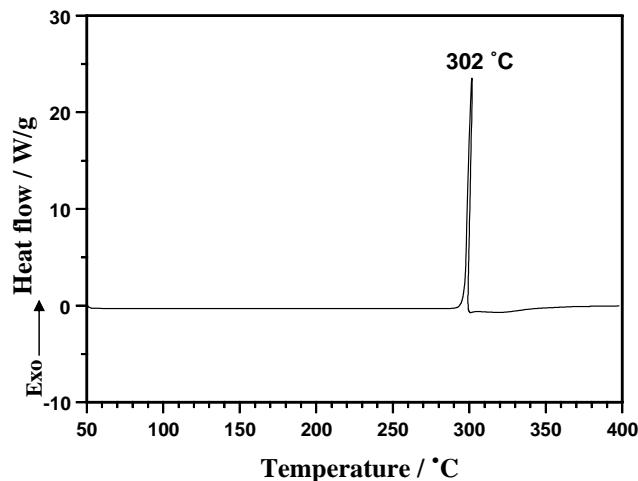


Fig. 1. DSC analysis of Cyagard. Open pans, heating rate 10 °C/min, nitrogen flow 60 cm³/min.

The infrared pattern of Cyagard remarkably changed at 20% weight loss (Fig. 3, spectrum b). The bands of the alcoholic OH disappeared. Instead of them the new bands of P–OH appeared at 2680, 2300, 1638, 987 and 480 cm⁻¹ due to the (P)–O–H valence vibration, a combination of the O–H deformation vibration and 987 cm⁻¹, a combination of the P=O valence vibration and 480 cm⁻¹, the P–O–(H) valence vibration and the P=O deformation vibration, respectively [6]. The band at 1131 cm⁻¹ was shifted to 1167 cm⁻¹, which is likely to be caused by a new chemical environment at P=O [6]. Moreover, there was an increase in the intensity of the aliphatic bands at 2960, 2874, 1467 cm⁻¹, as compared to the intensity of the P=O band. A shoulder at 1722 cm⁻¹ points to the formation of a carbonyl compounds, and its position is characteristic for ketones [5].

This main IR pattern of the solid residue at 20% weight loss was kept during decomposition to 85% weight loss (Fig. 3, spectrum c). In addition, an increase in intensity of

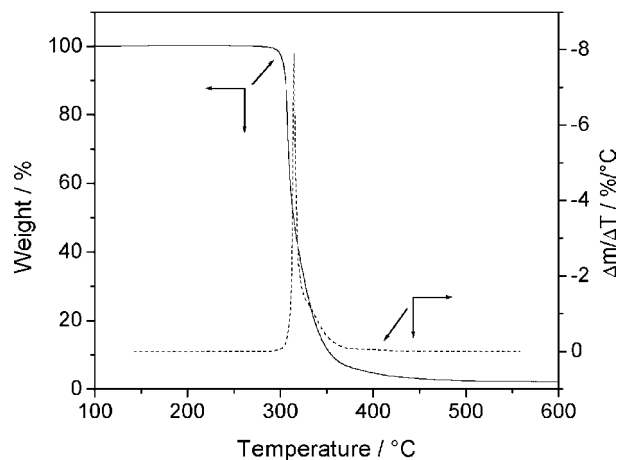


Fig. 2. Thermogravimetry of Cyagard. Nitrogen flow, heating rate 10 °C/min.

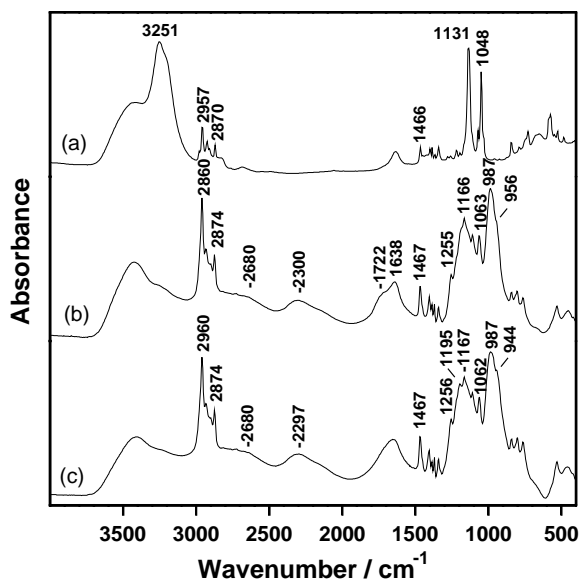


Fig. 3. Infrared spectra of initial Cyagard (a) and its solid products of the thermal decomposition collected in thermogravimetry in inert atmosphere at 20% (b) and 85% (c) weight losses.

peaks at 1195, 944 cm^{-1} ascribable to the P=O and P–O stretch in O=P–O–P=O was detectable indicating a condensation of the acidic P–OH groups to an anhydride structure.

These results indicate that Cyagard undergoes a conversion of P–C–OH bonds to P–OH and CH bonds. For this process, a formation of an intermediate P–OC ester bond is expected, and the support for the rearrangement was further found by studying the HBPs. Two rings of the HBPs were collected during the thermal decomposition of Cyagard. The upper ring was presented by a brown amorphous solid. Its IR spectrum (Fig. 4, spectrum a) shows a very strong absorption band of P–O–C at 1116 cm^{-1} and a strong absorption band of C–C in the phosphorus ester at 962 cm^{-1} .

A black liquid was found in the third ring. Its IR spectrum (Fig. 4, spectrum b) resembles that of the solid residue

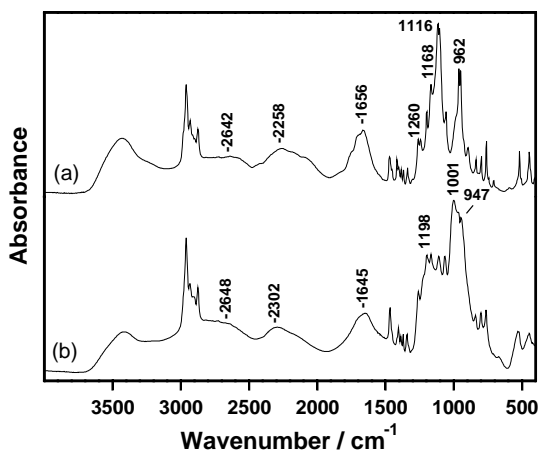


Fig. 4. Infrared spectra of the HBPs of Cyagard collected in the degradation apparatus in inert atmosphere at heating rate of 10 °C/min from 30 to 400 °C: (a) light HBP; (b) heavy HBP.

Table 1
Soluble HBPs emitted on the pyrolysis of Cyagard

Peak code	Molecular mass (m/z)	Compound
1	250	
2	252	
3	284	

(Fig. 3, spectra b and c) and this substance appeared from the volatilization of the low chain molecules containing P–O–P and P–OH groups.

The HBPs were further washed out by acetone, and the solution was subjected to the GC/MS analysis. Three soluble substances were identified from pyrolysis of Cyagard as evidenced in the gas chromatogram presented in Fig. 5. The structure of the substances is listed in Table 1, and their mass spectra are shown in Figs. 6–8. The mass spectral fragmentation pattern of the molecular ion of compound 1 supporting its structure is shown in Fig. 9. The molecular ion of compound 3 (Table 1, Fig. 8) exhibits two successive losses of C_4H_9 ($m/z = 227$) and C_4H_8 ($m/z = 171$), indicating the presence of two phosphorus atoms. The peaks at $m/z = 121$ and 163 are attributed to the $[(\text{CH}_3)_2\text{CHCH}_2\text{POOH}]^+$ and $[(\text{CH}_3)_2\text{CHCH}_2\text{PH}(=\text{O})\text{C}(=\text{O})\text{CH}(\text{OH})]^+$ ions correspondingly. The ions are formed from scission of the P–CH bond in the molecular ion.

The formation of the compounds 1 and 2 containing P–C or P–C–C bonds is indicative of the occurrence of a reduction of the alcoholic group, in addition to the formation of the P–O–P and P–OH groups.

As shown in Fig. 10, two main gaseous products are formed on the pyrolysis of Cyagard—acetaldehyde and water.

4. Discussion

Reportedly [7,8], phosphorus compounds bearing an alcoholic group in the α -position to a P–C bond are thermally unstable. When heated, α -hydroxyalkylphosphine [7] and hydroxymethylphosphine [9] undergo a rearrangement, resulting in the formation of phosphine oxides. As reported in [10,11], α -hydroxyalkyldialkylphosphine oxides which are adducts of disubstituted phosphine oxides and aldehydes (or ketones) decompose remarkably on melting and one of the

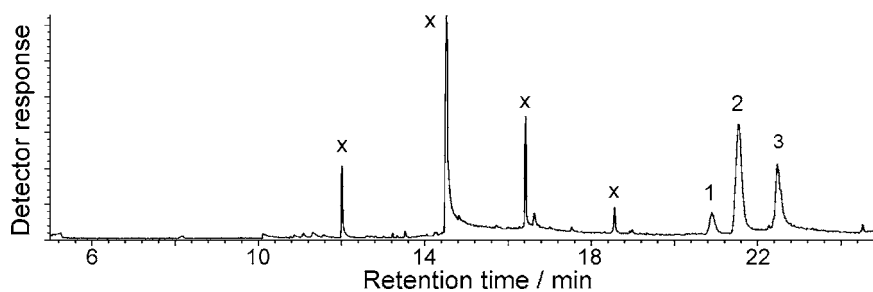


Fig. 5. Gas chromatogram of the soluble in acetone HBPs of Cyagard. The mass spectra of compounds (x) are masked by intense mass spectra of cyclosiloxanes that are likely to arise from column artifacts. Assignment of peaks 1–3 in Table 1.

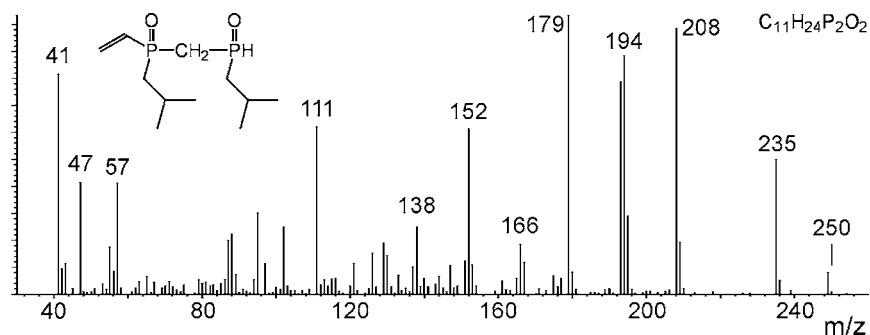


Fig. 6. Mass spectrum of product 1 (Table 1).

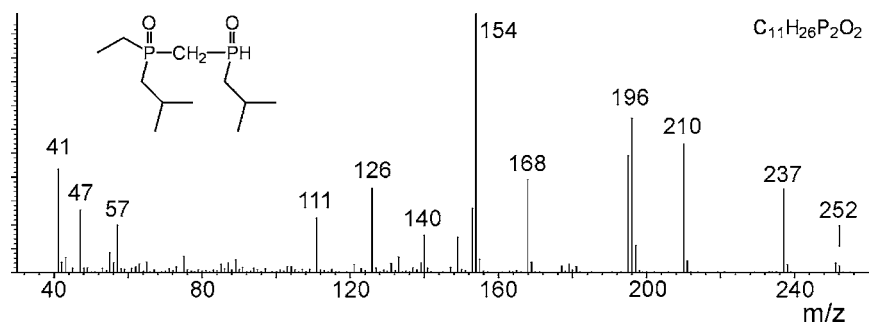


Fig. 7. Mass spectrum of product 2 (Table 1).

degradation reactions results in the formation of the initial disubstituted phosphine oxides and aldehydes (or ketones). However, in the presence of sodium hydroxide, the heating of α -hydroxyalkyldialkylphosphine oxides yields a sodium salt of dialkylphosphinic acids [10].

The results of the present study indicate that Cyagard undergoes a rearrangement of the P–C–OH bonds to the P–O–C ones (a phosphine oxide \rightarrow phosphinate \rightarrow phosphonate rearrangement), similar to that observed for dimethyl 2,2,2-trichloro-1-hydroxyethylphosphonate

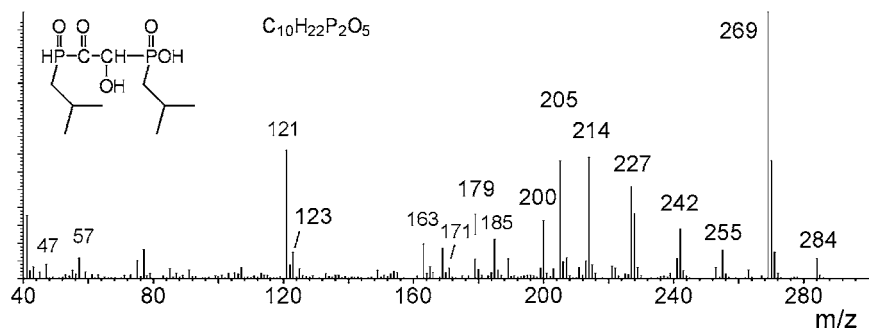


Fig. 8. Mass spectrum of product 3 (Table 1).

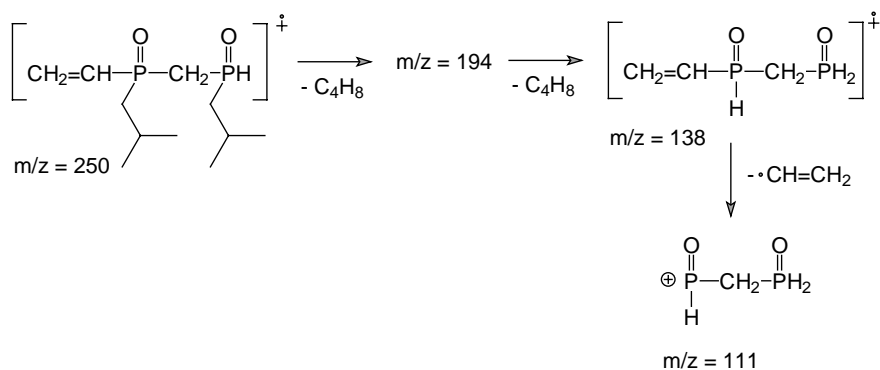
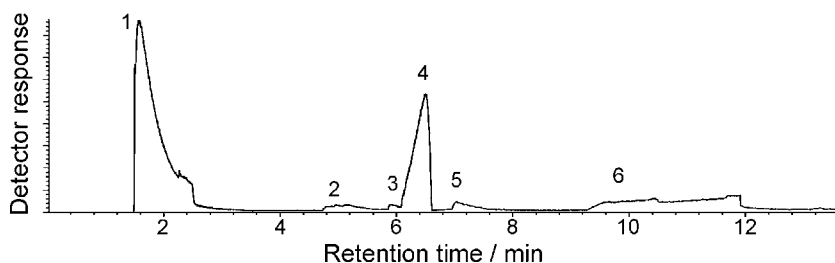


Fig. 9. Mass spectral fragmentation pattern of the molecular ion of compound 1 (Table 1).

Fig. 10. Gas chromatogram of the gaseous pyrolysis products of Cyagard: (1) acetaldehyde; (2) acetic acid ethenyl ester; (3) tetrahydrofuran; (4) H₂O; (5) benzene; (6) acetic acid.

[12], ethyl *N,N*-diethylamidophosphite [13] or dialkyl α -benzoyl- α -hydroxymethylphosphonates [14]. A possible mechanism of the formation of the P–O–H and P–O–C bonds for Cyagard is suggested in Fig. 11. In the first

step, the formation of an ester(II) can be speculated about, a typical reaction of which is scission of the ester bond [15], generating an unstable enol(III) along with an acid group. The compound(III) further rearranges to a more

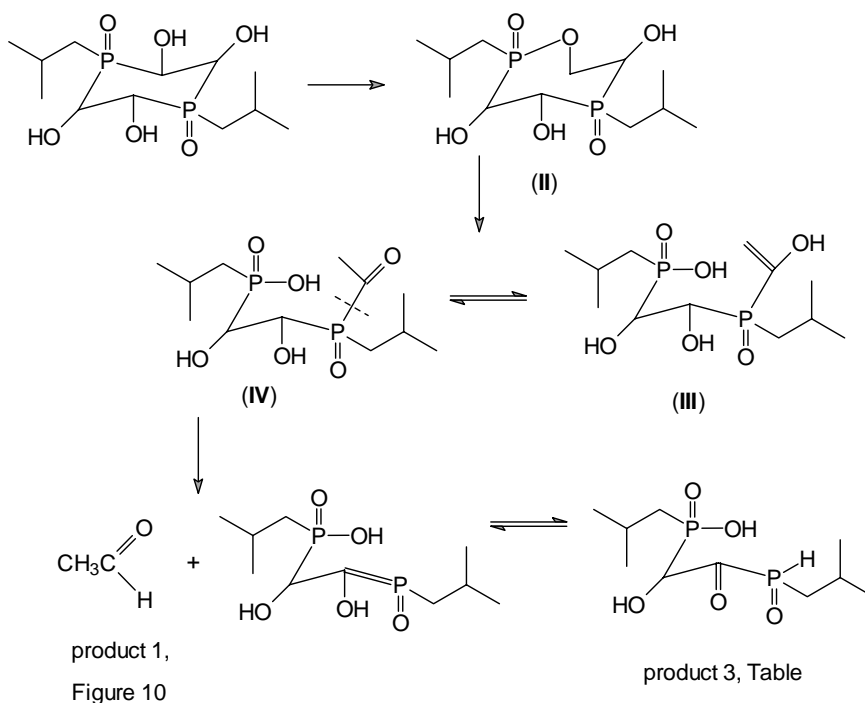


Fig. 11. Possible decomposition mechanism of Cyagard.

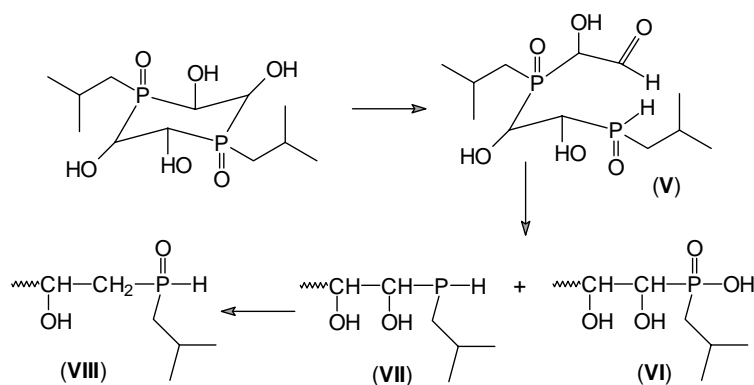


Fig. 12. Possible decomposition mechanism of Cyagard.

stable ketone(IV). The compound(IV) can undergo decomposition forming acetaldehyde (Fig. 10, product 1) and product 3 (Table 1).

The rearrangement (I \rightarrow II) is favored from the thermodynamical point of view: ΔH_{f298} (P–C) = 513 kJ/mol, ΔH_{f298} (P–O) = 597 kJ/mol [16]. Moreover, as shown for ethyl *N,N*-diethylamidophosphite [13] or dialkyl α -benzoyl- α -hydroxymethylphosphonates [14], this type of rearrangement exhibits an exotherm in differential thermal analysis. This is in agreement with the DSC data of Cyagard (Fig. 1). Finally, the rearrangement (I \rightarrow II) increases the amount of the aliphatic hydrogens, and this is in accordance with FT-IR data (Fig. 3).

It should be noted that Fig. 11 illustrates the thermal rearrangement, occurring on one phosphorus atom. However, the rearrangement is very likely to proceed on the both atoms.

The mechanism shown in Fig. 11 does not explain the occurrence of the reduction of the OH group. Fig. 12 illustrates a possible mechanism involving scission of the P–C bond, which is a usual decomposition mechanism of phosphine oxides [10]. The scission results in the formation of an intermediate(V) bearing an aldehyde and a secondary phosphine oxide group. The latter is thermally unstable [8], disproportionating to form a phosphinic acid(VI) and a secondary phosphine(VII). In its turn, the phosphine(VII) containing a α -hydroxy group is able to rearrange producing a phosphine oxide(VIII) [7]. In this way, a formation of the P–CH₂ bond occurs.

Reactions involving the aldehyde group are not exactly clear. They might be attacked by phosphines [8] to form phosphine oxides as shown in Fig. 13.

Condensation of the P–OH bonds contributes to the development of phosphorus anhydride structure and water. These

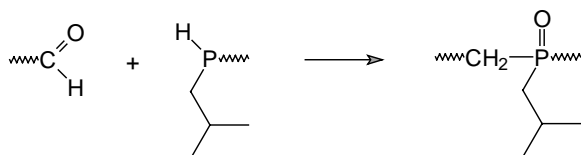


Fig. 13. Reduction of aldehyde group.

structures were detected in the heavy HBP (Fig. 4b) as well as in the solid pyrolysis products (Fig. 3b and c).

5. Conclusion: fire retardant effect

The P–C–OH bond strongly influences the thermal decomposition behavior of Cyagard due to the exothermic phosphine oxide \rightarrow phosphinate \rightarrow phosphonate rearrangement. This exothermic effect does not contribute positively to fire retardancy as brings about an additional warming up of the polymeric material.

The formation of the solid residue consisting of phosphorus acid moieties is likely to be a substantial part of fire retardancy. The acid coating acts as a physical barrier to the vaporization of fuel and can deactivate oxidation-active centers on the carbon [17].

In addition, vapor-phase fire retardancy involving flame chemistry can not be excluded, as phosphorus-containing moieties were detected in the HBPs of Cyagard. They might suppress combustion of the thermal decomposition products of HIPS.

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