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Thermal evolution of phosphorodiamidic acid as a model for nitrogen stability in phosphate glasses

Y. PARENT, L. MONTAGNE, G. PALAVIT
Laboratoire de Chimie des Matériaux Vitreux, Université des Sciences et Technologies de Lille, C5 2ème étage, 59655 Villeneuve d'Ascq Cedex, France

The thermal evolution at a heating rate of 3 °C min^{-1} of phosphorodiamidic acid, $HPO_2(NH_2)_2$, was studied up to 600 °C. Thermogravimetric analysis revealed three stages at 120, 320 and 600 °C. Nuclear magnetic resonance and Fourier transform-infrared analysis have been used to characterize the thermal products. At 120 °C, phosphorodiamidic acid condenses without any weight loss into an ammonium salt of P,P′-diamidoimidodiphosphoric acid. It is transformed at 320 °C into a more condensed product containing 17.7 wt% nitrogen and showing P–NH–P and P–O–P linkages. At 600 °C, the product still contains 10 wt% nitrogen. Phosphorus nuclear magnetic resonance shows that it is composed of nitrogen-containing Q^3 groups and ultraphosphate Q^3 groups. It is concluded that nitrogen cannot be held in the phosphate network if it contains hydroxyl groups, and that incorporation of nitrogen requires both reducing and nitriding conditions.

1. Introduction

The incorporation of nitrogen into phosphate glasses is appreciated because the resulting enhanced reticulation of the phosphate network improves the glass durability without significantly reducing the thermal expansion coefficients. Phosphorus nitride oxide glasses are obtained by remelting the glass in an ammonia or nitrogen atmosphere [1], or by adding a nitride such as AlN or Mg_3N_2 to the batch conversion [2]. Another field of interest of nitrogen-containing phosphate glasses has emerged recently, because porous glasses of the P_2O_5–SiO_2–B_2O_3 system are prepared with ammonium hydrogen phosphates. The reductions which result from nitrogen–phosphorus reactions in the thermal treatment of this glass lead to the formation of so-called "hydrogen microfoams (gas–ceramics)" [3]. Such materials are developed for microelectronic packaging. Marchand obtained phosphorus oxynitride glass of the H–P–O–N system by reaction of P_2O_5 with NH_3 at 700 °C [4]. Such glasses seem to have a fairly good stability.

Phosphorus compounds containing phosphorus–nitrogen covalent bonds are of interest as phosphorus oxynitride glass precursors. Moreover, the characterization of the thermal evolution and stability of such compounds is useful in the understanding of the mechanism of nitrogen incorporation in phosphate glasses. The phosphoro amidates have such P–N bonds. Watanabe and co-workers have reported the thermal evolution of phosphoro amidic acid and salts, but were mainly concerned with hydrated compounds which always evolve into metaphosphate compositions without nitrogen [5, 6].

In a previous paper [7], we described the structure and properties of anhydrous phosphorodiamidic acid at room temperature. The thermal evolution up to 120 °C has been also presented [8]. We propose here the thermal evolution up to 600 °C of the anhydrous phosphorodiamidic acid. The different stages that occur have been recorded with thermal analysis, and the products have been characterized using nuclear magnetic resonance (NMR) and Fourier transform-infrared spectroscopies (FT–IR).

2. Experimental procedure

2.1. Phosphorodiamidic acid preparation and thermal treatment

Phosphorodiamidic acid was prepared by the method described by Klement *et al.* [9]. In order to obtain a very pure and anhydrous compound, recrystallization of the phenyl ester was carried out twice after dissolution in ethanol at 80 °C. The phosphorodiamidic acid was then dried under vacuum at room temperature. The thermal treatment of phosphorodiamidic acid was carried out in a tubular furnace under dry flowing argon (0.1 l min^{-1}). The heating rate was 3 °C min^{-1}. The sample was removed when the temperature reached the programmed level.

2.2. Chemical analysis

The phosphorodiamidic acid was dissolved in water and the amount of phosphorus was determined after complete hydrolysis as pyrophosphates by the gravimetric method [10]. Total nitrogen was determined

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by the Kjeldahl procedure [10], and ammonium content by ammonia distillation [10]. The titration of the phosphorodiamidic acid gave a pK_a value of 4.9 which is the same as reported by Peacock and Nickless [11]. The chemical analysis of phosphorodiamidic acid, compared with the calculated values in parentheses, is (wt %): P 32.2 (32.3); N 27.6 (29.2); NH_4^+ 0.3.

2.3. Spectroscopic analysis

The ^{31}P magic angle spinning-nuclear magnetic resonance (MAS-NMR) spectra were recorded at 121.5 MHz (spinning rate 15 KHz) on an MSL300 and at 40.5 MHz (spinning rate 3.8 KHz) on a CXP100 Bruker spectometer. The chemical shifts were relative to an external H_3PO_4 reference, negative shifts being upfield. The sample heated at 600 °C was sensitive to hydrolysis, so it was ground in a glove box and transferred in a closed rotor. The Conventional Q^n symbol will be used, n is the number of phosphate tetrahedra shared by a phosphate group.

The infrared analysis was carried out on a Perkin–Elmer M1710 spectrometer, using the KBr disc method. When hydrolysis was encountered, the sample was dispersed in sodium-dried Nujol oil.

2.4. Thermal analysis

Differential thermal analysis and thermogravimetric analysis were carried out on a combined TG-DTA92 apparatus of Setaram. A platinum crucible filled with 20 mg sample was used; the experiment was conducted in an argon atmosphere at a heating rate of 3 °C min^{-1}.

3. Results

3.1. Thermal analysis

Fig. 1 shows the DTA and TGA curves of diamidophosphoric acid. An endothermic peak appears at 110 °C that is not associated with weight loss. A succession of endothermic effects occurs from 125–300 °C, accompanied by a weight loss of 15.6%. An important endothermic peak also occurs at 300 °C. Another weight loss, with a broad endothermic signal, is observed between 395 and 600 °C. The cumulated weight loss up to 600 °C is 25%. Chemical analysis shows that no phosphorus is lost during the thermal treatment. The assignments of the observed thermal phenomena will be proposed in the discussion, after the structural data obtained by NMR and FT–IR.

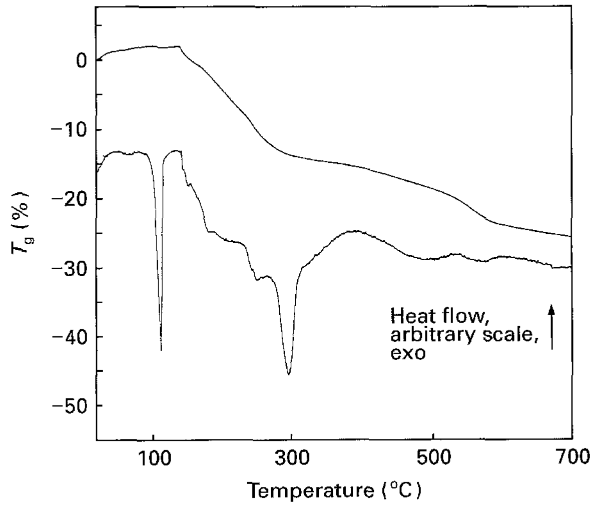


Figure 1 TG and DTA curves of phosphorodiamidic acid (heating rate 3 °C min^{-1} in argon).

TABLE I Nitrogen analysis of the thermal products of phosphorodiamidic acid. Δm: weight loss measured by TGA, NH_4^+: ammonium content, N_T: total nitrogen content, NH_3: evolved ammonia (calculated from the composition).

T (°C)	Δm (wt %)	NH_4^+ (wt %)	N_T (wt %)	NH_3 (wt %)
120	0	15.2	27.6	0
320	15.6	0	17.3	16.6
600	25	0	9.9	24.3

3.2. Analysis of nitrogen content

Total nitrogen, ammonium and ammonia contents have been checked at each step of the thermal evolution characterized by thermal analysis. The results are reported in Table I. It is concluded that only ammonia (NH_3) is evolved up to 600 °C.

3.3. ^{31}P NMR

The ^{31}P MAS–NMR spectra of diamidophosphoric acid heated at 120, 320 and 600 °C are shown in Fig. 2. The spectrum of the 120 °C heated product shows two signals at 0 and − 4 p.p.m. They are attributed to the following compound: NH_2–PO(OH)–NH–PO(ONH_4)–NH_2 which was previously identified [8]. Owing to the lower screening effect of ammonium compared to a proton, the signal at 0 p.p.m. is due to [–NH–PO(ONH_4)–NH_2] group, the signal at − 4 p.p.m. to [NH_2–PO(OH)–NH–] group. This product is in accordance with a thermal condensation of phosphorodiamidic acid without weight loss. Small signals are detected at + 10.3, + 3.1, − 11.6 and − 22.6 p.p.m; they are not spinning sidebands because their positions do not change with the spinning rate. The last two indicate that some condensation occurs into P–O–P bonds because they are respectively attributed to terminal (Q^1) and internal (Q^2) phosphate units. The + 10.3 and + 3.1 peaks refer to phosphorus in ammonium salts of phosphorodiamidic acid.

The spectrum of the 300 °C heated sample shows three broad signals at 0, − 10 and − 23 p.p.m. Linked with the infrared data interpretation, which will be detailed below, they are attributed to condensation products of the 110 °C compound. The structural units concerned are shown in Fig. 3. The signal at 0 p.p.m. is attributed to Q^2 units containing two nitrogen atoms, i.e. a Q^2 phosphate unit with two phosphorus–nitrogen linkages [12]. The nitrogen induces a lower screening effect on the phosphorus nucleus than oxygen. The

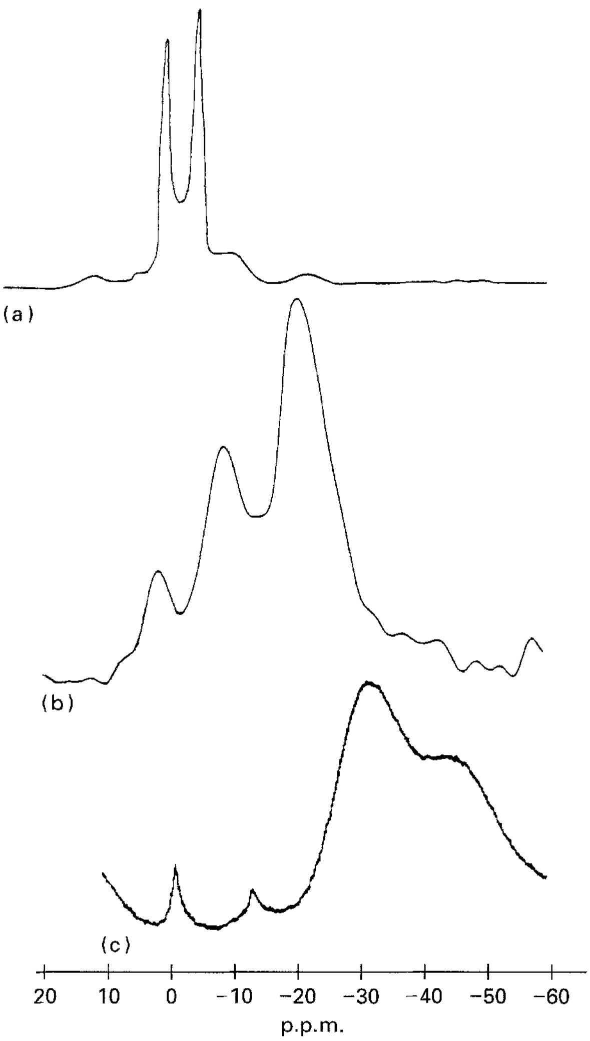
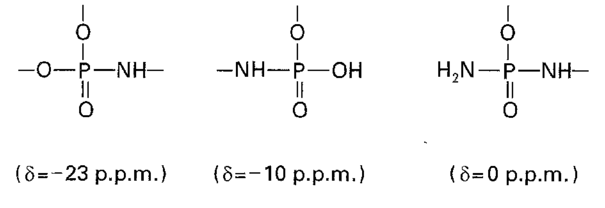


Figure 2 ^{31}P MAS–NMR spectra of the (a) 120 °C, (b) 320 °C and (c) 600 °C heated samples.



$-O-\overset{\overset{|}{O}}{\underset{\underset{O}{\|}}{P}}-NH-$ $-NH-\overset{\overset{|}{O}}{\underset{\underset{O}{\|}}{P}}-OH$ $H_2N-\overset{\overset{|}{O}}{\underset{\underset{O}{\|}}{P}}-NH-$

Figure 3 Structural units proposed for the 320 °C heated sample.

signal at − 10 p.p.m. is attributed to Q^2 units with one nitrogen atom; the signal at − 23 p.p.m. is attributed to the Q^3 unit with one nitrogen atom.

The spectrum of the 600 °C heated sample contains two broad bands at − 35 and − 45 p.p.m., and two narrow weak peaks at 0 and − 15 p.p.m. The two broad bands are attributed to condensation products of the 300 °C sample: the − 45 p.p.m. signal is due to phosphorus in Q^3 sites [13], i.e condensation products with loss of nitrogen, whereas the − 35 p.p.m. is attributed to Q^3 sites containing phosphorus–nitrogen linkages. The narrow peaks at 0 and − 15 p.p.m. are attributed to Q^0 and Q^1 type hydrolysis products, or uncondensed precursor groups. The attribution was confirmed by the acquisition of spectra with shortening of the recycling time from 200 s to 5 s. The broad bands are progressively suppressed, whereas the narrow ones remain unchanged. The absence of rotation bands and the short relaxation time suggest the assignment of the narrow peaks to a "mobile phase" (i.e. Q^0 and Q^1), as reported by Grimmer and Wolf [13], and the bands with long relaxation time to condensed groups.

3.4. Infrared spectroscopy

The spectra of the thermal product of phosphorodiamidic acid are shown in Fig. 4. On the spectrum of the 120 °C heated sample, the absorption band at 3074 cm^{-1} is attributed to N–H stretching vibrations of the (P)–NH–(P) bridges [14]. The three bands at 3385, 3269 and 1586 cm^{-1} correspond, respectively, to the antisymmetric (ν_{as}), symmetric (ν_s) and bending (δ) vibrations of the (P)–NH_2 group. The ν_{as} and ν_s vibrations of PO_2 groups are located at 1210 and 1065 cm^{-1} [15] ; the ν_{as} and ν_s vibrations of P–NH–P at 870 and 696 cm^{-1}, respectively [15]. The 957 cm^{-1} band is attributed to P–O(H) groups. The bending mode of NH_4^+ appears at 1467 cm^{-1}. Bending vibrations of P–O are situated at 512 cm^{-1}.

On the spectrum of the 320 °C heated sample, the stretching vibration of the N–H bond is visible at 3130 cm^{-1} [14], and the bending mode at 1470 cm^{-1}. Some (P)–NH_2 vibrations are visible as shoulders at 3200 cm^{-1} (ν) and 1398 cm^{-1} (δ). P=O group absorb at 1253 cm^{-1}, P–O–P at 906 (ν_{as}) and 733 cm^{-1} (ν_{as}). Notice that P=O and P–O–P vibrations are observed at a lower frequency than in the polyphosphates, because the lower electronegativity of nitrogen compared to oxygen induces a diminution of the electronic density on the phosphorus–oxygen bonds. The P–NH–P mode is present as a shoulder at 696 cm^{-1}. No NH_4^+ group is visible on the infrared spectrum, as established by chemical analysis. These attributions confirm the interpretation of the ^{31}P NMR spectrum.

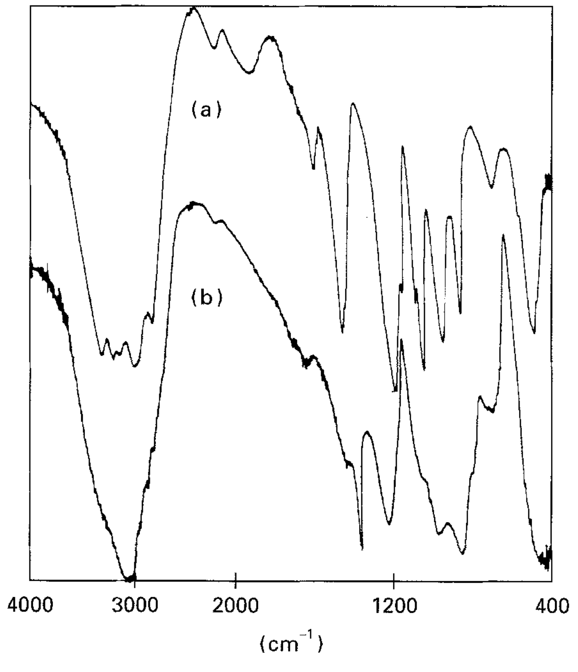


Figure 4 Infrared spectra of the (a) 120 °C, (b) 320 °C heated samples (KBr disc).

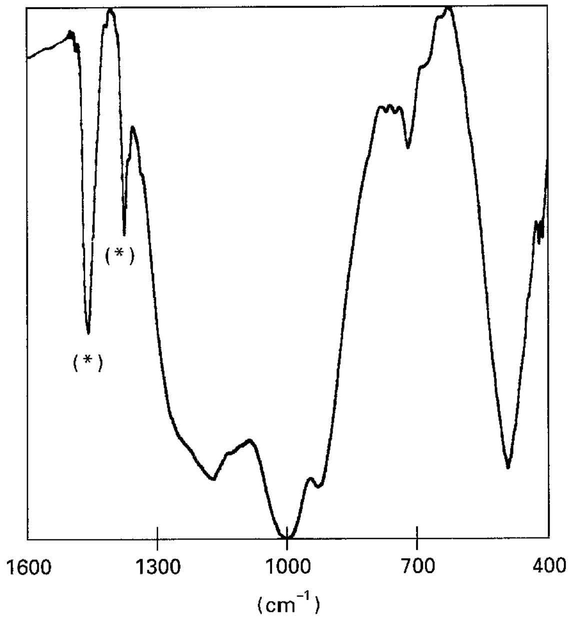


Figure 5 Infrared spectrum of the 600 °C heated sample (*) Nujol absorption bands.

The infrared spectrum of the 600 °C heated sample, recorded in Nujol oil, is shown in Fig. 5. The strong band at 1153 cm^{-1} is characteristic of P–O$^-$ vibration in a nitrogen-containing phosphate network [16], the P=O vibration being visible at 1253 cm^{-1}. Condensations would lead to the formation of P–N(P)–P or P=N– groups, but the P=N vibration, reported in the 750–830 cm^{-1} range [17], is absent. A small band is present at 690 cm^{-1}, it is attributed to the P–N(P)–P vibration [12].

4. Discussion

Infrared and NMR analysis of the 120 °C heated phosphorodiamidic acid show the presence of P–NH–P, P–NH$_2$, and PO$_2$ groups in a dimeric unit. The heating at 120 °C of the phosphorodiamidic acid leads to the formation of the ammonium salt of P,P′-diamidoimidodiphosphoric acid [8]. The transformation is an internal condensation by NH$_2$ groups which occurs without weight loss. Such a compound was also identified during the ageing of phosphorodiamidic acid at room temperature [7].

When temperature is raised up to 300 °C, the sample loses only ammonia. This weight loss can find its origin in the following reactions:

$$\text{P–O–NH}_4^+ \rightarrow \text{P–OH} + \text{NH}_3 \quad (1)$$

$$\text{P–NH}_2 + \text{P–OH} \rightarrow \text{P–O–P} + \text{NH}_3 \quad (2)$$

$$\text{P–NH}_2 + \text{P–NH}_2 \rightarrow \text{P–NH–P} + \text{NH}_3 \quad (3)$$

$$\text{P–NH–P} + \text{P–NH}_2 \rightarrow \text{P–N(P)–P} + \text{NH}_3 \quad (4)$$

As infrared analysis concluded the disappearance of NH$_4^+$ groups, Reaction 1 is mainly encountered when the temperature is raised. Reaction 3 also occurs because the product heated at 300 °C contains P–NH$_2$ and P–NH–P groups. Finally, condensation leads to three phosphorus environments (described on Fig. 3), as revealed by NMR.

After thermal treatment up to 600 °C, both NMR and infrared denote a highly condensed phosphate network. NMR spectrum shows that the condensed phase coexists with an uncondensed phase which originates from hydrolysis products or uncondensed groups. The thermal treatment indeed consists in a heating rate at 3 °C min^{-1}, in order to observe only thermal evolution products. So it is clear that a few parts of the initial product will not react under these conditions. Moreover, the infrared spectrum only shows residual NH groups which can be detected as a weak shoulder at 696 cm^{-1}. So the condensation leads to an ultraphosphate network containing 10 wt % nitrogen. As no P=N groups are seen in the infrared spectrum, it is concluded that nitrogen is incorporated as tertiary amine groups P–N(P)–P.

5. Conclusion: consequences of nitrogen stability in a phosphate network

The structure of the 600 °C heated product is intermediate between PON and P_2O_5. As the phosphorodiamidic acid contains both P–OH and P–NH$_2$ groups, it condenses into P–O–P and P–N–P linkages, with nitrogen losses. As a matter of comparison, the thermal condensation of $PO(NH_2)_3$ leads to PON [18] which is very stable upon hydrolysis, whereas H_3PO_4 condenses into unstable P_2O_5. The reactivity of the 600 °C product confirms the proposed mechanism of condensation of the phosphorodiamidic acid, i.e. a condensed network intermediate between PON and P_2O_5.

Otherwise, the thermal condensation of anhydrous sodium phosphorodiamidate gives sodium polyimidophosphates [19], whereas the hydrate of phosphorodiamidate leads to polyphosphates with nitrogen loss [5]. So we conclude that the presence of hydroxyl groups, or water, in the precursor leads to a condensation mechanism with nitrogen loss, which has a negative effect on the obtention of phosphorus oxynitride glasses.

This suggests that the incorporation of nitrogen in phosphate glasses [1, 12, 20], performed either by reaction of molten glass with ammonia, or by incorporation of a nitride in the precursors, is possible not by the formation of P–NH–P groups from P–OH groups, but only if *both* nitriding and reducing conditions are joined. These conditions are realized with long-term experiments under an ammonia atmosphere or reducing gaseous atmosphere. This is confirmed in the glasses of the H–P–O–N system, obtained by reaction of phosphorus oxide with ammonia at 700 °C for several days, which are stable upon hydration [4]. Marchand [4] reports that they lose ammonia when heated at 500 °C under an inert atmosphere. Ammonia can be released if the glass contains P–OH groups, with the same mechanism as described for phosphorodiamidic acid.

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