

# Structure and properties of phosphorodiamidic acid: $\text{HPO}_2(\text{NH}_2)_2$ at room temperature

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At room temperature, phosphorodiamidic acid ( $\text{HPO}_2(\text{NH}_2)_2$ ) has a mobile hydrogen, which leads to  $\text{P}-\text{NH}_3^+$  and  $\text{P}-\text{O}^-$  groups in limiting form. According to the spectroscopic analysis, a limiting (zwitterion) or a medium form (compound with mobile hydrogen) is prominent. This mobile hydrogen leads phosphorodiamidic acid to react with itself giving  $\text{P}-\text{N}(\text{H})-\text{P}$  bridges and ammonium. We obtained a major compound ammonium salt of diamido 1, 2 imidodiphosphate which is present as  $^{31}\text{P}$  MAS NMR, a crystallographic nonequivalency.

## 1. Introduction

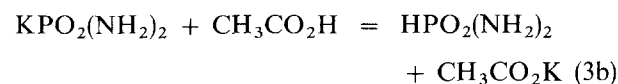
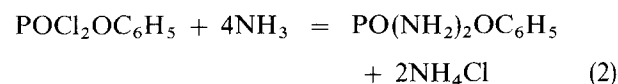
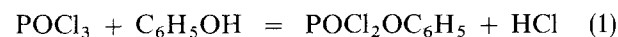
Incorporation of nitrogen into phosphate glasses improved their chemical durability without reducing significantly the thermal expansion coefficient. In general, phosphorus oxynitride glasses are prepared by remelting the glass in an ammonia or nitrogen atmosphere at temperatures above the glass transition temperature [1]. These glasses can also be prepared by additions to the glass of nitrated compounds such as  $\text{AlN}$  and  $\text{Mg}_3\text{N}_2$  [2].

In the present work, we used compounds with P–N covalent bonds as phosphorus oxynitride glass precursors. Among the phosphorus nitrogen compounds, amidophosphates have now been well studied, particularly, by Watanabe and Coll who reported several salts of phosphoroamidic and phosphorodiamidic acid [3, 4]. For phosphorodiamidic acid, only the synthesis is well known; the structure and behaviour at room temperature are not well described. Therefore, we present here a structural model and a discussion of the stability of this acid at 20 °C.

## 2. Experimental procedure

### 2.1. Phosphorodiamidic acid preparation

Phosphorodiamidic acid was prepared by the method described by Klement *et al.* [5]. The synthesis occurs in three steps:



In order to obtain a very pure and anhydrous phosphorodiamidic acid, the recrystallization of the phenyl

salt was carried twice in ethanol at 80 °C. The phosphorodiamidic acid was then dried under vacuum at room temperature.

### 2.2. Chemical analysis

The product was dissolved in water and the amount of phosphorus and nitrogen in the solution was determined by gravimetric technique and the Kjeldahl method, respectively.

The acidic titration of the phosphorodiamidic acid was also carried out. The  $\text{p}k_a$  value (4.9) was found to agree with that given by Peacock and Nickless. Chemical analysis of the product gave the following results:  $\text{NH}_4^+$  0.3%, N 27.6%, P 32.16%; the calculated contents of the elements for  $\text{HPO}_2(\text{NH}_2)_2$  were  $\text{NH}_4^+$  0%, N 29.17%, P 32.26%.

### 2.3 X-ray diffraction

X-ray diffractograms were recorded with nickel-filtered  $\text{CuK}_\alpha$  radiation using a Phillips PW.1010 diffractometer.

### 2.4. Fourier transform–infrared spectroscopy

Infrared spectra were recorded on a Perkin–Elmer M1710 spectrophotometer by means of the KBr disc method.

### 2.5. $^{31}\text{P}$ nuclear magnetic resonance (NMR) measurement

$^{31}\text{P}$  NMR proton-decoupled spectra of samples were recorded at 32.4 MHz on a WP80 Bruker spectrometer after dissolution in water. The NMR chemical shifts are reported relative to external 85% orthophosphoric acid, with negative shifts being down field.

$^{31}\text{P}$  CP MAS NMR were recorded at 32.4 MHz on a 200 MHz Bruker spectrometer. The magic angle

spinning (MAS) NMR chemical shifts are reported relative to external  $\text{H}_3\text{PO}_4$ , negative shifts being down field.

## 2.6 $^{15}\text{N}$ NMR measurement

$^{15}\text{N}$  NMR spectra of samples dissolved in water were recorded at 40.6 MHz on a AM400 Bruker spectrometer. The  $^{15}\text{N}$  was present in natural abundance. The MAS NMR chemical shifts are reported relative to external liquid ammonia with negative shifts being down field.

## 2.7. $^1\text{H}$ MAS NMR measurement

Spectra were recorded at 100.1 MHz on a CXP100 Bruker spectrograph. The MAS NMR chemical shifts are reported relative to external tetra methyl silane with negative shifts being up field.

## 3. Phosphorodiamidic acid structure

### 3.1. Results

#### 3.1.1. Infrared analysis

Phosphorodiamidic acid has been studied only by means of infrared analysis by Steger [7], but unfortunately its spectrum is not clearly resolved between 700 and  $1400\text{ cm}^{-1}$ . The product exhibits the infrared spectrum shown in Fig. 1b. Absorption peaks at 1246 and  $1134\text{ cm}^{-1}$  are attributed to  $\nu_{\text{as}}$  and  $\nu_{\text{s}}$   $\text{PO}_2$  respectively. At 3400 and  $3284\text{ cm}^{-1}$  we observed very strong and narrow absorptions which are attributed to  $\nu_{\text{s}}$  and  $\nu_{\text{as}}$  of  $\text{NH}_2$  groups. We did not observe bands in the regions  $3100\text{--}3000\text{ cm}^{-1}$  and  $2360\text{--}2200\text{ cm}^{-1}$  which would correspond to P-OH vibrations.

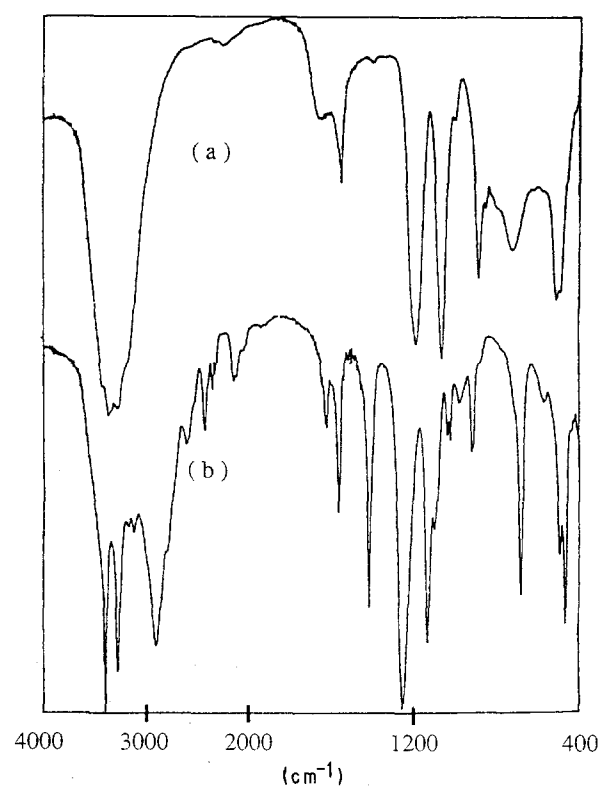


Figure 1 Infrared spectra of (a) sodium salt of phosphorodiamidic acid, and (b) phosphorodiamidic acid.

Moreover the spectrum of  $\text{NaPO}_2(\text{NH}_2)_2$ , Fig. 1a, is very different from that of  $\text{HPO}_2(\text{NH}_2)_2$ . The spectrum of phosphorodiamidic acid exhibits absorptions at 2908, 2807 and 2618,  $2438\text{ cm}^{-1}$  which are attributed to  $\nu_{\text{as}}\text{NH}_3^+$  and  $\nu_{\text{s}}\text{NH}_3^+$ . The complete attribution of the bands is reported in Table I. It is interesting to note that the stretching vibrations of the  $\text{PO}_2$  groups at 1246 and  $1134\text{ cm}^{-1}$  in phosphorodiamidic acid shift to lower frequencies in the sodium salt: 1200 and  $1080\text{ cm}^{-1}$ . This behaviour is different from that observed for  $\text{NaHPO}_3\text{NH}_2$  and  $\text{Na}_2\text{PO}_3\text{NH}_2$  where the stretching vibration of the  $\text{PO}_3$  groups have the same frequency.  $\text{NaHPO}_3\text{NH}_2$  is considered to form a zwitterion [7-9]. The spectra of  $\text{NaHPO}_3\text{NH}_2$  and  $\text{Na}_2\text{PO}_3\text{NH}_2$  are very different.  $\text{Na}_2\text{PO}_3\text{NH}_2$  does not exhibit absorptions due to  $\nu_{\text{as}}\text{NH}_3^+$  and  $\nu_{\text{s}}\text{NH}_3^+$  at 2920, 2860 and 2610,  $2482\text{ cm}^{-1}$ . Moreover, there is a great shift for  $\nu\text{ P-N}$  between the salt ( $830\text{ cm}^{-1}$ ) and the acid ( $710\text{ cm}^{-1}$ ).

In the same way, the bending vibration of N-H groups shifts to greater frequencies for the phosphorodiamidic acid. The absorptions of the  $\text{NH}_2$  groups are very narrow, in comparison with absorptions of  $\text{NH}_3$  groups which are very broad. The attribution of the spectrum proposed also indicated a zwitterion form for phosphorodiamidic acid, as for  $\text{NaHPO}_3\text{NH}_2$ .

#### 3.1.2. $^{31}\text{P}$ NMR

$^{31}\text{P}$  NMR liquid data for phosphorodiamidic acid are contradictory. Nielsen *et al.* [10] give for this compound a peak at  $-0.2\text{ p.p.m.}$  and Van Wazer and Callis [11] a peak at about  $-3.5\text{ p.p.m.}$  with also minor peaks at  $+10$  and  $+25\text{ p.p.m.}$  (the latter authors verified by X-ray diffraction that it had been hydrolysed).

TABLE I Attribution of the infrared absorption bands of phosphorodiamidic acid and the sodium salt of phosphorodiamidic acid

$\text{NaPO}_2(\text{NH}_2)_2$	$\text{PO}_2(\text{NH}_2)(\text{NH}_3)$	Attribution
3370	3400	$\nu_{\text{as}}\text{NH}_2$
3300	3284	$\nu_{\text{s}}\text{NH}_2$
3160		
	2908	$\nu_{\text{as}}\text{NH}_3$
	2807	
	2618	$\nu_{\text{s}}\text{NH}_3$
	2438	
	2154	
	1630	$\delta_{\text{as}}\text{NH}$
	1568	
1580	1416	$\delta_{\text{s}}\text{NH}$
1205	1246	$\nu_{\text{as}}\text{PO}_2$
1160		
1085	1134	$\nu_{\text{s}}\text{PO}_2$
1070	1098	$\rho\text{NH}_2$
	1022	
	975	
	910	$\nu\text{ P-NH}_2$
	682	$\nu\text{ P-NH}_3$
480	570	$\rho\text{PO}_2$
	494	
	465	

To avoid the problem of hydrolysis we employed  $^{31}\text{P}$  MAS NMR. The spectrum obtained, Fig. 2, shows a peak at 0 p.p.m. relative to external  $\text{H}_3\text{PO}_4$ . This value is very different from that obtained for the sodium salt at +14.6 p.p.m. This difference between the salt and the acid compound was observed for  $\text{Na}_2\text{PO}_3\text{NH}_2$  (+8.9 p.p.m.) and  $\text{NaHPO}_3\text{NH}_2$  (+3 p.p.m.).

### 3.1.3. $^1\text{H}$ NMR

No data are available for  $^1\text{H}$  NMR of phosphorodiamidic acid. However,  $^1\text{H}$  NMR of the phenyl salt of phosphorodiamidic acid has been reported [12], and the chemical shift of H in  $\text{NH}_2$  groups is at +4.6 p.p.m. The  $^1\text{H}$  NMR is reported in Fig. 3; we observe with or without spinning only one peak at +4.7 p.p.m. with 500 Hz half-height width.

We recorded  $^1\text{H}$  NMR as a function of temperature, the spectra obtained are given in Fig. 4. At 240 K, a broad peak appeared, which became larger as temperature decreased.

## 3.2. Discussion

Infrared analysis and  $^{31}\text{P}$  NMR show several particularities for phosphorodiamidic acid. For the  $^{31}\text{P}$  NMR there is a great shift between the acid and the salt in the liquid and solid states. Infrared analysis does not show absorption of OH groups, but rather absorptions of  $\text{NH}_2$  and  $\text{NH}_3^+$  groups. Therefore, a zwitterion form of this compound should exist, as for

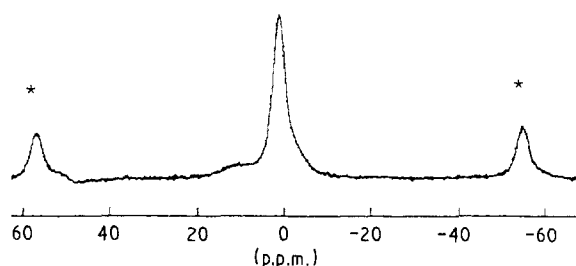


Figure 2  $^{31}\text{P}$  MAS NMR spectrum of diamidophosphoric acid. Spinning rate 4500 Hz. (\*) Spinning sidebands.

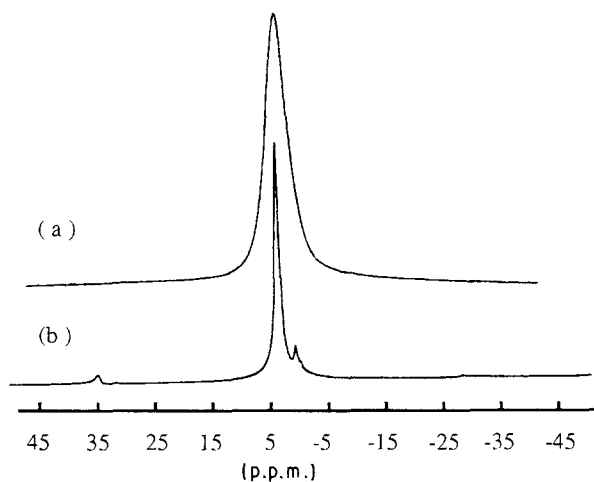


Figure 3  $^1\text{H}$  MAS NMR spectra (a) without spinning, and (b) with spinning at 30 000 Hz of phosphorodiamidic acid.

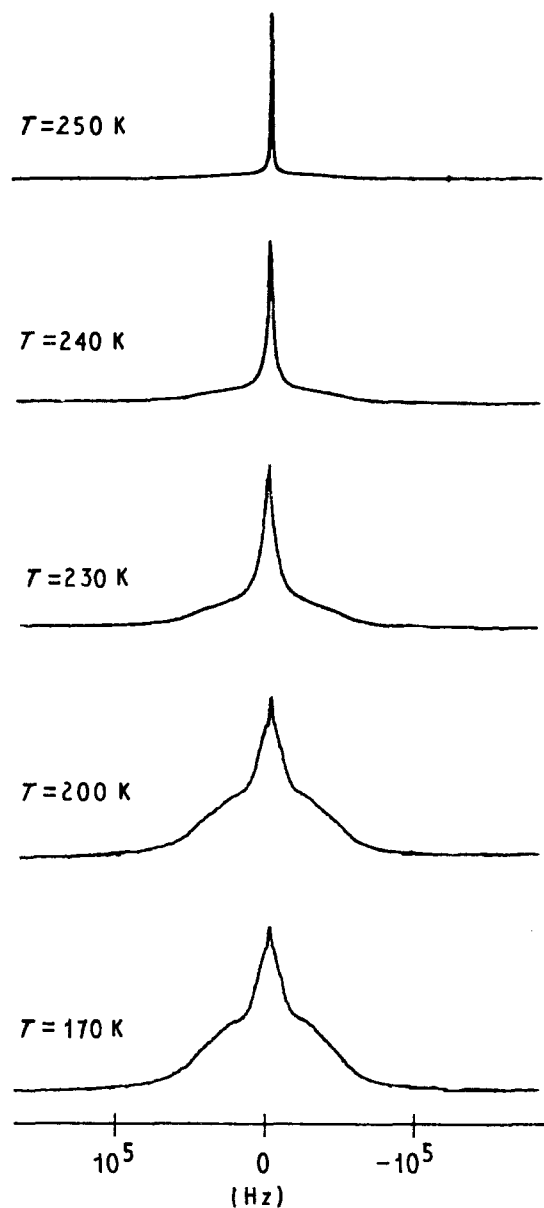


Figure 4  $^1\text{H}$  MAS NMR spectra of phosphorodiamidic acid as a function of temperature.

monoamidophosphoric acid. However, this zwitterion should only be a limiting form of the acidic compound, due to the short observation time of the infrared analysis. As for monosodium phosphorodiamidic acid [13], there should be a hydrogen bond system for phosphorodiamidic acid. Every phosphorodiamidic acid molecule should be linked in a continuous three-dimensional network by hydrogen bonds. Moreover, the  $^1\text{H}$  MAS NMR spectra show only one peak, so there is only one type of hydrogen, which is very mobile. The mobility of the hydrogen is revealed by the small half-height line width.

## 4. Evolution of phosphorodiamidic acid at 20°C

### 4.1. Results

#### 4.1.1. X-ray analysis

The X-ray diffraction patterns of the phosphorodiamidic acid recorded after 1, 140 and 1370 days are shown in Fig. 5. The intensities of the diffraction peaks decrease with time. New peaks appear with

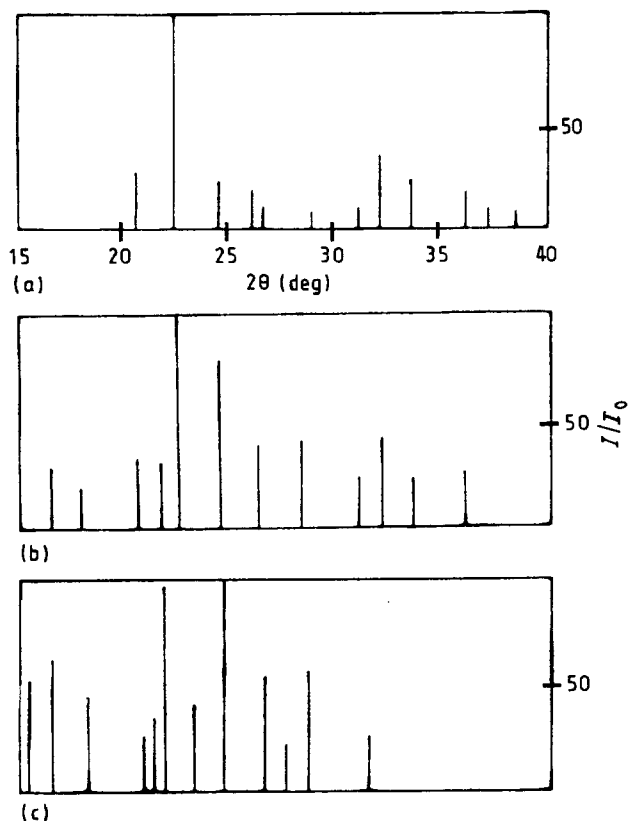


Figure 5 X-ray diffractogram of phosphorodiamidic acid after (a) 1, (b) 140, and (c) 1370 days.

time, but it has not yet been possible to identify the new species (none were detected on the diffractogram of the ammonium salt of phosphorodiamidic acid and/or ammonium orthophosphates which are due to the hydrolysis).

#### 4.1.2. Infrared analysis

Infrared analysis of phosphorodiamidic acid evolution is shown in Fig. 6. Several important modifications

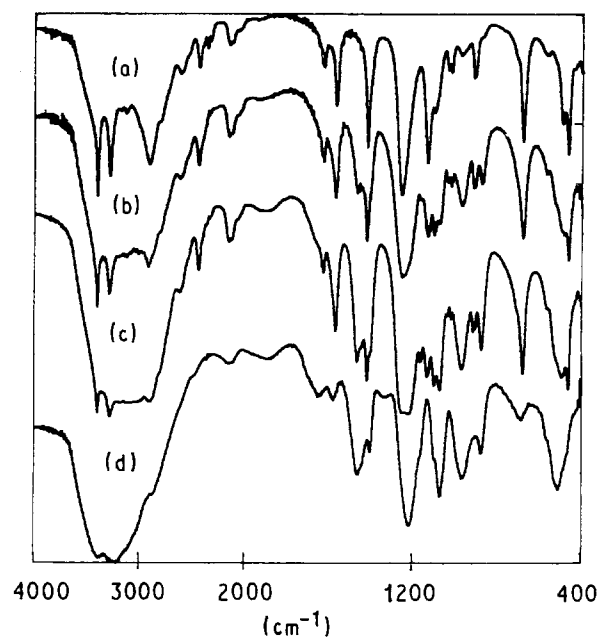


Figure 6 Infrared spectra of phosphorodiamidic acid after (a) 6, (b) 35, (c) 180 and (d) 880 days.

appear with time. Firstly the absorption of  $\text{NH}_4^+$  groups at  $1460\text{ cm}^{-1}$  increases. Secondly the absorption of  $\nu_{\text{as}}\text{ PO}_2$  at  $1246\text{ cm}^{-1}$  shows first a shoulder, then a splitting. This phenomenon is indicative of a new compound very similar to phosphorodiamidic acid. At  $880$  and  $690\text{ cm}^{-1}$  we observed absorptions attributed to  $\text{P-O-P}$  and/or  $\text{P-N(H)-P}$  bonds. The absorptions of  $\text{NH}_2$  groups at  $3400$  and  $3284\text{ cm}^{-1}$  become less and less separated with time. At  $3000\text{ cm}^{-1}$  a very broad absorption peak appears which could be explained as a reinforcement of hydrogen bonding.

#### 4.1.3. Evolution of ammonium

Infrared analysis shows the presence of ammonium. Measurement of the evolution of ammonium is shown in Fig. 7, in which fast evolution during the 5 first months is observed. After 25 months, the rate of ammonium evolution is close to zero.

#### 4.1.4. $^{31}\text{P}$ NMR

$^{31}\text{P}$  MAS NMR spectra are shown in Fig. 8. A new signal appears after 39 days at  $-3.8$  p.p.m. which is only a shoulder, but it becomes stronger with time. After 58 or 880 days the signals at  $+0.3$  and  $-3.8$  p.p.m. have the same intensities. These two peaks are not due to a quadrupolar splitting, because when the Larmor frequency is changed the shift between the two peaks does not change. After 58 days new weak signals at  $-11$  and  $-22$  p.p.m. were observed, which are assigned to polyphosphates end and middle groups, respectively.

$^{31}\text{P}$  liquid NMR of phosphorodiamidic acid which has evolved for 180 days in the solid state is shown in Fig. 9. Multiplets were seen at  $-8$  and  $-22$  p.p.m. which are due to polyphosphates end and middle groups. These two signals represent 30% of the total phosphorus. The signal at  $+0.3$  p.p.m. in  $^{31}\text{P}$  MAS NMR is also present in the liquid state, but it is better resolved and presents three peaks at  $+0.1$ ,  $-0.9$  and  $-1.3$  p.p.m. This signal represents 60% of

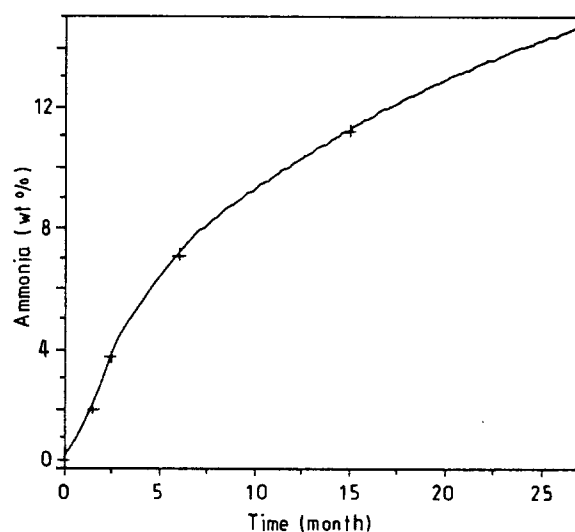


Figure 7 Evolution of ammonia as a function of time.

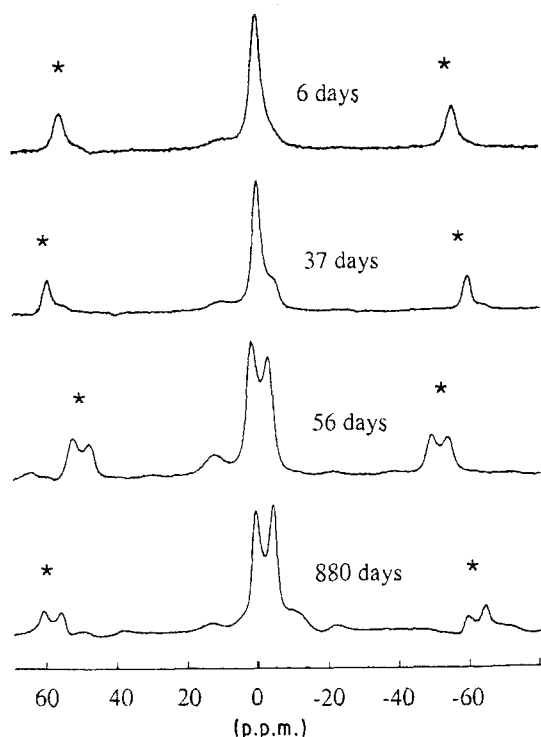


Figure 8  $^{31}\text{P}$  (CP) MAS NMR spectra of phosphorodiamidic acid as a function of time. Spinning rate 4500 Hz. (\*) Spinning sidebands.

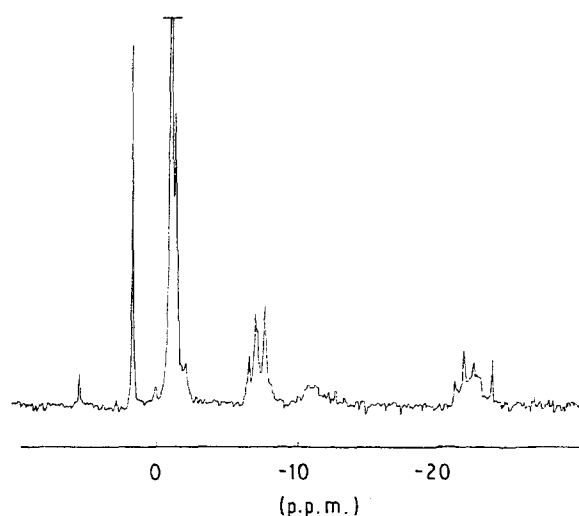


Figure 9 Liquid  $^{31}\text{P}$  NMR spectrum of diamidophosphoric acid after 180 days.

the total phosphorus. In  $^{31}\text{P}$  liquid NMR, a new peak is seen at 1.7 p.p.m., which represents 10% of the total phosphorus. The signal at  $-3.8$  p.p.m. in  $^{31}\text{P}$  solid NMR disappears. This is attributed to the hydrolysis of the product, or to the disappearance of a crystallographic nonequivalency in the solid state.

#### 4.1.5. $^{15}\text{N}$ NMR

The  $^{15}\text{N}$  liquid NMR spectrum of phosphorodiamidic acid after 180 days is shown in Fig. 10. There is a singlet at  $-360$  p.p.m. which is due to ammonium, and a multiplet at  $-339$  p.p.m. The intensities of the multiplet at  $-339$  p.p.m. correspond to doublet with  $J = 25$  Hz and a triplet with  $J = 23$  Hz, thus nitrogen is linked to one (doublet) and two (triplet) phosphorus.

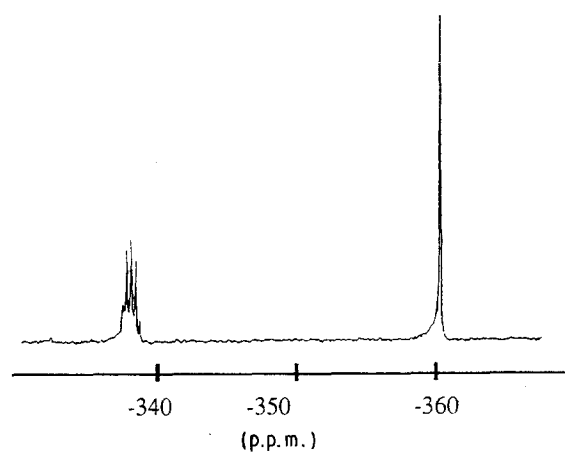


Figure 10  $^{15}\text{N}$  liquid NMR spectrum of phosphorodiamidic acid after 180 days.

## 4.2. Discussion

The phosphorodiamidic acid transformation leads to the disappearance of its diffraction peaks and at the same time the appearance of ammonia and P-O-P and/or P-N(H)-P bridges detected by infrared analysis. In addition, using  $^{15}\text{N}$  NMR, we observed that the compound which appears exhibits P-N(H)-P bridges and P-NH<sub>2</sub> groups. This major new product is detected by its  $^{31}\text{P}$  MAS NMR peaks at  $+0.3$  and  $-3.8$  p.p.m.

Our results agree with a mechanism of condensation reaction based on the mobile hydrogen of phosphorodiamidic acid which reacts with itself giving amidoimido diphosphates and ammonia (Fig. 11). Ammonia reacts with the acidic form giving the ammonium salt (Fig. 12).

An ammonium salt of diamido 1, 2 imidodiphosphate which is present as two different forms of phosphorus in the solid state, was obtained as a major compound. One phosphorus is present as an acid function and the other as an ammonium salt function. A small amount of polyphosphates was detected as a minor product of partial hydrolysis.

This reaction of amidophosphates with acidic compounds (like P-NH<sub>3</sub><sup>+</sup>) has already been observed. Riejsele and Somieski studied the reaction of PO(NH<sub>2</sub>)<sub>3</sub> with HCl in the solid state and observed the formation of P-N(H)-P bridges, P-N(P)-P cross-links and NH<sub>4</sub>Cl by an S<sub>N</sub>2-type mechanism. Furthermore, Watanabe and Sato [15] studied the reaction of salts of monoamidophosphoric acid with HCl, and observed only the formation of P-O-P bridges and NH<sub>4</sub>Cl, whereas for phosphorodiamidic salts they observed the formation of P-O-P and P-N(H)-P bridges [16].

## 5. Conclusion

The structure of monomeric phosphorodiamidic acid (HPO<sub>2</sub>(NH<sub>2</sub>)<sub>2</sub>) is described by taking into account hydrogen bonds and hydrogen transfer for limiting forms. This monomer is not the most stable thermodynamic form. The structural model proposed allows us to propose that the diamido 1, 2 imidodiphosphate is produced by a mechanism which involves an initiation step by the (P)-NH<sub>3</sub><sup>+</sup> species.

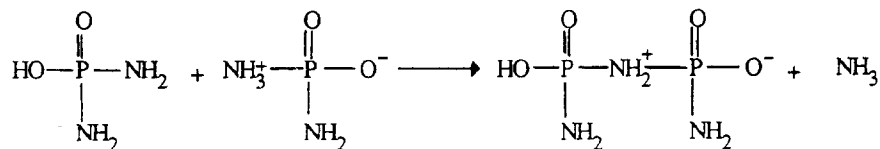


Figure 11 Mechanism of condensation of phosphorodiamidic acid.

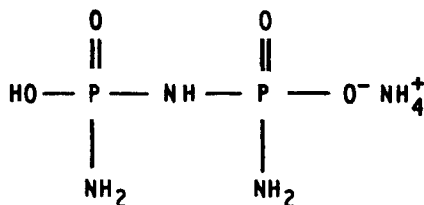


Figure 12 Diamido 1, 2 imidodiphosphate.

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Received 21 July  
and accepted 5 November 1992