July, 1993] © *1993 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***66***, *1963—1966(1993)* 1963

Thermal Condensation of Phosphorodiamidic Acid: $HPO_2(NH_2)_2$

K. Kowalczyk, * Y. Parent, and G. Palavit
Université des Sciences et Technologies de Lille, C$_5$2$^{\text{ème}}$étage, 59655 Villeneuve d'Ascq cedex, France

(Received October 19, 1992)

Phosphorodiamidic acid disappears when it is heated at 110 °C. It condenses, giving the ammonium salt of *P*,*P*′-diamidoimidodiphosphoric acid. The value of the enthalpy for this reaction is -3.6 kJ mol^{-1}. We determined the apparent activation energy for the condensation reaction by two different methods: -Differential Scanning Calorimetry, -Measuring out ammonium. We obtained by these two methods the same apparent activation energy: 120 kJ mol^{-1}.

The incorporation of nitrogen into phosphate glasses improves their chemical durability without significantly reducing their thermal expansion coefficient.[1,2] In general, phosphorus nitride oxide glasses are prepared by remelting the glass under an ammonia or nitrogen atmosphere at temperatures above the glass transition temperature.[1] These glasses can also be prepared by adding a nitride, such as: AIN, Mg_3N_2.[2]

We propose to use compounds with a phosphorus-nitrogen covalent bond as phosphorus nitride oxide glass precursors. Among phosphorus nitrogen compounds phosphoramidates are now well studied; particularly, Watanabe and Coll have reported on several salts of phosphoramidic and phosphorodiamidic acid.[3,4]

In a previous paper we described the structure and properties of phosphorodiamidic acid at room temperature.[5] We propose in this paper a study of the thermal stability of this acid.

Experimental

Phosphorodiamidic Acid Preparation. Phosphorodiamidic acid is prepared by a method described by Klement.[6] In order to obtain a very pure anhydrous phosphorodiamidic acid, recrystallization of the phenyl ester is carried out twice after dissolving in ethanol at 80 °C. The phosphorodiamidic acid is then dried under vacuum at room temperature.

Analysis. The product was dissolved in the water and the amount of phosphorus in the solution was determined by a gravimetric technique. Total nitrogen was determined by the Kjeldahl method. Nitrogen present as ammonium ions was determined by an ammonia distillation method without decomposition by use of concentrated sulfuric acid. Acidic titration of the phosphorodiamidic acid was also carried out. The pK_a value (4.9) is the same as that reported by Peacock.[7] A chemical analysis of the product gave the following results: NH_4^+, 0.3%; N, 27.6%; P, 32.2%. The calculated contents of the elements for $HPO_2(NH_2)_2$ were: NH_4^+, 0%; N, 29.2%; P, 32.3%. After a thermal treatment at 110 °C a chemical analysis gave the following results: NH_4^+, 15.2%; N, 27.2%; P, 31.9%.

X-Ray diffractograms were recorded with nickel-filtered Cu *Kα* radiation using a Phillips PW.1010 diffractometer. The X-ray diffractogram of phosphorodiamidic acid was the same as that reported by M. L. Nielsen.[8] After a thermal treatment (110 °C) the X-ray diffraction peaks of phosphorodiamidic acid disappeared; the resulting product was not well-crystallized.

The IR spectra were recorded on a Perkin–Elmer M1710 spectrometer by means of the KBr disc method.

The ^{31}P NMR proton-decoupled spectra of the 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, the negative shifts being downfield.

The ^{31}P CP MAS NMR spectra were recorded at 161.97 MHz on an AMX-S 400WB Bruker spectrometer, at a spinning rate of 15000 Hz. The MAS NMR chemical shifts are reported relative to the external H_3PO_4, the negative shifts being downfield.

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

A differential scanning calorimetry (D.S.C.) analysis was carried out using a Setaram DSC 111.

Results and Discussion

Thermal Condensation of Phosphorodiamidic Acid. A D.S.C analysis of phosphorodiamidic acid was carried out at various heating rates under several atmospheres (air, vacuum, nitrogen). We did not observe any important modifications under the experimental conditions. We therefore present in Fig. 1 the D.S.C. curves of phosphorodiamidic acid in air at a heating rate of 1 °C mn^{-1}. We observed during the first run (Fig. 1a) an endothermic peak at 79 °C; during a second run (Fig. 1b) we did not observe this phenomenon.

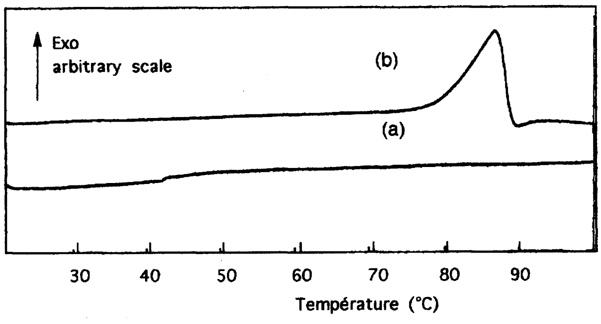


Fig. 1. D.S.C. curves for phosphorodiamidic acid with a heating rate of 1 °C mn^{-1} in air (a) first heating and (b) second heating.

There was no weight loss during the endothermic phenomenon, and the enthalpy was -37.6 J g^{-1}.

We show in Fig. 2 the infrared spectrum of phosphorodiamidic acid after a thermal treatment at 110 °C. We observed large modifications between the spectrum before and after a thermal treatment at 110 °C.

First, the stretching vibrations at 3400 and 3284 cm^{-1} attributed, respectively, to v_{as} and v_s NH_2 in the acid were larger for the compound at 110 °C. However we looked for thermal product absorptions at 3385, 3269 and 1586 cm^{-1}, which could be attributed to the (P)–NH_2 groups, and at 3074 cm^{-1}, which could be attributed to the (P)–NH–(P) groups. Secondly, the stretching vibrations attributed to v_{as} and v_s NH_3 in phosphorodiamidic acid disappeared after the thermal treatment. We looked for the products heated at the 110 °C absorption peaks at 2864, 2112, 1882 and 1467 cm^{-1}, which were attributed to the ammonium ion. The 870 and 696 cm^{-1} bands were attributed to the P–O–P and/or P–N(H)–P bonds and the 1210 and 1065 cm^{-1} bands to the stretching vibrations of the PO_2 groups.

Phosphorodiamidic acid after a heat treatment underwent a transformation. We observed by X - ray diffraction the disappearance of the acid. This transformation leads to the appearance of ammonium, which was proved by two chemical analyses: ^{15}N NMR and infrared. However, all of the nitrogen of phosphorodiamidic acid was not converted into ammonium. We, indeed, observed by infrared and ^{15}N NMR spectroscopies the formation of P–N(H)–P bridges and the retention of P–NH_2 groups. The principal new product was characterized by its ^{31}P CP MAS NMR peaks at 0 and -4.1 ppm.[9]

We propose the following mechanism for the thermal condensation of phosphorodiamidic acid: in a first step it reacts with itself giving *P*,*P*′-diamidoimidodiphosphoric acid and ammonia. In the second step ammonia reacts with one acidic group, giving an ammonium salt. We therefore obtained as a major compound the ammonium salt of *P*,*P*′-diamidoimidodiphosphoric acid, which presents in the solid state a crystallographic nonequivalency. We also observed a small quantity of polyphosphates and the ammonium salt of phosphorodiamidic acid.

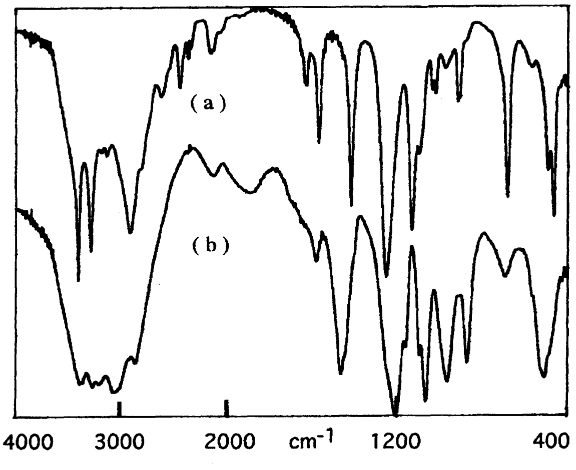


Fig. 2. Infrared spectra of (a) phosphorodiamidic acid and (b) phosphorodiamidic acid after a thermal treatment at 110 °C.

The condensation of phosphoramidates (carrying P–NH_2 groups) in an acidic medium has already been observed.[10—12] We described in another article the condensation of phosphorodiamidic acid with time, which follows the same mechanism.[5] Phosphorodiamidic acid is not thermodynamically stable and condenses with time. If it is heated at 110 °C the condensation is greatly accelerated.

Kinetic Analysis. A Kinetic study of the thermal condensation of phosphorodiamidic acid was realized by the Kissinger method[13] by exploiting the D.S.C runs shown in Fig. 3. As the heating rate increases, both the initial transition and the peak maximum were shifted to higher temperatures (Table 1). The theoretical work of Kissinger indicates that the activation energy of the condensation reaction is defined by as follows:

$$\frac{d\ln(\phi/T_{max}^2)}{d(1/T_{max})} = -E/R.$$

Here ϕ is the heating rate, T_{max} the temperature of the D.S.C. peak maximum, E the activation energy and

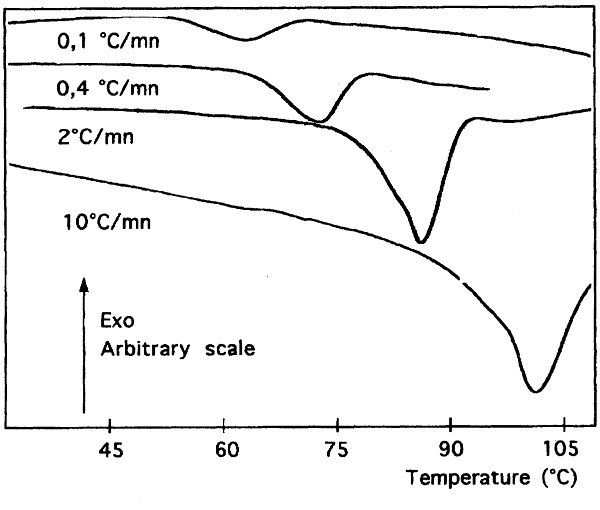


Fig. 3. D.S.C. curves for phosphorodiamidic acid with various heating rates in air.

Table 1. Kinetic Data for the Thermal Condensation of Phosphorodiamic Acid

Heating rate	ΔH	$T_{initial}$	T_{max}	$1/T_{max}$	$\ln(\Phi/T_{max}^2)$
(°C mn^{-1})	J g^{-1}	K	K	(×1000)	
0.1	−34.65	323	336	2.98	−13.94
0.4	−34.69	330	345	2.90	−12.60
2	−37.12	347	361	2.77	−11.08
10	−32.94	335	372	2.69	−9.54

R the perfect-gas constant. The plot of $\ln(\phi/T^2_{\max})$ versus $1/T_{\max}$ is linear, the slope being equal to $-E/R$. The apparent activation energy for the condensation reaction was estimated to be 120 kJ mol^{-1}. The results are shown in Fig. 4 and Table 1.

The previous spectroscopic study confirms that the condensation of phosphorodiamidic acid is characterized by the appearance of ammonium. Ammonium measurements were therefore used to investigate the condensation of phosphorodiamidic acid at 293 and 328 K. The ammonium weight versus the reaction time at 293 and 328 K is shown in Fig. 5. The rate of the appearance of ammonium increases with temperature. After a long time, the ammonium percentage was constant at 12.5 weight %. This transformation obeys first-order kinetics, which can be represented as follows:

$$\ln \frac{N_0 - N_\infty}{N_t - N_\infty} = kt.$$

Here N_0 and N_∞ are, respectively, the ammonium weight at the beginning (0%) and at the completion (12.5%) of the reaction; N_t is the value after time t and k is the rate constant. The first-order kinetic plot of $\ln[(N_0-N_\infty)/(N_t-N_\infty)]$ versus time at 293 and 328 K was found to be linear, as is shown in Fig. 6. The rate constant at 293 K is 4.21×10^{-8} s^{-1} and 6.59×10^{-6} s^{-1} at 328 K. An arrhenius calculation gave the activation energy: 115 kJ mol^{-1}.

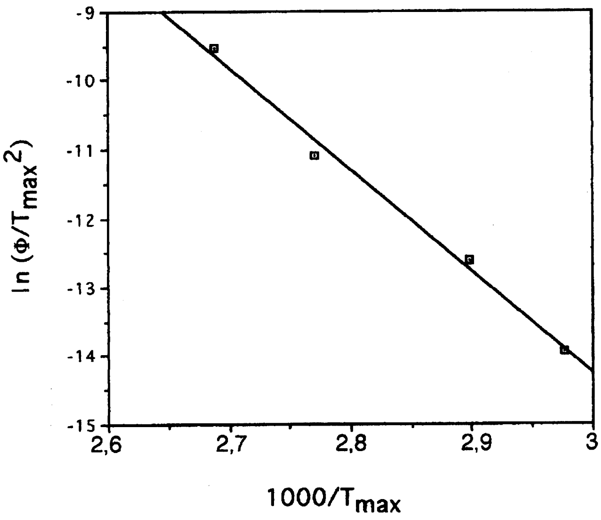


Fig. 4. The Kissinger plot for D.S.C. curves of phosphorodiamidic acid. $\ln(\Phi/T^2_{\max}) = 29.89 - 14712/T_{\max}$. Linear correlation coefficient $r^{\wedge 2}$: 0.992.

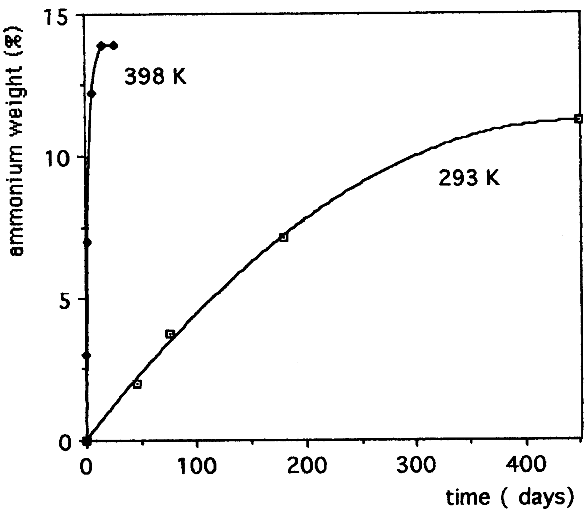


Fig. 5. Evolution of the ammonium weight as a function of time at 293 and 328 K.

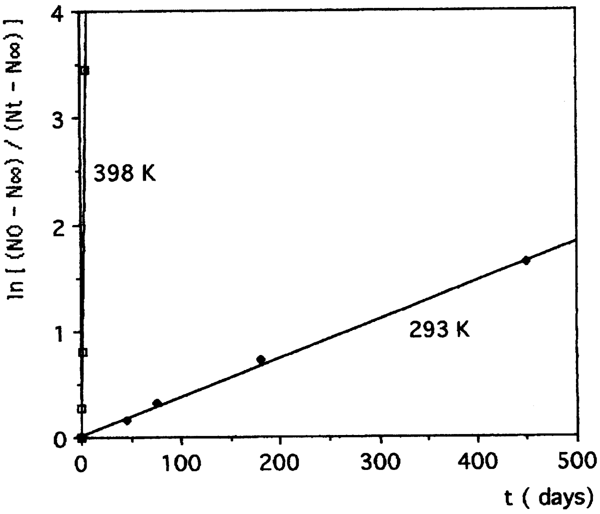
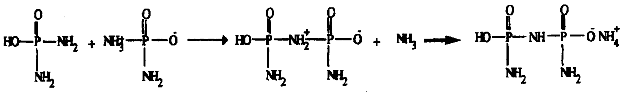


Fig. 6. First-order kinetic plots of $\ln[(N_0-N_\infty)/(N_t-N_\infty)]$ versus the time for isothermal condensation. $y=6.98\times10^{-2}+0.57\times r^{\wedge 2}$: 0.992 at 328 K, $y=1.87\times10^{-2}+3.64\times10^{-3}\times r^{\wedge 2}$: 0.992 at 293 K.

We obtained by these two different methods almost the same activation energy: 120 kJ mol^{-1}. Moreover, we measured for the condensation reaction of phosphorodiamidic acid the enthalpy: -3.61 kJ mol^{-1}. These two values are greatly different from those obtained by Shimasaki and Coll[14] for the condensation of different salts of phosphoramidic acid. They obtained values between -25 and -44 kJ mol^{-1} for the enthalpy, and between 150 and 210 kJ mol^{-1} for the activation energy. They proposed the following condensation mechanism:

This mechanism involves the formation of P–O–P bridges and gives polyphosphates as the resulting product. The condensation mechanism that we propose is:



and involves the formation of P–N(H)–P bridges.

The lower are the values of the enthalpy and activation energy, the lower is the condensation temperature; moreover, the difference in the condensation mechanism is probably due to the zwitterion structure of the raw material (phosphorodiamidic acid).5) The formation of a small amount of polyphosphates during the condensation of phosphorodiamidic acid, however, could be explained by the appearance of the ammonium salt of *P*,*P'*-diamidoimidodiphosphoric acid, which could carry out condensation with a mechanism involving the formation of P–O–P bridges.

We thank Mr. Schimpf of the BRUKER society for the ^{31}P CP MAS NMR analysis of our samples.

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