601. *Phosphorus–Nitrogen Compounds. Part III.*[1] *Phosphams.**

By M. C. Miller and R. A. Shaw.

The thermal decomposition of aminophosphazenes with six- and eight-membered rings, in a nitrogen atmosphere, up to 1000° has been studied by thermogravimetric analysis. Observations have been made on the suitability of a number of crucible materials. Two phosphams, differing in density, are reported, and their structures discussed.

PHOSPHAM, $(NPNH)_n$, has been described a number of times but, as Van Wazer[2] states, " It is difficult to tell whether or not the material described as phospham by one author is the same as [that called] phosphorus nitride by another." Earlier work has been summarised,[3] but it is worth noting that the thermal decomposition in vacuum of hexa-aminocyclotriphosphazatriene, $N_3P_3(NH_2)_6$, and of octa-aminocyclotetraphosphazatetraene, $N_4P_4(NH_2)_8$, was reported[4] to give successively phospham, triphosphorus pentanitride $(N_5P_3)_n$, and phosphorus mononitride $(NP)_n$.

Recently, phospham has been the subject of renewed synthetic and spectroscopic investigations.[5,6] As the controlled ammonolysis of phosphorus pentachloride leads to a complex mixture of cyclic and open-chain chlorophosphazenes,[3] which can be further ammonolysed under more drastic conditions, it appeared probable that phospham, as normally prepared by the reaction of ammonia with phosphorus pentachloride accompanied or followed by strong heating, would contain the basic units derived from various ring and possibly open-chain structures[7] randomly linked together and thus giving amorphous materials. In attempts to obtain more ordered structures, the thermal decomposition of pure hexa-aminocyclotriphosphazatriene and octa-aminocyclotetraphosphazatetraene was studied:

$$N_3P_3(NH_2)_6 \longrightarrow [(NPNH)_3]_n + NH_3$$

$$N_4P_4(NH_2)_8 \longrightarrow [(NPNH)_4]_n + NH_3$$

The thermal decomposition of the aminophosphazenes up to 1000° at atmospheric pressure was studied under oxygen-free nitrogen. In the initial preparative work silica

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[1] Part II, Shaw and Stratton, *J.*, 1962, 5004.

[2] Van Wazer, " Phosphorus and Its Compounds," Interscience Publ., Inc., New York, 1958, Vol. I, p. 331.

[3] Shaw, Fitzsimmons, and Smith, *Chem. Rev.*, 1962, **62**, 247.

[4] Moureu and Rocquet, *Compt. rend.*, 1933, **197**, 1643; 1934, **198**, 1691; 1935, **200**, 1407; *Bull. Soc. chim. France*, 1936, **3**, 821, 829, 1801.

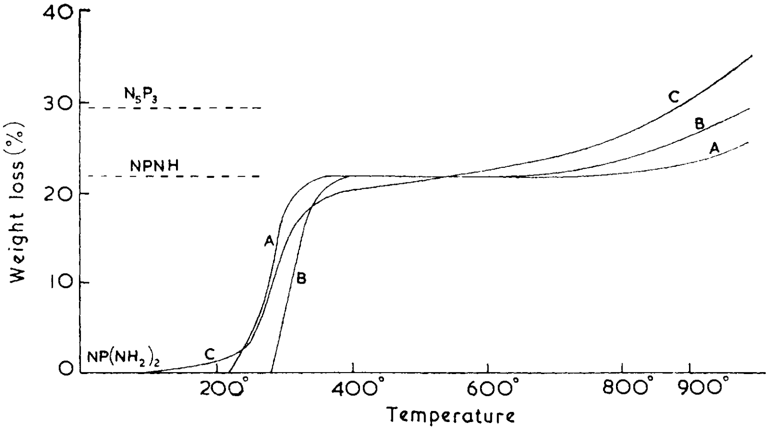
[5] Audrieth and Sowerby, *Chem. and Ind.*, 1959, 748; *Chem. Ber.*, 1961, **94**, 2670.

[6] Steger, *Angew. Chem.*, 1957, **69**, 145; *Chem. Ber.*, 1961, **94**, 266; Lunkwitz and Steger, *Naturwiss.*, 1961, **48**, 552.

[7] Shaw, " Symposium on Macromolecules," Wiesbaden, October 1959; *J. Polymer Sci.*, 1961, **50**, 21.

crucibles were used. Though it was possible to obtain a phospham from the hexa-amino-compound with a new crucible, successive use of the same one led to products having higher phosphorus contents than required for phospham, and attack on the crucible was observed. No phospham was obtained from the octa-amino-compound even when using new crucibles. The position was further complicated when it was found that phosphams undergo a very slow decomposition above 550—600°, with a decrease in phosphorus content (formation of N_5P_3[4] would require an increase), even in crucibles (*e.g.*, alumina) in which no surface effects were observed; for instance, when phosphams were heated in alumina crucibles at 720° for 400 hours under oxygen-free nitrogen, 10% by weight was lost. Noble-metal crucibles, tried in thermogravimetric analysis studies, showed severe attack in the case of platinum and palladium, slight attack on iridium and rhodium, and none on ruthenium, parallelling the increase in melting point of the eutectic of the noble metal with its phosphide poorest in phosphorus. Calcium fluoride crucibles were also attacked.

As aminophosphazenes are relatively strong bases,[8] it is possible that they, or their decomposition products, underwent basic reaction with the silica crucibles. More basic materials such as alumina or thoria proved quite satisfactory, and the former was adopted for all subsequent thermogravimetric studies and larger-scale preparative work. Thermogravimetric curves of the phospham reaction in a number of different crucible materials are shown in the Figure. Some difficulty was experienced in obtaining absolutely flat plateaux, owing, it is believed, to the long time taken for the last traces of ammonia to diffuse out of the macromolecular phospham. Further evidence for some diffusion control comes from the preparative work (see Experimental section).



Thermogravimetric analysis of octa-aminocyclotetraphosphazatetraene.
Crucible material: (A) alumina or thoria; (B) ruthenium; (C) alumina containing residues from pyrolysis of a silicone polymer.

When the thermal decompositions were carried out in alumina vessels under oxygen-free nitrogen, phosphams of satisfactory analyses were obtained. Thermogravimetric studies indicated a single decomposition beginning around 230° (280° in ruthenium). This was confirmed by studies on the hot-stage microscope which showed that the aminophosphazenes do not melt or sublime. The reaction occurs in the solid state, the crystals being shattered, presumably by the ammonia gas formed within them. The expected weight loss occurred, and no further decomposition was observed (for the duration of a run at a heating rate of 1·4°/min.) until about 900°.

Like Audrieth and Sowerby,[5] we had hoped to use infrared spectroscopy to differentiate

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[8] Feakins, Last, and Shaw, *Chem. and Ind.*, 1962, 510.

between the phosphams produced from hexa-amino- and octa-amino-phosphazenes. The spectra[9] indicated the presence of N–H bonds, but failed to give any evidence concerning the different nature of the two phosphams prepared. This was obtained from density measurements. Phospham prepared from hexa-aminocyclotriphosphazatriene has a density of 2·17 ± 0·04 g./c.c. and that from octa-aminocyclotetraphosphazatetraene of 2·43 ± 0·04 g./c.c. (determined by toluene displacement). In case the difference was due to easier penetration of the relatively large toluene molecule into the pores of one of the phosphams than of the other, density determinations by hydrogen displacement were carried out, and values of 2·21 ± 0·02 and 2·49 ± 0·02 g./c.c., respectively, were obtained. These slightly greater values probably approximate more nearly to the true density of these macromolecular, amorphous solids, but the difference supports the belief that, although not crystalline, the two products are distinct. One possible explanation of this is that the two phosphams are based on six- and eight-membered rings, respectively, randomly linked by NH bridging groups; and, in consequence, the nitrogen in the ammonia liberated in the pyrolysis comes only from elimination between amino-groups and not from the ring-nitrogen. It is worth noting that, in the aminophosphazenes and in the majority of other phosphazenes, compounds based on eight-membered rings are more dense than their six-membered analogues.

The phosphams obtained are white, or off-white, infusible solids, amorphous to *X*-rays. They are insoluble in all solvents which do not decompose them. It is probable that there are as many phosphams as there are aminophosphazenes (or their chlorophosphazene precursors). In contrast to the work of Bode and Clausen[10] who thermally decomposed anilinophosphazenes to phenylphosphams and reported reconversion of these with aniline into the original anilino-compounds with retention of ring size, we, like Steinman,[11] failed to reconvert the phosphams into the amino-compounds. The phosphams were heated with liquid ammonia, and the cooled products extracted with water, but paper chromatography failed to reveal even traces of aminophosphazenes. Attempts to induce the phosphams to crystallise by keeping them for prolonged periods at elevated temperatures showed that some decomposition occurred (see above).

It must be emphasised that the above results, although checked in numerous experiments, may apply only to the reaction conditions stated. The differences with the findings of other workers may be due to variations in experimental conditions such as the type of crucible material, pressure, etc. It is possible that our findings, especially regarding the variations encountered with different crucibles, may have a bearing on other studies of high-temperature reactions, such as chemical, kinetic, and equilibria measurements and the testing of thermal stability.

EXPERIMENTAL

Hexachlorocyclotriphosphazatriene and octachlorocyclotetraphosphazatetraene were recrystallised to constant m. p. from light petroleum (b. p. 60—80°). Ether was dried over sodium. "White-spot" nitrogen was passed over phosphorus pentoxide and over manganous oxide. The aminophosphazenes were prepared from the corresponding chloro-compounds by treating their ether solution at −33° with liquid ammonia,[5] and the by-product, ammonium chloride, was removed by a method due to Klement and Koch.[12] The crude compounds were purified by recrystallisation from a minimum quantity of water. The pure aminophosphazenes were characterised by elementary analysis, infrared spectroscopy, density measurements, and paper chromatography, as shown in the Table.

Crucibles and their Sources.—Materials tried were: alumina, porcelain, and calcium fluoride (The Royal Worcester Porcelain Co. Ltd.); ruthenium, iridium, rhodium, palladium, and platinum (The International Nickel Co. Ltd.); thoria (The Morgan Crucible Co.); silica (Vitrosil Co. Ltd.).

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[9] Steger, personal communication.

[10] Bode and Clausen, *Z. anorg. Chem.*, 1949, **258**, 99.

[11] Steinman, Ph.D. Thesis, University of Illinois, 1942.

[12] Klement and Koch, *Chem. Ber.*, 1954, **87**, 333.

Aminophosphazenes.

	$N_3P_3(NH_2)_6$	$N_4P_4(NH_2)_8$	Calc.
Analysis: P (%)	40·4	40·3	40·2
N (%)	54·9	54·6	54·5
d^{20} (g./c.c.) (±0·04)	1·68	1·77	
Ring vibrations (cm.$^{-1}$)	1177	1240	
R_F	0·41	0·30	

Typical Preparation of a Phospham.—Hexa-aminocyclotriphosphazatriene (2·328 g.) was heated under oxygen-free nitrogen in an alumina crucible at 340° for 22 hr., cooled, and weighed. The loss in weight was 0·514 g. (calc., 0·515 g.). Heating for shorter periods led to incomplete weight loss. The quantity of ammonia evolved, determined by dissolution in water and titration with acid, was 0·510 g. Heating the sample for a further 4 hr. produced no further weight loss.

Products from hexa-aminocyclotriphosphazatriene had d^{20} 2·17, 2·17, 2·16 (all ±0·04) (Found: P, 51·3, 51·7, 51·6; N, 46·4, 46·4, 46·6. $(NPNH)_n$ requires P, 51·60; N, 46·4%), *d* being determined by toluene displacement. Products from octa-aminocyclotetraphosphazatetraene had d^{20} 2·43, 2·43, 2·44 (all ±0·04) (Found: P, 51·7, 51·5, 51·5; N, 46·6, 46·5, 46·4%).

Chromatography.—Paper chromatography (descending) was carried out on Whatman No. 1 paper using the following eluent: [13] propan-2-ol 100 ml.; dimethylformamide 100 ml.; ethyl methyl ketone 100 ml.; water 195 ml.; and 25% ammonia solution 5 ml. The chromatogram was developed by spraying with cold nitrous acid solution (sodium nitrite–70% acetic acid), followed by ammonium molybdate (1%) in perchloric acid (10%), and then exposure to ultraviolet light.

Density Determinations.—Densities were determined in a 10-c.c. density bottle with "AnalaR" toluene as the displacement liquid. Samples were degassed under toluene (2 hr. under reduced pressure) and then placed in a thermostat at 20°

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[13] Bieberacher, *Z. anorg. Chem.*, 1956, **285**, 86.