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Studies on Nitrogen-Phosphorus Compounds. XXII.[1] The Synthesis and Properties of Phosphoric Aniline Diamide

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In order to develop fireproof materials, a new compound, phosphoric aniline diamide, was prepared by employing phosphorus oxychloride, aniline, and ammonia as the starting materials. The conditions for the synthesis and the characteristics of the product have been investigated. Phosphoric aniline diamide can be prepared in the following way: 2 moles of aniline are added to 1 mole of phosphorus oxychloride diluted with chloroform, and the precipitate of aniline hydrochloride, a by-product, is separated from the solvent by filtration. A mixture of phosphoric amide and ammonium chloride is formed by the reaction between an excess of gaseous ammonia and the above filtrate at −10—20°C, and is then separated from the mother liquor. Crude phosphoric amide is extracted from the mixture with ethanol, and subsequent re-extraction with acetone yields the pure product with the formula $PONHC_6H_5(NH_2)_2$. The product thus obtained is composed of a white crystalline powder, soluble in water, ethanol and acetone but insoluble in various organic solvents. The compound shows its own characteristic X-ray diffraction pattern and IR absorption bands. Upon heating, the product melts at about 140°C; condensation occurs by de-ammoniation above 170°C, and conversion into insoluble condensed amidophosphates takes place.

Inorganic compounds with P–N bonds are of interest because of their covalency and the possibility of introducing different substituents into the phosphorus atom, and also because most of the compounds polymerize at moderate temperatures. As typical P–N compounds, phosphoric amides, the following types are known: $PO(OH)_2NH_2$, $POOH(NH_2)_2$, $PO(NH_2)_3$, $PONR_2(NH_2)_2$, $PO(OR)_2NH_2$, $POOR(NH_2)_2$, and $PONHR(NH_2)_2$. Some of these compounds have already been prepared by a reaction between the corresponding phosphoric chloride and ammonia at low temperatures.[2–4]

The author has also synthesized the phosphoric amides of $PONR_2(NH_2)_2$ type.[5] In this work, phosphoric aniline diamide, which is expected to have an excellent flame resistance because it contains an aromatic radical in its molecule, was initially formed by a reaction between phosphorus oxychloride, aniline, and ammonia in chloroform as the reaction medium. The pure product was then isolated from ammonium chloride by using ethanol and acetone as extractive solvents. In this paper an experimental study of the preparation and properties of this new compound is described.

Experimental

Synthesis. The flow sheet for the synthesis of phosphoric aniline diamide is shown in Fig. 1. The phosphoric amide can be prepared in the following way: 0.1 mole (15.3 g) of phosphoric oxychloride was placed in a three-necked flask and diluted with 100ml of chloroform. To this was added a solution containing 0.2 mol (18.6 g) of aniline in 80 ml of chloroform at room temperature. The precipitate of aniline hydrochloride (R·1) was separated by filtration from a solution containing phosphoric aniline dichloride. The above filtrate (SR1) was then added, drop by drop, into another three-necked flask containing some ammoniacal chloroform at −15—20°C, simultaneously the reactant in the flask was vigorously stirred while a moderate basicity was maintained by passing gaseous ammonia into it. Thus, a mixture (R2) of phosphoric amide and ammonium chloride was precipitated. This was kept standing overnight and was then separated from the mother liquor (SR2). R2 was put into a stoppered Erlenmeyer flask containing 300 ml of ethanol and stirred. Thus, phosphoric amide and a portion of ammonium chloride contained in R2 were dissolved in ethanol, and the residue (R3) of ammonium chloride was isolated from the ethanol solution (SR3). Crude

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[1] a) The article was presented at the 26th Annual Meeting of the Chemical Society of Japan, Tokyo, April 4, 1972. b) Part XXI of this series: E. Kobayashi, *Nippon Kagaku Kaishi*, **1972**, 38.

[2] H. N. Stockes, *J. Amer. Chem. Soc.*, **15**, 198 (1893); *ibid.*, **16**, 123; 140 (1894).

[3] R. Klement and O. Koch, *Chem. Ber.*, **87**, 333 (1954).

[4] M. Goehring and K. Niedenzu, *ibid.*, **89**, 1769 (1956).

[5] E. Kobayashi, *Kogyo Kagaku Zasshi*, **74**, 1780 (1971).

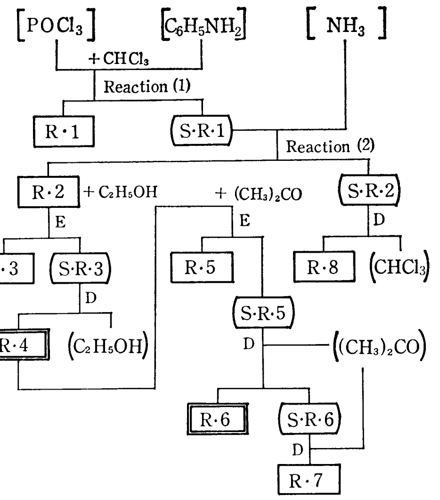

Fig. 1. Flow sheet for synthesis of phosphoric aniline diamides. R·1; $C_6H_5NH_2\cdot HCl$, R·2; Mixture of phosphoric amide and NH_4Cl, R·3 and R·5; NH_4Cl, R·4; Crude phosphoric amide, R·6; Pure phosphoric amide, R·7 and R·8; Sub-product, D; Distillation, E; Extraction.

phosphoric amide (R4) including ammonium chloride as an impurity was obtained by the vacuum distillation of SR3. A large amount of acetone was poured into R4, and the mixture was stirred for several hours at 35°C. Thus, phosphoric aniline diamide alone was dissolved in acetone. The resulting residue (R5) of ammonium chloride was isolated from the acetone solution (SR5). When the above extractions was incomplete because of the low solubility of phosphoric aniline diamide in acetone, it was necessary to use acetone for the reextraction. Pure phosphoric aniline diamide (R6) was precipitated fron an acetone solution concentrated by vacuum distillation at 40°C: R6 was separated by filtration from the mother liquor (SR6) and finally vacuum-dried over phosphorus pentoxide.

Analysis. A sample solution for determining the phosphorus, total nitrogen, and chlorine was prepared as follows: 0.2—0.8 g of a solid sample was weighed exactly and dissolved in water, the volume of the solution being adjusted to 250 ml.

The phosphorus content was determined gravimetrically as magnesium pyrophosphate. The total nitrogen content was determined by Kjeldahl's method. The chlorine content was determined gravimetrically as silver chloride.

The molecular weight of the product was determined with a Mechrolab model 301A vapor-pressure osmometer. The powder diffraction pattern was obtained by using a Rigaku-Denki model [2001 diffractometer with Ni-filtered Cu$K\alpha$ radiation, with 20 KVP and 5 mA. The infrared absorption spectrum was measured with a Hitachi model EPI-S2 infrared spectrophotometer applying the method of KBr disks. The differential thermal analysis (DTA) and thermogravimetric measurements (TGA) were performed simultaneously in a nitrogen atmosphere and at a heating rate of 5°C/min with a Rigaku-Denki model DC-Cl-S thermal analyser.

Results and Discussion

Synthesis of $PONHC_6H_5(NH_2)_2$. The results of the synthesis and analysis of phosphoric amides are summarized in Table 1.

Reaction between Phosphorus Oxychloride and Aniline. Phosphoric aniline dichloride and aniline hydrochloride are formed by the reaction of 1 mol of phosphorus oxychloride with 2 mol of aniline as follows.

$$POCl_3 + 2C_6H_5NH_2 \longrightarrow PONHC_6H_5Cl_2 + C_6H_5NH_2\cdot HCl \quad (1)$$

$$POCl_3 + 4C_6H_5NH_2 \longrightarrow PO(NHC_6H_5)_2Cl + 2C_6H_5NH_2\cdot HCl \quad (1')$$

$$POCl_3 + 6C_6H_5NH_2 \longrightarrow PO(NHC_6H_5)_3 + 3C_6H_5NH_2\cdot HCl \quad (1'')$$

Chloroform was chosen as the medium for the reaction because it does not react with phosphorus oxychloride. Further, chloroform dissolves phosphoric aniline dichloride, but aniline hydrochloride is insoluble in it. Carbon tetrachloride used for the previous synthesis of phosphoric amides[4,5)] was not suitable, since phosphoric aniline dichloride is insoluble in carbon tetrachloride.

For a mole ratio of 2: 1 of $C_6H_5NH_2$ to $POCl_3$, 11.7—14.1 g of R–1 was obtained. These typical results approached the theoretical yield (12.9 g) of aniline hydrochloride. The analytical values of R–1 also agreed with the calculated values of each component in the $C_6H_5NH_2\cdot HCl$, so that confirmation of Eq. (1) might be expected. However, in the experiments at mole ratios of 4: 1 and 6: 1, it was found that Eqs. (1)′ and (1)″ respectively are not invariably completed.

Reaction between SR1 and Ammonia. A mixture (R–2) of phosphoric amide and ammonium chloride was precipitated by a reaction between the filtrate SR1 containing phosphoric aniline dichloride and ammonia as shown by

$$PONHC_6H_5Cl_2 + 4NH_3 \longrightarrow PONHC_6H_5(NH_2)_2 + 2NH_4Cl \quad (2)$$

In this case, a large amount of R–2 was obtained with a mole ratio of 2: 1 of $C_6H_5NH_2$ to $POCl_3$. The high yield of crude phosphoric amide extracted from the above R2 with ethanol was expected as a matter of course. The yield of R2, however, decreased with an increase in the mole ratio of $C_6H_5NH_2$ to $POCl_3$, and the yield of R8 as a by-product increased. It is conceivable that the reaction product (R8) dissolves in chloroform because of non-polarity with the excess of combined aniline, since, on the synthesis of this phosphoric amide, the mole ratio of 2: 1 of $C_6H_5NH_2$ to $POCl_3$ was just what was expected. When the effects of the reaction temperatures on the yields of R2 and R8 were observed, no apparent difference was recognized at −15—20°C. However, it is evident that the polymerization by deammoniation of phosphoric amides is prevented when Reaction (2) takes place at low temperatures and when diffusion of the heat of reaction is kept smooth, and consequently, a high yield of orthophosphoric amide might be expected. At reaction temperatures above 20°C, there is a probability of the formation of condensed products. The resulting product is reddish-brown, a color which frequently appears in aniline salts.

Table 1. Synthesis and analysis of phosphoric aniline diamides

No.	Reaction conditions					Yield					
	$POCl_3$ (g)	$C_6H_5NH_2$ (g)	N/P	Reaction[a] (1) (°C)	Reaction[a] (2) (°C)	R·1 (g)	R·2 (g)	R·3 (g)	R·4 (g)	R·6 (g)	R·8 (g)
1	15.3	18.6	2.0	−10∼−12	−10∼−15	11.7	23.8	9.9	13.0	11.5	2.2
2	15.3	18.6	2.0	−10	−10	13.6	22.6	9.9	12.5	11.4	1.8
3	15.3	18.6	2.0	0	0	13.1	23.1	9.8	13.1	11.0	1.9
4	15.3	18.6	2.0	0±1	0±1	12.7	26.7	15.1	4.9	—	—
5	15.3	18.6	2.0	10	10	13.8	23.1	8.7	13.6	11.1	2.6
6	15.3	18.6	2.0	20	20	14.2	21.5	8.4	12.1	10.2	5.4
7	15.3	37.2	4.0	0±2	0	24.2	11.7	7.6	5.2	3.5	11.7
8	15.3	55.8	6.0	0	0	37.0	6.3	3.8	1.7	1.3	25.0

Analysis of R·4					Analysis of R·6					
pH	P (%)	N (%)	Cl (%)	P:N:Cl (atomic ratio)	pH	P (%)	N (%)	P:N (atomic ratio)	Mp (°C)	MW
6.08	15.0	21.8	6.2	1.00:3.21:0.36	4.51	18.1	24.9	1.00:3.04	141—144	171
6.60	13.3	21.0	7.7	1.00:3.50:0.57	4.48	17.8	23.5	1.00:2.92	140—143	164
6.31	13.7	21.3	6.9	1.00:3.44:0.44	4.51	17.6	23.9	1.00:3.00	138—144	
5.90	14.1	19.6	3.1	1.00:3.08:0.02		17.8	24.5	1.00:3.04	142—146	168
						C; 41.1	H; 6.1			
6.40	13.1	21.7	7.0	1.00:3.67:0.46	4.59	17.9	23.9	1.00:2.95	143—146	
6.28	14.2	23.0	7.9	1.00:3.58:0.53	4.59	17.6	22.8	1.00:2.88	140—144	157
						C; 39.5	H; 6.0			
6.32	13.8	20.9	10.2	1.00:3.35:0.73	4.50	18.1	24.0	1.00:2.98	142—144	
5.90	10.2	20.0	15.6	1.00:4.35:1.34	4.55	18.0	24.1	1.00:2.96	139—150	169
						Cl; 0.1				
				(C; 42.11)[a] (H; 5.89)		(18.10)	(24.55)	(1.00:3.00)		(171)

a) (1): Reaction between $POCl_3$ and $C_6H_5NH_2$.
(2): Reaction between NH_3 and SR 1.
b) Numerals in parentheses indicate the calculated values of the composition of $PONHC_6H_5(NH_2)_2$.

Extraction of Crude Phosphoric Amide from R2. The R2 product consists of phosphoric amide and ammonium chloride. The two compounds cannot be easily separated because their reactions with various solvents resemble each other; that is, both materials are soluble in water and methanol, and insoluble in such organic solvents as chloroform, carbon tetrachloride, petroleum ether, and benzene. The author therefore chose ethanol and acetone as the solvents because they have a suitable polarity for the extraction of phosphoric amide from R2. Acetone does not dissolve ammonium chloride, but phosphoric amide is a little soluble in it, so that the direct extraction of phosphoric amide, by using acetone is not an efficient treatment. Thus, ethanol which also dissolves a small amount of ammonium chloride was used in the first extraction of phosphoric amide from R4. The residue R4 was a light yellowish-brown powder, containing 13—15% P, 20—23% N, and 3—8% Cl, as shown in Table 1. It is soluble in water, the solution being almost neutral. The P: N: Cl atomic ratios of the products were 1.0: 3.0—3.6: 0.0—0.6, in which the values of Cl correspond to the values of nitrogen which exceed 3.0. It might be understood that crude phosphoric amide R4 is contaminated with ammonium chloride.

Extraction of Phosphoric Aniline Diamide. In the preliminary experiments, it was confirmed that phosphoric aniline diamide is slightly soluble in acetone, but not ammonium chloride. Therefore, the pure phosphoric aniline diamide R6 was obtained from R4 by a previous method. However, because of the low solubility of phosphoric aniline diamide in acetone, a tendency for this compound to remain in the R5 residue was often observed in the chemical analysis of R5 and on the basis of X-ray diffraction data. An efficient extraction of phosphoric aniline diamide may also be expected by using a solvent in which 2—5 vol% of ethanol is added to acetone.

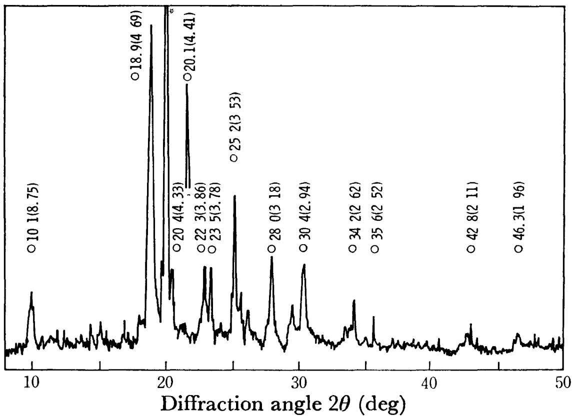

Fig. 2. X-ray diffraction spectrum of phosphoric aniline diamide. Numerals near peaks indicate distances (Å) between planes in crystals.

Properties of PONHC$_6$H$_5$(NH$_2$)$_2$. *X-Ray Diffraction*: Phosphoric aniline diamide is a white, crystalline powder. Each crystal is a tetragonal plate 5—30 μ in size, as determined by means of microphotography. The X-ray diffraction pattern is shown in Fig. 2. Three strong diffraction lines at 4.69, 4.41, and 3.53 Å can be used for identification. So far, single crystals of phosphoric aniline diamide of a suitable size have not been obtained, and an accurate interpretation of the X-ray data is not possible.

Solubility with Various Solvents. Compound $PONHC_6H_5 \cdot (NH_2)_2$ is soluble in water; its solubility is 3.49% at 0°C, and 5.66% at 25°C, and the pH of a 1% aqueous solution is 4.5. This compound is insoluble in such organic solvents as chloroform, carbon tetrachloride, petroleum ether, and benzene, but soluble in polar solvents such as methanol and ethanol, the solubility in the latter being 1.36% at 0°C and 2.39% at 25°C. The compound is slightly soluble also in acetone, the solubility being 0.23% at 0°C and 0.28% at 25°C. Therefore, on the complete extraction of R6 from R4, a large excess acetone is necessary for the treatment of R4.

Analysis of Purified Products. The percentage of each component in R6 agreed with that of the formula $PONHC_6H_5(NH_2)_2$. The P: N atomic ratios almost reached 1: 3, as shown in Table 1. The molecular weight of R6, as measured in the ethanol solution, was close to the calculated value (171.14) for this formula.

In the cases of Nos. 7 and 8, where the $C_6H_5NH_2/POCl_3$ mole ratios are 4: 1 and 6: 1, respectively, small amounts of R6 are obtained; the products can actually be denoted by $PONHC_6H_5(NH_2)_2$. The following process seems to take place: when 2 or 3 mol of aniline replace chlorine atoms in phosphorus oxychloride in Reactions (1) and (2), the part of which amount is greater than that of a connecting C_6H_5NH radical is replaced by NH_2 radical from ammonia giving rise to the formation of $PONHC_6H_5(NH_2)_2$.

Infrared Absorption Spectra. Previously, the infrared absorption spectra of $PO(NH_2)_3$ had been investigated by Stenger,[6] and those of $PON(C_2H_5)_2(NH_2)_2$ (crude) by the author,[5] but not the IR of $PONHC_6H_5(NH_2)_2$. The results are shown in Fig. 3.

In this spectrum, the absorption bands may be assigned as follows: There are N–H stretching vibrations at 3350 and 3220 cm^{-1}, the C–C stretching vibrations in aromatic compounds at 1600 and 1489 cm^{-1}, the C–N stretching vibrations in aromatic secondary amines at 1407 cm^{-1}, the N–H bending mode in secondary amines or the C–N stretching vibrations at 1291 and 1238 cm^{-1}, and the P–O stretching vibration at 1140 cm^{-1}, while the absorption bands in the range of 1075 and 873 cm^{-1} are related to the NH_2 radicals. The assignment of the absorptions at 748 and 690 cm^{-1} is difficult. However, because though these peaks can be generally considered to represent the P–N stretching vibrations, the characteristic peaks of aniline as a raw material have also appeared at the same locations.

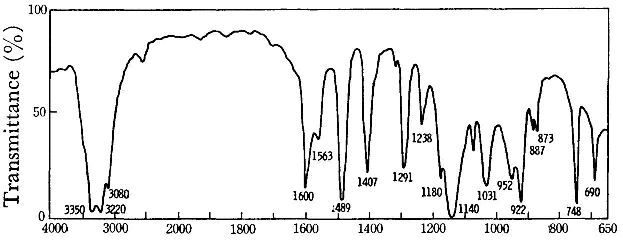

Fig. 3. Infrared spectrum of phosphoric aniline diamide.

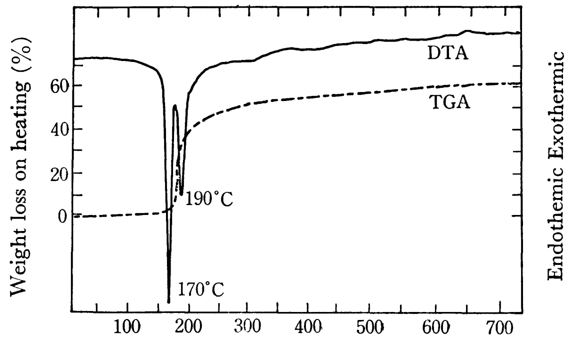

Fig. 4. DTA and TGA curves for phosphoric aniline diamide. Sample; 100 mg, Heating rate; 5°C/min, Current gas; Nitrogen 0.31/min

Change in Product by Heating. When phosphoric aniline diamide is used in fireproof material its effect can be expected. In fact, both paper and fiber immersed in aqueous solutions of R4 or R6 exhibited a remarkable fireproof character. Both R4 and R6 reacted with formalin to form resinous products which are insoluble in water and fireproof. Upon heating, the $PONHC_6H_5(NH_2)_2$ melted at about 140°C and commenced condensation with deammoniation. The compound bubbled above 170°C after it formed a fire-resistant film.

The DTA and TGA curves for $PONHC_6H_5(NH_2)_2$ are shown in Fig. 4. Two endothermic peaks resulting from melting and condensation in the heated product appeared at 170 and 190°C, respectively. In this case condensation was recognized by the loss in weight shown by the TGA curve. Conversion of the phosphoric amide into the insoluble condensed phosphates was also confirmed by paper chromatography.

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[6] E. Stenger, *Z. Anorg. Allg. Chem.*, **310**, 114 (1961).