The Formation of $N_3P_3(NH_2)_6 \cdot H_2O$ and $N_3P_3(NH_2)_6 \cdot HCl$ from the Reaction Product between $(NPCl_2)_3$ and Ammonia

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(Received March 19, 1971)

In the course of the synthesis research into $N_3P_3(NH_2)_6 \cdot H_2O$ as a fireproof material, some experiments have been made on the reaction between $(NPCl_2)_3$ and liquid ammonia, a new adduct, $N_3P_3(NH_2)_6 \cdot HCl$, was found to be formed. The reaction conditions for the formation and the characteristics of the adduct have been investigated.

Previous studies have indicated that an ammonolysis of phosphonitrilic chlorides takes place very slowly.[1] Audrieht and Sowerby[2] have also reported that the complete replacement of the chlorine atoms in the phosphonitrilic chlorides could be achieved within 48 hr. However, in this study, the reaction between $(NPCl_2)_3$ and a large excess of liquid ammonia has been completed within several hours in an autoclave with an electro-magnetic stirrer, and the rate of reaction was accelerated by the addition of dioxane as the solvent to this reaction system. The reaction product is a mixture of $N_3P_3(NH_2)_6$ and NH_4Cl.

It has been reported that the addition of ethanol to an aqueous solution of the reaction product causes the precipitation of $N_3P_3(NH_2)_6 \cdot H_2O$.[3] However, the author found the following facts when he used this separation procedure.

After the ammonia involved in the reaction product was completely excluded under reduced pressure, the product was dissolved in water. The adduct, $N_3P_3(NH_2)_6 \cdot HCl$, was then precipitated by the addition of ethanol to the aqueous solution.

Found: P, 34.2; N, 46.5; Cl, 12.6%; P : N : Cl atomic ratio, 3.0 : 9.0 : 1.0. Calcd for $N_3P_3(NH_2)_6 \cdot HCl$: P, 34.73; N, 47.12; Cl, 13.25%.

The analyses of the typical products did not give the $N_3P_3Cl_{6-n}(NH_2)_n$ formula, but $N_3P_3(NH_2)_6 \cdot HCl$. Therefore, the formation reaction may be expressed by the following equation:

$$N_3P_3(NH_2)_6 + 6NH_4Cl \rightleftarrows N_3P_3(NH_2)_6 \cdot HCl + 5NH_4Cl + NH_3$$

The equation was also confirmed by an examination of the reaction between $N_3P_3(NH_2)_6 \cdot H_2O$ and commercial ammonium chloride, and the heat of reaction was 1.24 kcal/mol (endothermic).

It is known[4] that the basicity of some aninophosphazens is comparable with that of parent amines, and adducts ($N_3P_3(NHR)_6 \cdot HCl$, where R is aliphatic amines) are formed with one molecule of hydrogen chloride even in the presence of ammonia. However, with the $N_3P_3(NH_2)_6 \cdot HCl$ adduct, it is considered that the molecule of hydrogen chloride can be removed with ammonia. In fact, $N_3P_3(NH_2)_6 \cdot H_2O$ was formed by the addition of ethanol to a reaction product solution that contained an excess amount of ammonia for the neutralization of hydrogen chloride in $N_3P_3(NH_2)_6 \cdot HCl$.

Found: P, 38.4; N, 51.7; Cl, 0.4%; P : N : Cl atomic ratio, 3.0 : 8.9 : 0.0. Calcd for $N_3P_3(NH_2)_6 \cdot H_2O$: P, 37.30; N, 50.61%.

Both compounds, $N_3P_3(NH_2)_6 \cdot H_2O$ and $N_3P_3(NH_2)_6 \cdot HCl$, are composed of a white crystalline powder, both dissolve in water (hydrate: the solubility at 25°C is 11.2 g anhydride/100 g soln; chloride: because of its high solubility, it could not be measured), but are insoluble in various organic solvents. The compounds showed their own characteristic IR absorption bands, as is shown in Fig. 1. Their DTA curves are distinguished from each other, and they were both converted by heating to phospham, which has an excellent flame resistance.

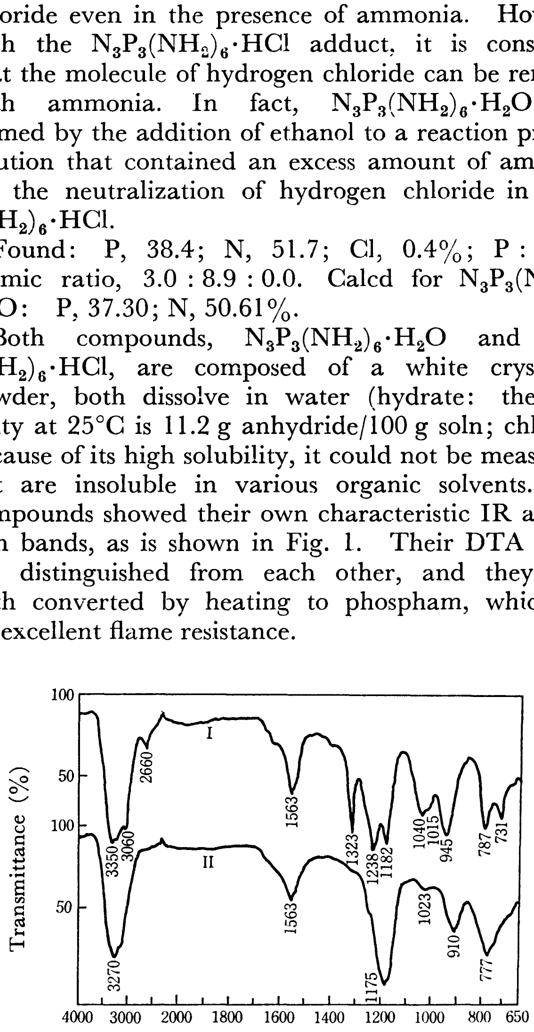

Fig. 1. Infrared spectra of trimeric phosphorus nitride diamides.
I: $N_3P_3(NH_2)_6 \cdot HCl$ II: $N_3P_3(NH_2)_6 \cdot H_2O$

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