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THE REACTION BETWEEN PHOSPHORUS TRIFLUORIDE-BORANE AND AMMONIA

THE SYNTHESIS OF TRIAMIDOPHOSPHORUS-BORANE, $(NH_2)_3PBH_3$

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Abstract—The reaction of unstable phosphorus trifluoride-borane and ammonia yields the new, stable compound, $(H_2N)_3PBH_3$.

A formal analogy between BH_3 and O is developed, and evidence is presented to indicate that the B—P bond is not broken during the ammonolysis of F_3PBH_3.

DIBORANE and excess phosphorus trifluoride react slowly at room temperature under a pressure of 8 atm to give F_3PBH_3 as the primary product.[1] The base displacement reaction between F_3PBH_3 and trimethylamine can be summarized by the equations:[1]

$$(CH_3)_3N + F_3PBH_3 \rightarrow (CH_3)_3NBH_3 + F_3P \quad (1)$$

$$F_3P + (CH_3)_3N_{(excess)} \rightarrow \text{Undefined products.}\dagger \quad (2)$$

It is tempting to extrapolate the behaviour of $N(CH_3)_3$ and to predict that a similar base displacement reaction might occur if ammonia were used as the base. On the other hand a well supported axiom of co-ordination chemistry indicates that the chemistry of ammonia can not be predicted from observations on trimethylamine. It was not suprising then to find in the original study[1] that ammonia reacts with F_3PBH_3 but no F_3P is liberated. An unidentified solid was obtained. A more proper description of the foregoing ammonia reaction is the subject of this paper.

The synthesis of $(H_2N)_3PBH_3$

When ammonia is allowed to react with F_3PBH_3 in diethyl ether over a gradually increasing temperature range from (−111–+25°C), the following process ensues:

$$6NH_3 + F_3PBH_3 \xrightarrow[-111-25°C]{Et_2O} 3NH_4F + (H_2N)_3PBH_3. \quad (3)$$

The product, triamidophosphorus–borane, is a new ether-soluble crystalline solid with a characteristic X-ray powder pattern. Its detailed structure has been worked out by NORDMAN[4] and its geometry is as expected from the above formula. It is stable (in dry air) when pure, but, like most borane compounds, its stability is

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† Although no definitive data on the F_3P—$N(CH_3)_3$ reaction products are available, GRIFFITHS and BURG[2] mention an unstable adduct at −78°C and HOLMES[3] has isolated a solid adduct of PCl_3 and $N(CH_3)_3$ at 0°C.

[1] R. W. PARRY and T. C. BISSOT, *J. Amer. Chem. Soc.* **78**, 1524 (1956).
[2] J. E. GRIFFITHS and A. B. BURG, *J. Amer. Chem. Soc.* **82**, 1508 (1960).
[3] R. R. HOLMES, *J. Amer. Chem. Soc.* **82**, 5285 (1960); *J. Phys. Chem.* **64**, 1295 (1960).
[4] C. E. NORDMAN, *Acta Crystalographica.* **13**, 535 (1960).

seriously reduced by small amounts of impurities. It is soluble in ethers, liquid ammonia and chloroform without decomposition, and dissolves in water with reaction, but the hydrogen evolution is slow unless the solution is acidified.

Observations on the mechanism of $(H_2N)_3PBH_3$ *formation*

In view of the high degree of dissociation of F_3PBH_3, particularly near room temperature, it was of some interest to determine whether the low temperature reaction was a direct ammonolysis, involving displacement of the fluorines of PF_3 by NH_2 groups, or whether the reaction proceeded in a more conventional fashion through a base displacement process involving the entire PF_3 molecule:

$$H_3N + F_3PBH_3 \rightarrow H_3NBH_3 + PF_3$$

$$PF_3 + 6NH_3 \rightarrow 3NH_4F + P(NH_2)_3$$

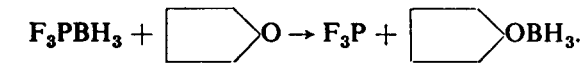
$$H_3NBH_3 + P(NH_2)_3 \rightarrow (H_2N)_3PBH_3 + H_3N$$

The first equation in the above sequence would be analogous to the reaction between trimethylamine and F_3PBH_3 [equation (1)]. A direct test of the postulated mechanism could be made by mixing H_3NBH_3, PF_3, and NH_3. If the reaction proceeded as described above, $(H_2N)_3PBH_3$ and NH_4F should appear as products. Experimentally it was found that no $(H_2N)_3PBH_3$ could be detected in the products and the original H_3NBH_3 could be recovered unchanged. These data support the postulate that the reaction proceeds through direct attack of NH_3 on F_3PBH_3 without initial rupture of the P—B bond.

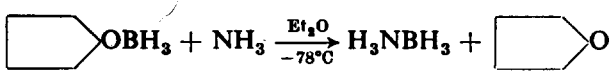
The role of reaction conditions

In the reaction of B_4H_{10} and B_2H_6 with ammonia it was found that direct attack of ammonia on the boron hydride gave a non-symmetrical cleavage of the double bridge bond, whereas a preliminary attack upon the boron hydride by a relatively strongly basic ether such as tetrahydrofuran, followed by a subsequent displacement of the ether with NH_3, resulted in a symmetrical cleavage product. A similar observation can be made involving F_3PBH_3 and NH_3.

At −78°C no more than 15 per cent of the original F_3P was displaced from F_3PBH_3 by tetrahydrofuran over a ½ hr period. These data support the earlier qualitative observation that the weak base, diethyl ether, does not displace F_3P at −111°C; (no visible evidence for dissoc.) hence, it is not unreasonable to postulate direct interaction between F_3PBH_3 and ammonia in diethyl ether at −111°C or −78°C. On the other hand, F_3PBH_3 in tetrahydrofuran at 0°C is more than 90 per cent dissociated in accordance with the equation:



As expected, addition of ammonia to this solution, after PF_3 has been removed, gives a quantitative yield of N_3NBH_3.



In the original study[1] trimethylamine was allowed to react with F_3PBH_3 without any solvent. The formation of PF_3 and $(CH_3)_3NBH_3$ was observed just as in the low

temperature reaction in ether. On the other hand when ammonia was allowed to react with F_3PBH_3 *without solvent*, variable amounts of hydrogen gas were evolved and undefined solid and liquid products were obtained. Neither $(H_2N)_3PBH_3$ nor H_3NBH_3 could be detected in the products.

The reactions of F_3PBH_3 *and* F_3PO

It has been noted on many occasions that the BH_3 group is isoelectronic with the oxygen atom and indeed certain early molecular orbital arguments of MULLIKEN[5] compared BH_3 and the oxygen atom, and B_2H_6 and the oxygen molecule. While detailed physical analogies (e.g. magnetic properties, spectra, molecular energy levels, etc.) were rendered inapplicable by fundamental geometric differences resulting from the lower symmetry of the BH_3 group, it is tempting to examine the chemistry of certain BH_3 adducts to see if useful chemical correlations can be found between BH_3 and 0. It is immediately apparent that if PF_3 is used as a reference base, BH_3 is a much weaker acid than is the 0 atom; however, certain formalistic analogies still exist. The ammonia reaction is typical since it has been shown in this study that the reaction of F_3PO and NH_3 is comparable to that of F_3PBH_3 and NH_3 and may be written as:

$$6H_3N + F_3PO \rightarrow 3NH_4F + (H_2N)_3PO$$

The $(H_2N)_3PO$ is an ether insoluble white solid which is identical to the product prepared by KLEMENT and KOCH[6] from the ammonolysis of $POCl_3$. In a formal sense the analogy between F_3PBH_3 and F_3PO may be drawn. It may be profitably extended to other systems such as H_3BCO[7] for low temperature processes where the weaker acid strength of BH_3 does not introduce alternative complicating reactions.

EXPERIMENTAL

1. *Materials*

F_3PBH_3. This compound was prepared and purified using the literature method.[5]

Ammonia. Commercial reagent grade ammonia was dried and stored over sodium before use.

Ether. Solvents of the best grade were dried and stored over $LiAlH_4$ before use. All reactions were conducted in the vacuum system unless otherwise specified.

2. *The synthesis and characterization of* $(H_2N)_3PBH_3$

An ethyl ether solution of F_3PBH_3 at −111°C was frozen with liquid nitrogen and an excess of ammonia was condensed into a 20 mm reaction tube attached to the vacuum line. See Table 1 for typical data on quantities used. The temperature was then allowed to rise slowly with stops as follows: 2 hr at −111°C, 2 hr at −78°C, 5–6 hours at −35°C, and 2–7 days at 25°C. The tube was then opened; the ether solvent was distilled away, and the solid mixture of $(H_2N)_3PBH_3$ and NH_4F was separated by leaching the $(H_2N)_3PBH_3$ from the mixture with ethyl ether and/or liquid ammonia. When the reaction was carried out in liquid ammonia instead of ethyl ether, and the solid $(H_2N)_3PBH_3$ was extracted from the residue with liquid ammonia, yields of recovered product were high (92 per cent) but it was slightly yellow in colour, indicating lower purity. Analytical data were obtained on a purified sample for product characterization. (Found: hydridic hydrogen, 3·21; N, 45·5; B, 12·1. Calc. for $(H_2N)_3PBH_3$: hydridic hydrogen, 3·25; N, 45·23, B, 11·65%). A molecular weight of 98 was found in liquid ammonia solution. Calculated for $(H_2N)_3PBH_3$ is 92. Characterization of the product was completed by the single crystal X-ray study of NORDMAN[4] which gave an unequivocal structure.

[5] R. S. MULLIKEN, *Chem. Rev.* **41**, 207 (1947); *J. Chem. Phys.* **3**, 635 (1935).
[6] R. KLEMENT and O. KOCH, *Ber. Dtsch. Chem. Ges.* **87**, 333 (1954).
[7] J. C. CARTER and R. W. PARRY, Paper No. 22 presented before the Division of Inorganic Chemistry at the 137th National Meeting of the American Chemical Society. Cleveland, Ohio, April (1960).

Even if the initial ratio of NH_3 to PF_3BH_3 was one or less, no evidence for PF_3 liberation was ever detected; instead NH_4F was formed and *unreacted* F_3PBH_3 was recovered from the system.

It was noted that the reaction between NH_3 (in excess) and F_3PBH_3 to form $(H_2N)_3PBH_3$ is not complete at low temperatures. When the system was not allowed to warm above −78°C, the ratios of unrecovered ammonia to F_3PBH_3 ranged from 3·9 to 4·4. This suggests a formation of intermediate compounds $(H_2N)_2PFBH_3$ and $H_2NPF_2BH_3$.

$$F_3PBH_3 + 2NH_3 \rightarrow NH_4F + \mathit{H_2NPF_2BH_3}$$

$$H_2NPF_2BH_3 + 2NH_3 \rightarrow NH_4F + \mathit{(H_2N)_2PFBH_3}$$

Indeed, when the NH_4F precipitate was filtered out from such a reaction mixture, a clear ether solution could be obtained. From this solution a white precipitate, (NH_4F), formed again slowly when warmed to a higher temperature. Even if the mixture was kept at −35°C for several hours, the product obtained after solvent removal was always contaminated with a viscous liquid which slowly decomposed to give a yellowish appearance, and the yield of purified $(H_2N)_3PBH_3$ was only 20–30 per cent on the basis of F_3PBH_3 used.

TABLE 1.—TYPICAL DATA FOR SYNTHESIS OF $(H_2N)_3PBH_3$

Reactants added			Materials recovered				
F_3PBH_3 (mmole)	NH_3 (mmole)	Ether (solvent) (ml)	NH_3 (mmole)	NH_4F (mmole)	H_2 (mmole)	$(H_2N)_3PBH_3$ (mmole)	Yield (%) $(H_2N)_3PBH_3$
1·05	6·040	5	*	*	0·024	0·837	82·4
2·70	25·99	10	10·88	6·72	0·077	2·020	75·0
1·70	0·5 ml liq.	0	*	3·78	0·018	1·570	92·0

* Not determined.

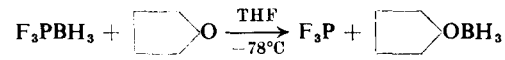
3. *The reaction between* H_3NBH_3, PF_3 *and* NH_3

In order to test a mechanism involving initial displacement of PF_3 by NH_3, followed by displacement of the NH_3 by newly formed $P(NH_2)_3$, the following reaction was carried out. One of two similar runs is described. A sample of H_3NBH_3 (0·709 mmole) was weighed into a reaction tube (volume = 50 cm^3) equipped with a break-off tip. A 10 ml sample of diethyl ether was added then a quantity of PF_3 (0·782 mmole) was condensed into the system. When the reactor was allowed to warm up to −78°C, no external signs of reaction could be detected. After the system was again frozen with liquid nitrogen, an excess of ammonia was condensed into the reaction vessel and the tube was sealed. The temperature was raised stepwise as follows: −111°C for 1 hr, −78°C for ½ hour, 25°C for one week. When the tube was opened to the vacuum system, no H_2 was found; a mixture consisting of a solid precipitate of NH_4F (X-ray) and an unidentified compound of phosphorus was filtered off. [Ratio NH_3/F_3P consumed in one reaction was about 3·4 instead of the expected six for simple ammonolysis.] Ninety six per cent of the original H_3NBH_3 was recovered unchanged from the filtrate. It was identified as H_3NBH_3 on the basis of its X-ray powder pattern and by measurement of the H_2 produced on acid hydrolysis (1·285 mM H_2 from 13·4 mg sample; theory for H_3NBH_3 is 1·30 mM H_2).

4. *The system* F_3PBH_3–*tetrahydrofuran–ammonia*

a. *Low temperature* (−78°C). A sample of F_3PBH_3 amounting to 1·21 mmole was condensed into a reaction tube; then about 5 ml of tetrahydrofuran (THF) was condensed in by cooling with liquid nitrogen. The system was allowed to warm slowly to −95°C and was maintained at that temperature for 1 hr. Pressure of the system was about 2 mm of Hg. The temperature was raised to −78°C and maintained for ½ hr. The pressure remained constant at 6 mm Hg while the temperature was held at −78°C. The volatile components were distilled out at −78°C and fractionated. A 1·01 mmole sample of undissociated F_3PBH_3, a PF_3 sample amounting to 0·180 mmole, and a trace

of a hydride (probably B_2H_6) which yielded 0·0545 millimole of H_2 on hydrolysis were obtained. The foregoing data indicate that the reaction



is no more than 15 per cent complete at −78°C under the conditions used. Such conditions are an order of magnitude more severe than those used in the diethyl ether study −(T = −111°C).

b. *High temperature* (0°C). A sample of F_3PBH_3 amounting to 1·01 mmole was condensed with about 5 ml of tetrahydrofuran; then the system was warmed to 0°C. To increase contact between vapour and liquid phases, the liquid was constantly agitated with a magnetically activated hopper type stirrer and the reactor was occasionally cooled with liquid nitrogen to condense the vapour into the liquid. After reaction for about 5 hr, the system was cooled to −78°C and volatile components were removed and fractionated. The first fraction consisted of 0·953 mmole of gas with a molecular weight of 88·4; the molecular weight for F_3P is 88·0. The second fraction amounted to 0·047 mmole of F_3PBH_3. A 3·49 mmole sample of NH_3 was introduced into the residual solution which had been held at −78°C. The solution was aged for 10 hr and filtered; then the solvent was distilled off. A sample of crude H_3NBH_3 weighing 31·7 mg (theoretical weight NH_3BH_3 based on F_3PBH_3 consumed is 29·8 mg) was recovered. The yield of purified product would be essentially quantitative. Apparently some ether still remained on the sample when it was weighed.

5. *The reaction of* F_3PO *and* NH_3

F_3PO was prepared by fluorinating $POCl_3$ with commercial ZnF_2. The vapour-pressure of the F_3PO was determined; results are comparable to the literature values of TARBUTTON *et al.*[8]

A sample of F_3PO (1·546 mMole) and an 18·51 mmole sample of NH_3 were sealed in a tube with 10 ml of ethyl ether. A white solid formed quite rapidly, even at −111°C. After 3 days of standing at room temperature, the tube was opened and solid materials were filtered off. No solids could be recovered by evaporating the solvent from the filtrate.

The solid on the filtering disk was leached with liquid ammonia. NH_4F remained on the disk and $(H_2N)_3PO$ was obtained from the filtrate by evaporating the solvent ammonia. The yield was 79 per cent based on the F_3PO used. The $(H_2N)_3PO$ was identical to an authentic sample prepared from $POCl_3$ by the method of KLEMENT and KOCH.[6]

[8] G. TARBUTTON, E. P. EGAN, JR. and S. G. FRARY, *J. Amer. Chem. Soc.* **63**, 1872 (1941).