336. *The Interaction of Phosphorus Pentachloride with Tertiary Amines.*

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Contrary to previous work it has been shown that phosphorus pentachloride and pyridine react to form a 1 : 1 addition compound. The reaction of phosphorus pentachloride with trimethylamine has been re-examined and shown to result in the formation of triethylammonium chloride, previously formulated as an addition compound of chlorine and the amine.

THE donor properties of phosphorus pentachloride with Lewis acids, such as tin tetrachloride and aluminium trichloride, are well established.[1] Conversely, the hexachlorophosphate anion must be regarded as the only established example of the phosphorus pentachloride molecule's acting as an acceptor. This ion is present in solid phosphorus pentachloride,[2] and Gutmann and Mairinger[3] report the formation of crystalline tetraethylammonium hexachlorophosphate. The mechanisms suggested for some reactions of

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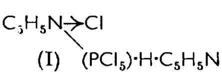
[1] See, *e.g.*, Abegg's " Handbuch der Anorganischen Chemie," Leipzig, 1907, III, **3**, 415; Groenveld, *Rec. Trav. chim.*, 1952, **71**, 594; Groenveld and Zuur, *ibid.*, 1953, **72**, 617.

[2] Clark and Powell and (independently) A. F. Wells, *J.*, 1942, 642.

[3] Gutmann and Mairinger, *Z. anorg. Chem.*, 1957, **289**, 279.

phosphorus pentachloride[4] formally involve the tetrachlorophosphorus(V) cation as an acceptor group. However, these species have not been isolated as true intermediates. In view of the stability of compounds such as the 2 : 1 addition compound of pyridine with silicon tetrachloride[5] and the 1 : 1 addition compound of pyridine with phosphorus pentafluoride,[6] we reinvestigated the reaction between phosphorus pentachloride and pyridine.

Work by Sell and Dootson[7] indicates that phosphorus pentachloride dissolved in phosphorus oxychloride does not react with pyridine, although it appears that their method of study would not have shown the presence of addition compounds. More recently Hutton and Webb[8] reported that the gradual addition of phosphorus pentachloride to dry pyridine gave an initial precipitate of pyridinium chloride. On further addition of phosphorus pentachloride a very hygroscopic solid was formed which the authors formulated as (I) although they did not indicate the source of the hydrogen chloride. An obvious criticism of this work, in which the reagents were directly mixed, lies in the difficulty of studying a reaction between a solid and a liquid to give a solid product.



(I)

$C_5H_5N{\rightarrow}Cl$; $(PCl_5){\cdot}H{\cdot}C_5H_5N$

We find that phosphorus pentachloride and pyridine react to give a 1 : 1 addition compound. The approximate stoicheiometry has been found by adding successive amounts of pyridine to phosphorus pentachloride in a vacuum system, while measuring the vapour pressure in the system after each addition. The results are shown in Fig. 1. The scatter towards the pyridine-rich end of the system is presumably due to incomplete reaction. These results point to the formation of a 1 : 1 addition compound of reasonable stability. Verification of this ratio was obtained by titrating pyridine with a solution of phosphorus pentachloride in carbon disulphide, the end-point being indicated by lack of further precipitation on addition of pyridine. The ratio found in this way was PCl_5 : py = 1 : 0·97. The solid product was removed by centrifugation, and completely analysed after excess of pyridine and carbon disulphide had been pumped away. The addition product sublimed readily *in vacuo*, and was hydrolysed rapidly and completely to phosphate, chloride, and pyridine.

These results suggest that phosphorus pentachloride can act as an acceptor. This seems to be at variance with some conclusions on the interaction of trimethylamine and triethylamine with phosphorus pentachloride in a vacuum system. Holmes and Bertaut[9] report that phosphorus trichloride is the volatile product of this reaction, while they formulate the solid products as $(Me_3N)_2,Cl_2$ and Et_3N,Cl_2 in each case. Their reaction scheme could thus be written

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2 \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ (1)$$

$$Cl_2 + 2Me_3N \longrightarrow (Me_3N)_2,Cl_2 \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ (2)$$

and

$$Cl_2 + Et_3N \longrightarrow Et_3N,Cl_2 \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ (3)$$

This does not agree with our results. Further, Hantzsch and Graf[10] state that " dichlorides of the form R_3N,Cl_2 are as yet scarcely known " and add that the addition compound of trimethylamine and chlorine is exceedingly unstable. This has been confirmed by Böhme and Krause.[11] The compound $(Me_3N)_2,Cl_2$ is not reported in the literature except as a private communication from an unnamed investigator.[9] Examination of Holmes and Bertaut's results shows that the stoicheiometry required by equations (1), (2), and (3) is not exactly obeyed. The solid products of reaction might well by formulated as amine

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[4] Newman and Wood, *J. Amer. Chem. Soc.*, 1959, **81**, 4300.
[5] Hulme, Leigh, and Beattie, *J.*, 1960, 366, and references therein.
[6] Woolf, *J. Inorg. Nuclear Chem.*, 1956, **3**, 285.
[7] Sell and Dootson, *J.*, 1898, **73**, 432.
[8] Hutton and Webb, *J.*, 1931, 1518.
[9] Holmes and Bertaut, *J. Amer. Chem. Soc.*, 1958, **80**, 2980.
[10] Hantzsch and Graf, *Ber.*, 1905, **38**, 2154.
[11] Böhme and Krause, *Ber.*, 1951, **84**, 170.

hydrochlorides. We reinvestigated the interaction of triethylamine with phosphorus pentachloride, to determine whether the initial stage involved dehydrogenation of the amine.

On rapid addition of an excess of triethylamine to a solution of phosphorus pentachloride in carbon disulphide, a white precipitate, almost exclusively of triethylammonium chloride was formed immediately (mixed m. p. and infrared spectra). The interaction of phosphorus pentachloride with triethylamine thus results in dehydrogenation of the amine. A test for diethylvinylamine with 2,5-dichloro-3,6-dimethoxy-*p*-benzoquinone[12] was negative.

The reduction of active metal halides with trialkylamines has been observed with titanium tetrachloride[13] and vanadium tetrachloride.[14] Further, our results do not conflict with the available experimental results of Holmes and Bertaut.

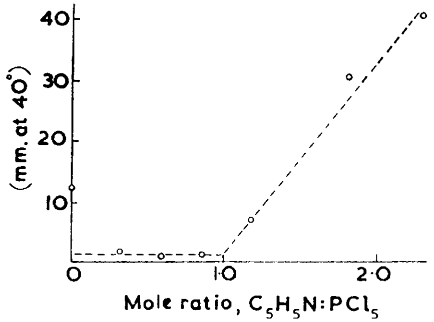

FIG. 1. *Vapour pressure–composition diagram for the addition of pyridine to phosphorus pentachloride.*

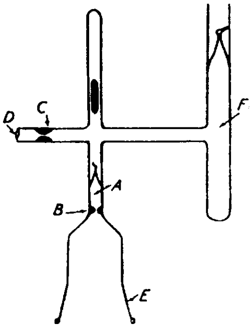

FIG. 2. *Apparatus used in the hydrolysis of the* 1 : 1 *addition compound of pyridine and phosphorus pentachloride.*

Experimental.—All work was carried out either in a vacuum system (complete absence of grease) or in a dry-box under nitrogen.

Reagents. Triethylamine. We were not able to remove the primary and secondary amines by the method suggested by Holmes and Bertaut.[9] Primary and secondary amines were removed by using benzenesulphonyl chloride followed by fractional distillation. The primary and secondary amines then totalled less than 0·05% of the product. The triethylamine was dried (CaH_2) and distilled *in vacuo* into ampoules which were then sealed. Carbon disulphide. This was dried over calcium hydride and distilled. Phosphorus pentachloride. This was sublimed *in vacuo* into ampoules which were then sealed.

Analysis of the complex. The 1 : 1 compound of phosphorus pentachloride and pyridine reacted violently with water so that hydrolysis was carried out in a sealed system (Fig. 2). The sample was introduced into *A* in a dry-box and the vessel was then stoppered. The apparatus was taken from the dry-box, the stopper removed, and the sample pumped out by rapidly connecting *E* to a ground-joint on the vacuum system. Water was introduced into *F*, and the apparatus joined to the vacuum system at *D*. After outgassing of the water, constriction *C* was sealed, and similarly after outgassing of the solid, constriction *B* was sealed. The thin glass septum separating *A* and *F* was broken to allow the sample to hydrolyse by carefully tipping it from *A* into the water in *F*. After hydrolysis the solution was transferred to a standard flask and made up to be about 0·2N with respect to nitric acid. Chloride was determined gravimetrically as silver chloride, phosphorus by precipitation as phosphomolybdate with ignition to $P_2O_5,24MoO_3$, and pyridine spectrometrically (Unicam S.P. 500; 255 mμ) as the pyridinium ion after removal of interfering anions by means of an ion-exchange resin

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[12] Buckley, Dunstan, and Henbest, *J.*, 1957, 4901.

[13] Antler and Laubengayer, *J. Amer. Chem. Soc.*, 1955, **77**, 5250.

[14] Fowles and Pleass, *J.*, 1957, 1674.

in the chloride form. The spectrometer was previously calibrated by using known pyridine solutions containing chloride.

Results. Found: Cl, $61{\cdot}5_1$, $61{\cdot}6_7$; C_5H_5N, $27{\cdot}7_4$; P, $10{\cdot}8_1$, $10{\cdot}7_7$. Calc. for PCl_5,C_5H_5N: Cl, 61·7; C_5H_5N, 27·5; P, 10·8%.

Reaction of triethylamine with phosphorus pentachloride (quantities are approximate). Phosphorus pentachloride (10 mmoles) was dissolved in carbon disulphide (70 c.c.), and triethylamine (20 mmoles) was rapidly added dropwise; 7 mmoles of apparently pure triethylamine hydrochloride were precipitated during the addition of the amine. M. p.s (sealed tubes, uncorr.); triethylamine hydrochloride 253—254°; product 248—250°; mixed m. p. 251—252°.

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