

The use of this average implies rapid transitions between vibrational states. The lines are about 10^6 sec.^{-1} broad and the experiments show that the excursion in frequency is at least $5 \times 10^6 \text{ sec.}^{-1}$ per second. The frequency of exchange as esti-

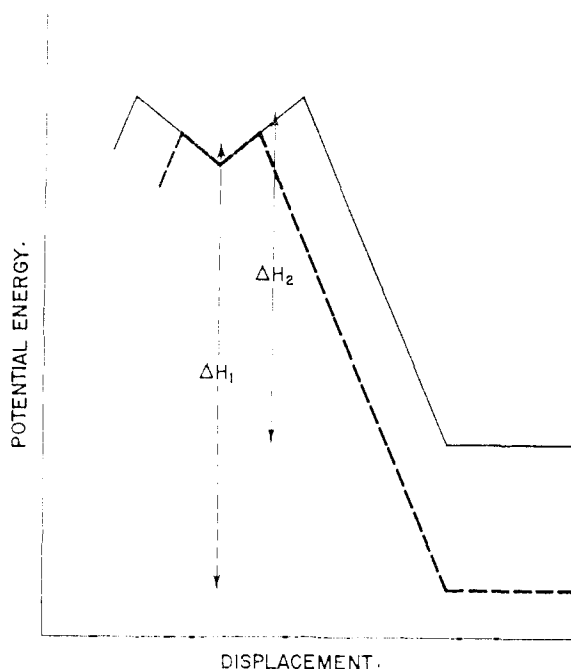


Fig. 5.—Idealized potential energy curve for displacement of sodium ion parallel to ring.

mated from the well-known formulas for exchange narrowing must be of the order 10^9 sec.^{-1} . The function $F(r_{\text{Na}})$ which gives the spin density for fixed positions of the sodium nucleus vanishes when r_{Na} lies in the plane P perpendicular to the naphthalene rings and passing through the 9 and 10 posi-

tions because of the antisymmetry of π_{m+1} relative to reflection in P . For positions of the sodium 2.5 Å. directly above the center of either of the rings numerical estimates suggest that the non-orthogonality mechanism alone provides spin density of the correct order of magnitude. Calculation of the dependence of coupling on temperature and properties of the solvent seems prohibitively difficult, but the highly idealized scheme shown in Fig. 5 seems to represent the qualitative features of the situation. The upper potential minimum corresponds to the equilibrium position of the sodium ion relative to the naphthalene in the ion pair. The displacement is parallel to the aromatic ring. The lower flat part corresponds to dissociation. For solvents in which ΔH of dissociation is large only a small range of excursion of sodium is permitted, while for those for which ΔH is small, large excursions are permitted. The diagram is thus in qualitative accord both with variations of coupling constants, with temperature, and with heat of dissociation.

The limiting value of the sodium coupling constant at low temperature in THF is very small and suggests that the equilibrium position of the sodium ion lies in the nodal plane P of the singly occupied orbital. In the other solvents it has not been possible to extend the measurements to low enough temperatures to obtain reliable limiting values of the coupling constant. The observed variations of coupling constant with temperature in the solvents other than THF is compatible either with a flat potential minimum or one displaced from the nodal plane.

The observations reported here reveal some of the potentialities of e.s.r. spectroscopy for direct demonstration of equilibria in solution. It is hoped that further work will lead to more detailed structural and kinetic information.

Acknowledgment.—Dr. R. E. Robertson carried out the computations of the sodium coupling constants. He will report his results in detail in a later publication.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY, SCHENLEY PARK, PITTSBURGH, PENNSYLVANIA]

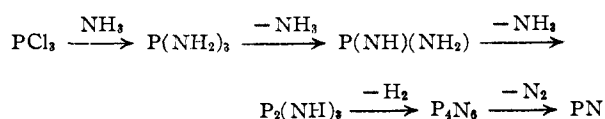
Phosphorus Nitrogen Chemistry. III. The Preparation and Properties of Phosphorus Tri-N-methylimide^{1,2}

BY ROBERT R. HOLMES

RECEIVED SEPTEMBER 6, 1960

The preparation of phosphorus tri-N-methylimide, $\text{P}_4\text{N}_6(\text{CH}_3)_6$, in high yield from the low temperature reaction of phosphorus trichloride and excess methylamine in the absence of solvent is reported, the product being the first member of a new class of phosphorus nitrogen compounds. Its reactions with methyl iodide, boron trichloride and oxygen are discussed. Physical properties indicate a cage structure analogous to phosphorus trioxide and is supported by chemical behavior. Its relation to other phosphorus nitrogen compounds is indicated.

Moureu and Wetroff³ summarized the reaction of phosphorus trichloride and ammonia by the set of equations



(1) Previous paper in the series: R. R. Holmes, *THIS JOURNAL*, **82**, 5285 (1960).

(2) Presented before the Inorganic Division at the 138th Meeting of the American Chemical Society, New York, N. Y., September, 1960; communication to the editor: **82**, 5509 (1960).

(3) H. Moureu and G. Wetroff, *Bull. soc. chim. (France)*, **4**, 918 (1937).

Some of the products are thought to be polymeric but little structural information is available and, in fact, doubt has been cast on some of the empirical formulations.⁴

If primary amines are used in place of ammonia, analogous compounds might be expected which one may work with more easily than ammonia.⁵ With primary aromatic amines a few compounds of the so-called "phosphorazo" class, P(NR)(NHR), have been characterized exhibiting dimeric behavior⁶ as well as one monomeric, crystalline substance,⁷ *p*-methoxyphenylamino-*N*-bis-(*p*-methoxyphenyliminophosphine), (CH₃OC₆H₄N)₂P₂. The "phosphorazo" compounds are analogous in formulations to the imide-amide of the ammonia series and the latter substance, (CH₃OC₆H₄N)₂P₂, is analogous to the imide, P₂(NH)₂. With primary aliphatic amines and phosphorus trihalides, the literature shows no successful characterizations of chlorine-free phosphorus nitrogen compounds.

This paper concerns the detailed study of the reaction of phosphorus trichloride with methylamine.

Experimental and Results

Apparatus.—High vacuum systems were used for part of the study. Transfer operations and weighings were carried out with the aid of a dry box.

Materials.—Reagents involved in vacuum line procedures were purified as follows: boron trichloride (Matheson) was purified over mercury and fractionated in the line, vapor pressure at 0°, 476 mm. Methyl iodide was distilled and fractionated in the line, vapor pressure at 0°, 140.5 mm. Tank oxygen was used after slow passage through a four-foot drying tube containing Drierite, potassium hydroxide and phosphorus pentoxide.

Reagents used outside the line were purified as follows: phosphorus trichloride (Baker and Adamson) was used directly. Tank methylamine (Matheson, anhydrous) was dried with barium oxide. Benzene (Fisher certified, thiophene-free) was dried over calcium hydride. Petroleum ether (range, 30–60°, Hommel and Co.) was distilled and dried over sodium ribbon.

The Phosphorus Trichloride-Methylamine Reaction.—Preliminary investigation on the slowness of the phosphorus trichloride-methylamine reaction after the initial vigor led to the use of a deep-well, all-glass Ace reaction kettle fitted with a dropping funnel for the trichloride (17.5 ml., 0.200 mole), a tube inlet for the amine (64.6 ml., 1.60 moles), a manually operated stirrer (stainless-steel rod, 1/4 inch diam. to break up the caked mass formed) and a nitrogen entrance for maintaining a positive pressure. The kettle assembly fitted into a gallon Dewar containing the coolant bath of carbon tetrachloride-chloroform with excess Dry Ice.

After condensation of the amine in the kettle the trichloride was added dropwise. The resulting yellowish solid and clear liquid was allowed to warm up slowly over a four-day period to room temperature and then heating to 50° to drive off excess amine.

The white solid mixture remaining was separated in a nitrogen atmosphere with petroleum ether using an all-glass filtration apparatus in conjunction with the dry box. The filtered solid was identified as pure methylamine hydrochloride by the m.p. 225–226°, same infrared spectrum of a Nujol mull as a known sample, and elemental analysis.

Anal. Calcd.: C, 17.79; H, 8.96; N, 20.74. Found: C, 18.20; H, 8.82; N, 20.52.

(4) J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1958, pp. 324–326.

(5) The close solubility of some of the products of the ammonia reaction and ammonium halide by-products creates separation problems not easily overcome.

(6) W. H. Grimm, A. Guenther and J. F. Morgan, *THIS JOURNAL*, **68**, 539 (1946).

(7) S. Goldschmidt and H. L. Krauss, *Ann.*, **595**, 193 (1955).

The product obtained by pumping off the petroleum ether was a crystalline white solid. Elemental analyses of sublimed and unsublimed samples were similar showing an empirical formulation P₂N₃(CH₃)₃.

Anal. Calcd.: C, 24.17; H, 6.08; N, 28.19; P, 41.56. Found (unsublimed): C, 23.92; H, 6.03; N, 28.19; P, 41.32.

Thus, the stoichiometry in excess amine corresponds to 2PCl₃ + 9CH₃NH₂ = P₂N₃(CH₃)₃ + 6CH₃NH₃⁺Cl⁻.

Properties of Phosphorus Tri-N-methylimide.—**General.**—The product, P₂N₃(CH₃)₃, m.p. 122.0–122.8°, b.p. (nitrogen atmosphere) 303–304° at 737 mm., was found to be soluble in benzene, toluene, *n*-hexane, ethyl ether, ethanol (with reaction), acetone and carbon tetrachloride. It is initially insoluble in water but dissolves slowly in a few days.

Infrared measurements in Nujol mulls and in benzene solution were nearly identical showing strong absorptions with rather sharp bands at 2860, 2790, 1440 and 1155 cm.⁻¹.

Molecular Weight.—Cryoscopic measurements on sublimed and unsublimed samples in benzene gave similar molecular weight results. Calcd.: 149.08. Found: 296 ± 15 indicating a molecular formulation, P₄N₆(CH₃)₆.

The electrical conductance of the benzene solution was negligible, showing that the cryoscopic measurements were not complicated by the presence of any significant amount of ionization.

The molecular formulation obtained cryoscopically is supported by vapor determinations (315 ± 8) using a dissociation tensiometer.⁸

Vapor Pressure Measurements.—The equation log *p* (mm.) = -3191/*T* + 8.476, governs the solid-vapor equilibrium from 72 to 121° from which the heat of sublimation, Δ*H*_s = 14.6 kcal./mole, is obtained. Treatment of the liquid-vapor data from 128 to 221° gives, log *p*(mm.) = -3146/*T* + 8.346, and the resulting values: heat of vaporization, Δ*H*_v = 14.4 kcal./mole; b.p. 302.5°; Trouton's constant, 25.0.

A heat of fusion of 0.2 kcal./mole is inferred. However, the heat of sublimation was obtained from the narrow range of pressure values (0.5 to 2.5 mm.) and subject to considerable uncertainty.

No time-pressure dependence was detected at the highest temperature of the vapor measurements.

N.m.r. Measurements.—Proton measurements at 60 Mcps. on benzene solutions of the compound showed one peak, having a one-two-one spin-spin splitting pattern. The latter data indicate equivalent protons each split by two equivalent phosphorus atoms. The chemical shift relative to water, +2.52 p.p.m., is characteristic of a N-CH₃ grouping.⁹ In addition the *J*_{P-H} coupling constant, 16.7 ± 0.6 c.p.s., is in the range characteristic of the P-N-C-H linkage.¹⁰

P³¹ measurements at 15.1 Mcps. on a benzene solution showed only one peak substantiating equivalent phosphorus atoms for the compound. The shift was +141 ppm. relative to P³¹ in pure PCl₃ determined by the substitution technique. Comparison of the line width relative to P³¹ in [N(CH₃)₂]₃P indicated 10 ± 2 protons were contributing to the broadening.

Reactions of Phosphorus Tri-N-methylimide. Reaction With Methyl Iodide.—Sublimed P₂N₃(CH₃)₃ was almost immediately soluble when mixed with excess methyl iodide at 0° in the line. Shortly afterwards a white solid precipitated out. Recovery of the unreacted methyl iodide after overnight stirring showed a 1:1 reaction took place corresponding to the formation of P₄N₆(CH₃)₆I. The product was soluble in water.

Reaction with Boron Trichloride.—The reaction of boron trichloride with P₂N₃(CH₃)₃ was studied in a bulb having a break tip, a side arm for introduction of the boron trichloride, a lower 8 mm. side arm appendage for collecting the product and appropriate seal off areas.

The sample (1.98 g., 6.64 mmoles) was dropped into the bulb and after evacuation sublimed onto the walls. Boron trichloride was condensed in (37.0 mmoles), the bulb sealed off from the line and the lower portion placed in an ice bath.

(8) R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

(9) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 272.

(10) Ref. 9, p. 351.

The bulb then was flamed just enough to melt the crystals coating the walls. As reaction proceeded more boron trichloride would volatilize from the 0° bath.

To complete the reaction the bulb was put in an oven for 20 min. at 147°. The clear liquid which first forms becomes yellowish and some white solid appears.

Analysis of the contents of the bulb resulted in the isolation of a small amount of phosphorus trichloride (1.5 mmoles), established by its vapor pressure and elemental analysis.

Anal. Calcd.: P, 22.56; Cl, 77.44. Found: P, 22.58; Cl, 77.70. The amount of boron trichloride recovered (8.0 mmoles) shows an over-all reaction mole ratio of boron trichloride to $P_4N_6(CH_3)_6$ of 4.4:1.

The main product formed, the clear liquid, reacts violently with water. It was further purified by distillation in vacuum. Elemental analysis yielded the composition $P_2N_3(CH_3)_3B_2Cl_3$.

Anal. Calcd.: C, 7.93; H, 2.00; N, 9.25; P, 13.64; B, 4.76; Cl, 62.43. Found: C, 7.75; H, 1.88; N, 9.11; P, 13.80; B, 4.70; Cl, 62.59.

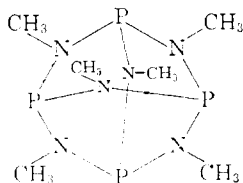
Based on the latter composition, a yield of about 60% (3.6 g., 8.0 mmole) was obtained. The weight relations involved indicated that the white solid formed should be a phosphorus nitrogen compound with a boron to chlorine ratio of approximately 2:3. However, no sample was separated in sufficient quantity for analysis.

Reaction With Oxygen.—No reaction of $P_4N_6(CH_3)_6$ (0.0930 g., 0.312 mmole) with oxygen (1.483 mmoles) took place at room temperature in a glass ampoule. However, on heating at 170°, a whitish solid formed within twenty minutes and the presence of some liquid was noted. Continued heating produced no significant change in the appearance of the products. On cooling, the liquid set to a glassy looking material. The recovered oxygen (0.824 mmole) did not contain any condensable materials and the reaction corresponded to 2.11 moles of oxygen per mole of $P_4N_6(CH_3)_6$. A nitrogen analysis on the whitish solid agreed with the formula $P_2N_3(CH_3)_3O_2$.

Anal. Calcd.: N, 23.21. Found: N, 23.03.

Discussion

The experimental results strongly indicate a cage structure analogous to that of phosphorus trioxide, P_4O_6 , containing a tetrahedral distribution of phosphorus atoms with oxygens strung along the edges, here, replaced by six N-CH₃ groups. The latter



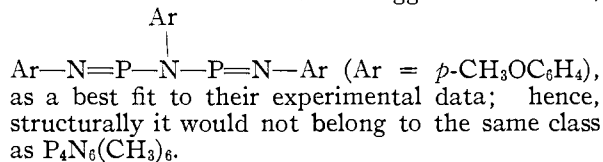
structure is made even more attractive when it is realized that the N-CH₃ group is isoelectronic with the oxygen atom.

The combination of elemental analyses, the molecular formula, $P_4N_6(CH_3)_6$, and the n.m.r. results form the main basis for the structural interpretation.¹¹

Chemical data are in agreement with the structural interpretation in that reactions might be expected to proceed toward a phosphorus pentoxide structure, P_4O_{10} , by coordinating the phosphorus atoms with electron acceptor groups since each phosphorus has an unshared pair in the trioxide structure. Reactions readily occurred with boron trichloride just above the melting point of the solid, with oxygen on heating at 170° and with methyl iodide at room temperature. However the nature of the products obtained from the boron trichloride reaction and the oxygen reaction are not completely understood and are at present being investigated more thoroughly.

Aside from the structure, the isolation of the substance $P_4N_6(CH_3)_6$ represents the first such characterization of a product from the reaction of a primary aliphatic amine and phosphorus trichloride and opens the way to other such substances. The analogous formulation, $P_2(NH)_3$, may possess a similar structure.

In the aromatic series, the compound of Goldschmidt and Krauss,⁷ $P_2(CH_3OC_6H_4N)_3$, is monomeric in benzene and has the suggested structure,



Acknowledgment.—This work was supported in part by the Office of Ordnance Research, U. S. Army, and this aid is gratefully acknowledged. The author also wishes to thank Dr. B. L. Brandau and Mr. J. A. Forstner in conducting the preparation of the phosphorus compound.

(11) It is noted that the low heat of fusion indicated here for $P_4N_6(CH_3)_6$, 0.2 kcal./mole, is comparable to that of α -white phosphorus (P, tetrahedral structure), 0.601 kcal./mole: see M. C. Sneed and R. C. Brasted, "Comprehensive Inorganic Chemistry," Vol. 5, D. Van Nostrand Co., Inc., Princeton, New Jersey, 1956, p. 107.