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The Descriptive Chemistry of Phosphorus Trioxide

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The chemistry of phosphorus trioxide is characterized by extremes. Thus CCl_4, $CHCl_3$, CH_2Cl_2, C_6H_6, $(C_2H_5)_2O$, $(CH_3)_2S$, dioxane, and $(CH_3)_4Si$ are nonreactive solvents at room temperature; whereas, liquid P_4O_6 added to $(CH_3)_2NCHO$, $(CH_3)_2SO$, $(CH_3O)_2SO$, CH_3OH, or AsF_3 reacts almost explosively to give a wide range of products including carbon char. Liquid P_4O_6 can be allowed to react smoothly but rapidly at room temperature with $P(OCH_3)_3$, $P[N(CH_3)_2]_3$, and $(CH_3CO)_2O$ and at elevated temperatures with PCl_3 and CH_3SiCl_3. These reactions involve a combination of scrambling, simultaneous oxidation–reduction and, in some cases under certain conditions, rearrangements similar to the Michaelis–Arbuzov one. The formation of amorphous white-to-orange network polymers is often found in the chemistry of P_4O_6. The white and light yellow ones appear to be polymeric phosphorus trioxide having various amounts of structure-terminating groups. The reaction of P_4O_6 with water, phosphorous acid, or pyrophosphorous acid gives evidence for the formation of unstable polyphosphorous acids, $H_2(P_nH_nO_{2n+1})$ for $n > 2$, containing phosphite middle groups, $HPO(O_{1/2}-)_2$.

Although phosphorus trioxide (P_2O_3) has been known for 150 years,[2] very little of its chemistry,[2b,3] other than air oxidation[4] has been reported. This is understandable in view of the great difficulty until recently[5] in preparing reasonably pure phosphorus trioxide[4,6] and its tendency (see below) to react violently at room temperature and/or to give a range of products including difficulty characterizable amorphous solids. The work described in this paper was originally directed toward making various new families of compounds in which triply connected phosphorus atoms, $:P\lessdot$, are held together by P–O–P linkages. This objective was never reached quantitatively, and the study was expanded into an extensive investigation of the descriptive chemistry of phosphorus trioxide—a chemistry summarized herein.

Experimental Section

Dimeric phosphorus trioxide, P_4O_6, was obtained several years ago from G. Mikulaschek of the University of Munich. The samples were prepared according to the standard method[6] and were freed[4] from dissolved white phosphorus by four successive ultraviolet irradiations each followed by high-vacuum distillation. The phosphorus trioxide thus produced exhibited a sharp melting point of 22.6° (lit. 23.8°) and was stored in sealed ampoules in the dark before use. After 2 years of storage, several of the ampoules were noticed to exhibit a trace amount of flocculent yellow precipitate, presumably the same amorphous yellow material which is discussed below.

Most of the organic solvents employed in this study (CS_2, CCl_4, $CHCl_3$, CH_2Cl_2, C_6H_6, ether, dioxane, acetone, and pyridine) were Mallinckrodt analytical grade, dried over alumina, except for the pyridine, which was distilled from calcium hydride. The dimethylformamide, dimethyl sulfoxide, dimethyl sulfide, and dimethyl sulfite were redistilled Eastman products, and the tetramethylsilane was obtained from Anderson Chemical Division of Stauffer Chemical Co. The AsF_3, $AsCl_3$, PCl_3, CH_3SiCl_3, and acetic anhydride were all commercial products which were redistilled. The $P[N(CH_3)_2]_3$ was prepared according to the literature.[7]

The proton and phosphorus nuclear magnetic resonance (n.m.r.) measurements were carried out on Varian A-60 and HR-100 spectrometers, respectively. The hydrogen spectra were thus taken at 60.0 Mc. and the phosphorus at 40.5 Mc. The chemical shifts in the proton spectra are reported with respect to dissolved tetramethylsilane and, in the phosphorus spectra, to 85% H_3PO_4 contained in a capillary. However, much of the experimental P^{31} referencing was to the P_4O_6 in the mixtures. In all cases, positive shifts were measured upfield.

Many of the measurements reported here were carried out by mixing the reagents, often after dilution with the appropriate solvent, in n.m.r. tubes in a dry bag under nitrogen. The usual precautions to avoid inadvertent contamination with moisture and oxygen were observed whenever applicable. Viscosities were measured on a Haake Rotovisco[8] with cone-plate attachment.

Results and Interpretation

Solvents for Phosphorus Trioxide.—The bird-cage structure,[4] P_4O_6, was found to be soluble to at least equal parts by volume in carbon disulfide, carbon tetrachloride, chloroform, methylene chloride, benzene, ether, dimethyl sulfide, dioxane, and tetramethylsilane. In all of these cases, there was no reaction even after several days at room temperature, as evidenced by the single, sharp P^{31} n.m.r. peak at *ca.* −113 p.p.m. (small solvent shifts)—the same resonance which is seen for liquid (molten) P_4O_6. On the other hand, a violent reaction is observed when P_4O_6 is added as a liquid to methanol, dimethylformamide, dimethyl sulfoxide, or dimethyl sulfite. In these cases, a yellow solid, some carbon char, and gaseous products are produced; and, under some conditions, the reactions are sufficiently violent to cause spontaneous flaming.

Dissolution is also readily effected in dry acetone but a white precipitate is seen to form immediately. When

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[2] (a) P. L. Dulong, *Mem. d'Arcueil*, **3**, 405 (1817); also see P. Hautefeuille and A. Perrey, *Compt. rend.*, **99**, 33 (1884). (b) T. E. Thorpe and A. E. H. Tutton, *J. Chem. Soc.*, **49**, 833 (1886); **57**, 545 (1890); **59**, 1023 (1891).

[3] L. Wolf, W. Jung, and M. Tschudnowsky, *Ber.*, **65B**, 488 (1932); E. Thilo, D. Heintz, and K. H. Jost, *Angew. Chem.*, **76**, 229 (1964). Also see J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, 1937, Vol. VIII, p. 899, for references prior to 1900.

[4] J. R. Van Wazer, "Phosphorus and Its Compounds," Interscience Publishers, New York, N. Y., Vol. I, 1958, p. 283.

[5] D. Heintz and E. Thilo, Deutsche Democratische Republic Patent 26660 (1960).

[6] L. Wolf and H. Schmager, *Ber.*, **62B**, 771 (1929).

[7] A. B. Burg and P. J. Slota, *J. Am. Chem. Soc.*, **80**, 1107 (1958).

[8] J. R. Van Wazer, J. W. Lyons, K. Y. Kim, and R. E. Colwell, "Viscosity and Flow Measurement," Interscience Publishers, New York, N. Y., 1963, p. 103.

cooling is used to avoid a rise in temperature due to the heat of the reaction, this precipitate is seen to form as finely divided particles, which later convert to a colorless gel. The precipitate as originally formed is highly reactive to water and alcohols. When P_4O_6 is combined with ten volumes of pyridine under nitrogen, a precipitate is also formed as separate flocs, the color of which changes from creamy yellow for the initial precipitate to a brownish yellow after 10 hr. at room temperature. This precipitate appears to oxidize readily since it is seen to blacken rapidly when in contact with air. It is unreactive with water at room temperature. Dimethyl sulfide reacts slowly with P_4O_6. Several days after two volumes of CH_3SSCH_3 were combined with one of P_4O_6, a gel formed in which $P(SCH_3)_3$ was seen to be a major soluble constituent by P^{31} n.m.r. (δ −124.5 p.p.m., J = 10 c.p.s.).

Reactions with Water and Phosphorous Acid.—As previously noted by Wolf, *et al.*,[3] shaking together of one or more volumes of water with liquid P_4O_6 without temperature control gives a yellow precipitate and a complicated mixture of acids of phosphorus. However, if the temperature is kept below 50–60° and the sample is occasionally shaken, the reaction proceeds smoothly to give only orthophosphorous acid. The shaking is necessary to avoid formation of a plug of the yellow precipitate at the interface between the aqueous phase and the P_4O_6.

When the reaction with water is properly controlled by cooling and shaking, it is found that addition of lesser amounts of P_4O_6 than correspond to the composition $3H_2O \cdot P_2O_3$ gives only orthophosphorous acid. For the composition region between $3H_2O \cdot P_2O_3$ and $2H_2O \cdot P_2O_3$, the correct stoichiometric mixture of ortho- and pyrophosphorous acids is formed and again all of the P_4O_6 reacts with the water. In this region, especially when approaching the $2H_2O \cdot P_2O_3$ composition, the yellow precipitate is readily produced through local overheating. For larger amounts of P_4O_6 than correspond to the composition of pyrophosphorous acid, $2H_2O \cdot P_2O_3$, the yellow precipitate is very difficult to avoid and there is also initially some unreacted P_4O_6 which appears as an essentially pure, colorless, separate phase.

Highly viscous fluids are produced by careful mixing of either ortho- or pyrophosphorous acids with P_4O_6 or with the white precipitates formed between P_4O_6 and small amounts of acetic anhydride (see below). In every case, the P^{31} n.m.r. shows that the soluble reaction products build up exclusively in the acid phase, with the P_4O_6 phase remaining pure (by n.m.r.) and colorless. Thus, the P_4O_6 phase slowly becomes incorporated into the acid phase, which is never seen to exhibit the n.m.r. resonance of the P_4O_6 molecule.

The initial addition of P_4O_6 to orthophosphorous acid proceeds stoichiometrically according to eq. 1. This

$$8H_3PO_3 \text{ (ortho)} + P_4O_6 \longrightarrow 6H_4P_2O_5 \text{ (pyro)} \qquad (1)$$

is achieved smoothly by dissolving the reagents in equal volumes of dry dioxane before combining them.

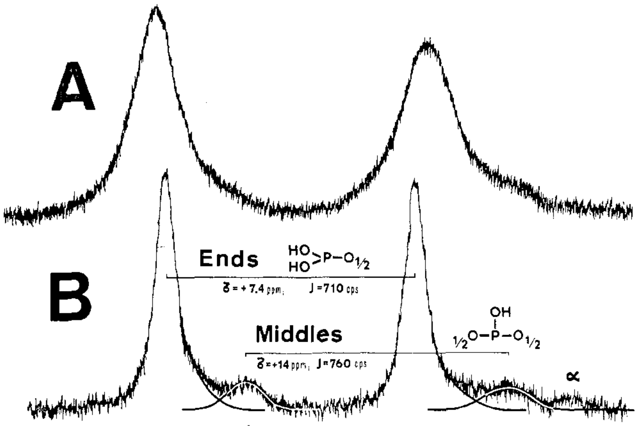
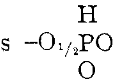


Figure 1.—P^{31} n.m.r. spectra of the condensed phosphorous acid exhibiting an over-all OH/P mole ratio of 1.85. The upper spectrum corresponds to the neat liquid and the bottom spectrum to a fresh solution in two volumes of dimethylformamide. The resonance labeled α in the lower spectrum at +27 p.p.m. increases slowly upon aging. The OH/P mole ratio calculated from the peak areas of the lower spectrum is 1.84.

With shaking, the reaction is complete within a few minutes and P^{31} n.m.r. shows only the presence of the ortho- and pyrophosphorous acids. Without shaking, phase separation occurs, with the dioxane distributing itself mainly with the P_4O_6.

More phosphorus than corresponds to the pyro- acid composition may be incorporated into the acid phase! This is done most readily either by the preceding dioxane-solution technique or by cautious but rapid stirring of the mixture of pyrophosphorous acid and P_4O_6 with a loose-fitting piston in a 5-mm. thin-walled n.m.r. tube, carefully avoiding local overheating which first results in yellow coloration followed by formation of a yellow precipitate. Essentially colorless samples containing more phosphorus than pyrophosphorous acid (H_2O/P_2O_3 = 2) have been obtained by this technique for H_2O/P_2O_3 mole ratios ≥ 1.85. Moreover, homogeneous liquids even more concentrated in phosphorus trioxide content can be made free of precipitate but showing a yellow coloration. The viscosities of the condensed phosphorous acids were found to be 1.06, 2.03, 12.75, 19.8, 37.0, 96.0, 490, and 2000 poises for over-all H_2O/P_2O_3 mole ratios of 5.95, 4.17, 2.54, 2.27, 2.06, 1.86, 1.6, and 1.5, respectively. It should be noted that the viscosity rises precipitously when the precipitate-free phosphorous acids become more condensed than the pyro-.

No resonance for orthophosphorous acid was seen in the n.m.r. spectrum of the colorless sample having a H_2O/P_2O_3 mole ratio of 1.85, and each peak of the P–H spin-coupling doublet corresponding to pyrophosphorous acid was broad and dissymmetric, indicating the presence of more than one compound. However, these coalesced resonances could not be resolved because of the high viscosity of the sample (see Figure 1A). Fresh dimethylformamide solutions of freshly prepared acids having more phosphorus than pyrophosphorous were found to be sufficiently stable to allow good n.m.r. measurements, and a typical spectrum is presented in

Figure 1B. The most reasonable explanation of this and related spectra is given by the assignments shown in the figure, where the middle group is  $-O_{1/2}\overset{H}{\underset{O}{P}}O_{1/2}-$. According to this interpretation, the P^{31} n.m.r. in dimethylformamide solution of the different building units involved in the structure of the phosphorous acids exhibited the following chemical shifts and coupling constants due to the P–H bond, with the coupling constants being in parentheses: neso (ortho) -3.2 p.p.m. (670 c.p.s.); ends, $+7.4$ p.p.m. (710 c.p.s.); and middles, $+14$ p.p.m. (760 c.p.s.).

This interpretation of the n.m.r. spectra in terms of polyphosphorous acids more condensed than the pyro- receives further support from the following evidence: (1) Addition of orthophosphorous acid (the neso compound) to a polyphosphorous acid causes the immediate disappearance of the middle groups with corresponding increase of the end group (as determined by P^{31} n.m.r.), indicating that reorganization equilibrium is reached rapidly. (2) Hydrolysis of freshly prepared polyacids gives only orthophosphorous acid, thus showing that the same oxidation state is maintained and that the molecule is held together by P–O–P linkages. (The hydrolysis reaction is very rapid, being too fast to be measurable by an automatic pH-Stat with which an entire titration may be completed in as short a time as 20 sec.)

Polyphosphorous Acids.—Upon aging at room temperature, the polyphosphorous acids more condensed than the pyro- become increasingly yellow and then a yellow precipitate forms. The time for initial occurrence of this precipitate (although difficult to reproduce precisely) becomes shorter and its subsequent rate of formation more rapid with an increasing amount of middle groups and with higher temperatures. Indeed at sufficiently high temperatures (>100°), the pyrophosphorous acid itself appears to decompose similarly. The n.m.r. spectra of aged dimethylformamide solutions or of fresh solutions of polyphosphorous acids (more condensed than the pyro-) which had been aged as neat liquids showed several P^{31} n.m.r. resonances (the major ones at $+5$ and $+27$ p.p.m.) not seen with the fresh preparations. Hydrolysis of these aged preparations gave, in addition to orthophosphorous acid, the usual yellow precipitate plus various amounts of orthophosphoric acid, indicating that oxidation–reduction processes occur during aging.

From the studies reported here on the polyphosphorous acids more condensed than the pyro- acid, we conclude that a metastable equilibrium is reached, involving a change of functionality between the various building units. The equilibria between the various phosphorous acids are thought to be described by the following set of constants.

$$K_0 = [\mathrm{H_2O}]\,[\text{pyro- acid}]/[\text{ortho- acid}]^2 \qquad (2)$$

$$K_1 = [\text{ortho- acid}]\,[\text{acid middle groups}]/[\text{acid end groups}]^2 \qquad (3)$$

For the system of phosphorous acids, H_2O–P_2O_3, K_0 and K_1 both appear to be smaller than 10^{-4}; whereas, for the phosphoric acid system,[9] H_2O–P_2O_5, $K_w = 2 \times 10^{-2}$ and $K_1 = 8 \times 10^{-2}$. Although there is no direct experimental evidence for an equilibrium of the form of eq. 2, we believe that the absence of detectable pyro- in the liquid ortho- acid must be due to a large negative enthalpy for the hydrolysis of pyrophosphorous acid rather than to lack of an appropriate reaction mechanism, as demonstrated by the rapid hydrolysis of the pyro-[10] and more condensed anions. On the other hand, the equilibrium of eq. 3 has been demonstrated to be rapid by the addition of the ortho- acid to an acid more condensed than the pyro- (*vide supra*). The pronounced instability of the polyphosphorous acids more condensed than the pyro- with respect to precipitation of the yellow solid and autoxidation–reduction reactions explains why previous investigators[11] who have carefully attempted to prepare these polyphosphorous acids were unsuccessful.

Reactions of P_4O_6 with Acetic Anhydride.—Combining various proportions of acetic anhydride with liquid P_4O_6 at 25°, both being dissolved in equal volumes of chloroform, leads to reactions which may be observed by P^{31} n.m.r. When a small amount of acetic anhydride is combined with P_4O_6 in the range $15 < P_4O_6/(CH_3CO)_2O < 40$, there is no observable change in the P^{31} n.m.r. spectrum, but after a period of about 10 hr. to 2 days at room temperature, the mixture is seen to have converted into a white solid. Vacuum evaporation of the chloroform and any excess P_4O_6 or acetic anhydride leaves a white powder which is amorphous to X-rays and highly reactive with water. Chemical analysis for C, H, and P corresponds to the incorporation of one acetyl group per 5–10 phosphorus atoms, depending on the preparation. This precipitate appears to undergo about the same reactions as does P_4O_6, but we were unable to find a nonreactive solvent for it. However, a P^{31} n.m.r. spectrum run immediately (10–30 sec.) after dissolution in dimethylformamide shows a main sharp resonance in the P_4O_6 region—a resonance which rapidly disappears in favor of others appearing in the spectral region corresponding to quadruply connected phosphorus. When the white precipitate is added to a chloroform solution of orthophosphorous acid, the predominant product is pyrophosphorous acid. All of this is interpreted to mean that the amorphous white solid is an acetyl-terminated polymeric form of phosphorus trioxide, *i.e.*, it consists primarily of phosphite branch groups, $P(O_{1/2}-)_3$, with an insufficient amount of terminating acetyl groups to reduce the three-dimensional molecular structures to finite size.

When the $P_4O_6/(CH_3CO)_2O$ mole ratio is $<\sim 10$, no white precipitate is formed; but in several days, the P^{31} n.m.r. resonance of P_4O_6 is seen to decrease while some other resonances which are downfield to it increase,

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(9) See pp. 726 and 747–754 of ref. 4.

(10) D. Grant, private communication and Ph.D. Thesis, University of Glasgow, Scotland.

(11) F. Hossenlopp and J. P. Ebel, *Bull. soc. chim. France*, 2229 (1965); D. Grant, D. S. Payne, and S. Skledar, *J. Inorg. Nucl. Chem.*, **26**, 2103 (1964).

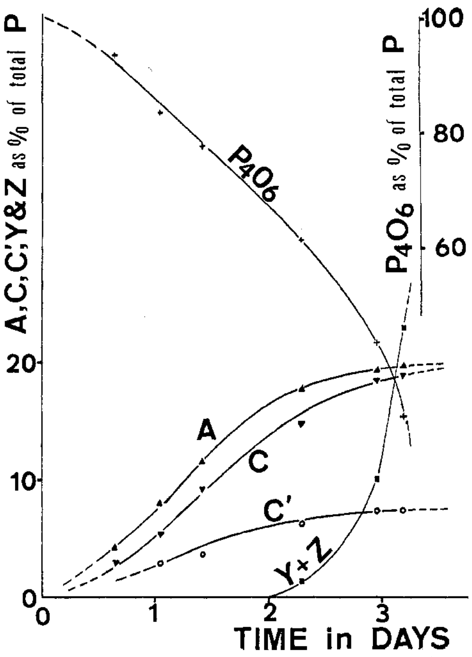

Figure 2.—Variation with time at 24° of the P^{31} n.m.r. resonances in an equimolar mixture of P_4O_6 with $(CH_3CO)_2O$. The resonances of this figure are those shown in the top spectrum of Figure 3.

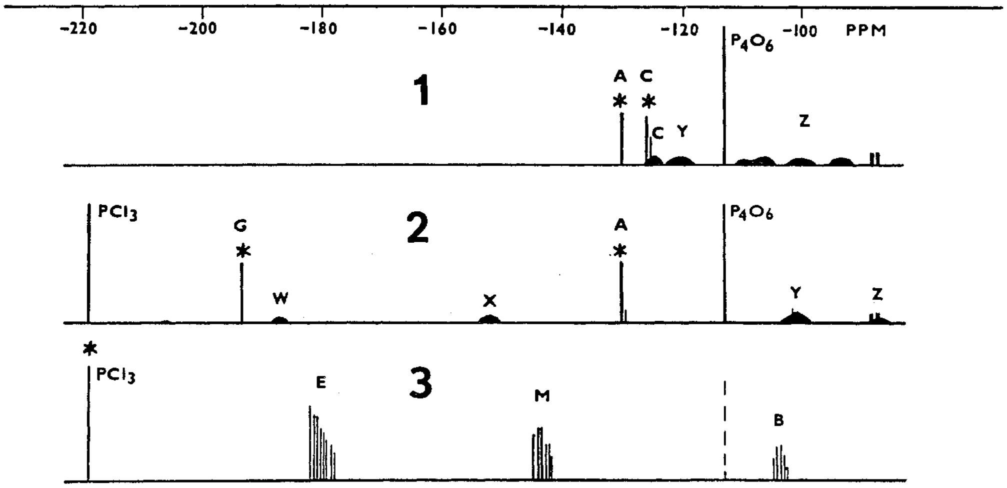

Figure 3.—P^{31} n.m.r. spectra of reaction products of phosphorus trioxide. The reagents used to obtain the various patterns shown are for spectrum 1, acetic anhydride; 2, phosphorus trichloride; and 3, methyltrichlorosilane. The asterisks denote the first resonances to appear in addition to those of the P_4O_6 and, in the case of spectrum 2, PCl_3.

as shown in Figure 2. The chemical shifts of these downfield resonances, labeled as A, C, and C′ in Figure 2, are shown in Figure 3. In about 4 days, a group of peaks upfield to P_4O_6 but still in the spectral region corresponding to triply-connected phosphorus (labeled Y and Z in Figure 3) are seen to appear and increase rapidly. Although there are small differences in the time scale from one run to another, rate curves such as the one shown in Figure 2 for this system may be readily reproduced. The H^1 n.m.r. spectra corresponding to the P^{31} data of Figure 3 give evidence of only the acetyl methyl group, appearing in the form of several highly overlapping peaks in the spectral region from 0 to 0.05 p.p.m. upfield from acetic anhydride. The poor resolution of these peaks prevented us from constructively correlating the H^1 and P^{31} spectra.

Before equilibrium is reached in this triply-connected-phosphorus system, a rearrangement takes place. After an irreproducible period at room temperature of about 4–7 days subsequent to mixing, the previously clear, limpid chloroform solutions corresponding to $P_4O_6/(CH_3CO)_2O$ < *ca.* 10 become viscous within a matter of a few minutes and then turn red. A gel-point is found for composition corresponding to P_4O_6 $(CH_3CO)_2O \simeq 3.5$. The color then progressively darkens to a deeply purple shade. P^{31} spectra taken within several minutes after the viscosities of the clear solutions began to rise and before any coloration was apparent showed complete conversion of all of the triply-connected phosphorus to quadruply-connected species; *i.e.*, the n.m.r. peaks were all in the range of −10 to +15 p.p.m. At the same time, the proton spectra were found to have changed very little.

It seems from this study that the initial reaction between P_4O_6 and acetic anhydride gives a range of new compounds in the family of acetyl polyphosphites (triply-connected-phosphorus atoms joined through oxygen bridges and with acetyl groups as monofunctional substituents). However, the system does not reach an equilibrium with respect to exchange of parts between molecules[12] but undergoes an Arbuzov-like rearrangement to give another set of new molecular structures, including acetyl polyacetylphosphonates.

Reactions with Trimethyl Phosphite, Methanol, or Tris(dimethylamino)phosphine.—Owing to the heat evolved in neat-liquid mixtures, $P(OCH_3)_3$ tends to react violently with P_4O_6 to give yellow and black solids. However, when chloroform is used as a solvent and the container is a thin-walled n.m.r. tube well thermostated at 25°, the reaction is moderated and gives an amorphous creamy yellow to orange-yellow precipitate and a solution exhibiting P^{31} n.m.r. chemical shifts

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[12] J. R. Van Wazer and K. Moedritzer, *Angew. Chem.*, in press.

ranging from that of trimethyl phosphite at −141 p.p.m. up to (for one sample) as high as +87 p.p.m. The reaction was capricious and obviously involved extensive oxidation and reduction. Reaction of P_4O_6 with methanol was even more violent, sometimes leading to flaming, and it was never satisfactorily tamed by use of solvents and cooling. Again an orange-yellow precipitate was always formed, and the characteristic odor of trimethyl phosphite was recognized.

Mixtures of $P[N(CH_3)_2]_3$ with P_4O_6 react rapidly but not violently, giving clear, single-phase products under optimum conditions. In order to obtain product homogeneity, it was necessary before mixing to dilute the reagents with equal volumes of dry chloroform. Then homogeneous liquids or glasses were produced, with equilibrium being attained too rapidly to be followed by n.m.r. The P^{31} n.m.r. patterns of the equilibrated mixtures were greatly complicated by spin–spin coupling between the hydrogens of the dimethylamino groups and the phosphorus. Since the resonances ranged from −123 to +20 p.p.m., it appeared that oxidation–reduction reactions had again occurred to give products involving both triply- and quadruply-connected phosphorus. The H^1 n.m.r. showed a large number of resonances, all in the spectral region expected for methyl groups bonded to nitrogen.

Reactions with Halogen Compounds.—PCl_3 is miscible with P_4O_6 and reaction between them is exceedingly slow at 25°. When neat mixtures are heated at 120°, a yellow precipitate appears in about 10–12 hr., and this increases in volume over a period of 1 month or more. When the reagents are combined with equal volumes of chloroform before mixing and then heated at 75°, the precipitate formed more slowly, first appearing as white flocs becoming slightly yellow with time. After vacuum drying under conditions where P_4O_6 or PCl_3 should be completely removed by volatilization, analysis of either the white flocs or the orange-yellow precipitate (both amorphous to X-rays) showed the presence of some chlorine (ranging up to as much as 10% Cl when a large proportion of PCl_3 was employed). This indicates that chlorine is incorporated in end or middle groups of the precipitate molecules. A typical n.m.r. spectrum taken from a chloroform solution in contact with the precipitate is shown in Figure 3. No shifts upfield of −85 p.p.m. were seen, so that all structures in solution are quite assuredly based on triply-connected phosphorus. In comparison with this reaction, phosphorus trioxide is found to react violently, with flaming, when mixed with AsF_3, and the reaction could not be properly tamed by use of solvents or cooling.

The reaction between CH_3SiCl_3 and P_4O_6, combined as neat liquids at 75°, led to a single-phase liquid or glass, with equilibrium being achieved within about 1 week depending on the exact ratio of the starting ingredients. H^1 and P^{31} n.m.r. showed that the chlorines of the silicon were practically completely transferred to the phosphorus in exchange for bridging oxygen atoms. Thus, for low starting proportions of phosphorus trioxide, all of the phosphorus was transformed to PCl_3. Furthermore, the gel point of the system was reached at an $Si/(Si + P)$ mole ratio of 0.40 ± 0.05. At the gel point, the P^{31} spectrum shown in Figure 3 was observed. From the variation of the proportions of the reagents with the areas of the groups of peaks labeled E, M, and B, we tentatively conclude that they are the end, middle, and branch groups obtained by permuting chlorine atoms with bridging oxygens. The formulas of these groups are $Cl_2PO_{1/2}$, $ClP(O_{1/2}–)_2$, and $P(O_{1/2}–)_3$, respectively. By comparing the proton spectra of the CH_3Si group in this system to that in the phosphorus-free system[13] CH_3SiCl_3 *vs.* $(CH_3Si)_2O_3$, it appears that some mixed polymers based on both phosphorus and silicon are formed. The P^{31} n.m.r. spectra exhibit reasonably sharp peaks beyond the gel point, even when the polymers are sufficiently cross linked so as to be hard glasses. With increasing cross linking, the resonances labeled B in Figure 3 are first seen to undergo pronounced viscosity broadening, followed by those labeled M. Since the equilibrium is such that the bridging oxygens are preferentially located on silicon and the chlorines on phosphorus, the phosphorus is congregated in end groups and PCl_3 and hence it is not surprising that there is a detectable P^{31} resonance for these structures, even in a hard glass. In order to explain the observance of phosphorus-based branch groups in the spectra, one might postulate that these branches preferentially occur at the ends of large molecules (as for a branch group having two ends attached to it) or in smaller molecules (three ends on a branch group).

Thermal Treatment of P_4O_6.—When P_4O_6 is heated in the range of 100–140°, it sooner or later undergoes chemical change consisting first of the appearance of several small resonances in the P^{31} n.m.r. spectrum, followed by precipitation of a solid, with the precipitate becoming increasingly yellow as more is deposited and with higher temperatures. The rate of these reactions is extremely variable, with the onset of precipitation ranging from 1 day to many months at 120°. Attempts to clarify the cause of this variability have not been fruitful, except for the finding that traces of water act as catalyst. When P_4O_6 is heated at temperatures greater than 150°, *e.g.*, 200°, the final products of the reaction are the mixture formulated as "PO_2"[14] and "red phosphorus" containing more or less oxygen, as previously observed.[2b]

The White and Yellow Precipitates.—Chemical analysis and X-ray investigation of the yellowish precipitates formed by thermal treatment of P_4O_6 or in the various reactions described above show that they are amorphous, generally insoluble materials of variable composition exhibiting an O/P mole ratio in the approximate range of 0.5 to 1.3 and varying amounts of terminating groups, such as methoxyl, hydroxyl, chlorine, etc. When these amorphous precipitates are

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[13] K. Moedritzer and J. R. Van Wazer, manuscript in preparation.

[14] D. Heintz, *Z. anorg. allgem. Chem.*, **336**, 137 (1965); K. H. Jost, *Acta Cryst.*, **17**, 1593 (1964).

nearly white, their O/P ratios are close to that of P_2O_3 (O/P $\leq$ 1.5) and they appear to react similarly.[15] When they are deep yellow or orange-yellow, they are quite unreactive at room temperature.

When various finely divided reactive solids were spread across the surface of a small piece of ice cooled on Dry Ice, the solutions obtained by allowing this ice to melt were promptly analyzed by P^{31} n.m.r. It was found that P_4O_6 gave 100% orthophosphorous acid and "PO_2" gave approximately 50% orthophosphorous and 50% phosphoric acids, of which about one-third was pyro- with the remainder being ortho-. The solutions resulting from reaction of the white and yellow precipitates all contained about three-quarters of the phosphorus as orthophosphorous acid. The precipitates formed by allowing P_4O_6 to react with PCl_3 or $P(OCH_3)_3$ showed the remainder of the soluble phosphorus to be orthophosphoric acid, with some (unreacted or precipitated) yellow material insoluble in water. As also found by Hossenlopp and Ebel,[11] the amount of H_3PO_4 found after hydrolysis increased in parallel with the amount of unreactive yellow precipitate and with the yellowish coloration of the material prior to hydrolysis.

As noted above, continued heating of liquid P_4O_6 yields a yellow precipitate, which may be structurally similar (but with P–O–P linkages) to amorphous red phosphorus, as envisaged by Pauling and Simonetta.[16] Investigations[17] of amorphous red phosphorus produced by heating white phorphorus in the presence of various catalysts have been interpreted to mean that the catalyst furnishes terminal groups to the network polymer made up of triply-connected phosphorus atoms. It is apparent from the work reported above that there is a continuous range of network polymers extending from nearly pure P_2O_3 to nearly pure phosphorus, with the color increasing from white through yellow, then orange, to red, as the phosphorus content increases. Presumably these polymers have highly complex structures involving P–P and P–O–P linkages as well as having some phosphorus atoms with unshared pairs of electrons and others of the phosphoryl variety. In addition, there are, of course, various structure-terminating groups, depending on the original composition and the thermal history. It is thought that the more reactive materials are those which have a predominance of P–O–P linkages and triply-connected phosphorus; *i.e.*, the precipitates first formed from P_4O_6 exhibit a structure and reactivity most closely related to this starting material.

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[15] A similar substance was presumably prepared from O_2 oxidation of P_4 in CCl_4 by B. Blaser, *Ber.*, **64B**, 614 (1931).

[16] L. Pauling and M. Simonetta, *J. Chem. Phys.*, **20**, 29 (1952); also see p. 117 of ref. 4.

[17] M. Ya. Kraft and V. P. Parini, *Dokl. Akad. Nauk SSSR*, **77**, 57 (1951); also see p. 114 of ref. 4.

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Complexes of Xenon Oxide Tetrafluoride[1]

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Xenon oxide tetrafluoride bears a strong resemblance to the halogen fluorides both in physical properties and chemical behavior. A number of physical properties of $XeOF_4$ have been measured. Xenon oxide tetrafluoride is a clear, colorless liquid freezing at −46.2°. Its electrical conductivity at 24° is 1.03×10^{-5} ohm^{-1} cm.$^{-1}$ and its dielectric constant is 24.6 at 24°. It is miscible with anhydrous HF, but its conductivity is not enhanced in such a solution. The addition of CsF or RbF to $XeOF_4$ increases its conductivity markedly. Xenon oxide tetrafluoride forms a series of addition compounds with the heavier alkali fluorides. The following complexes have been isolated: $CsF \cdot XeOF_4$, $3RbF \cdot 2XeOF_4$, and $3KF \cdot XeOF_4$. No reaction occurs with NaF. Thermogravimetric studies show that a number of intermediates are formed before final decomposition to the alkali fluorides. Xenon oxide tetrafluoride reacts with SbF_5 to form a complex of composition $XeOF_4 \cdot 2SbF_5$. A reaction also occurs with AsF_5 at −78°, but the complex is unstable at room temperature.

Introduction

Similarities between xenon fluorides and the halogen fluorides in their chemical bonding have been pointed out on a number of occasions.[2-4] It is to be expected that these analogies should be reflected in the chemical behavior of the xenon fluorides, and this has already been verified to some extent. It has been shown, for instance, that certain substances form complexes with xenon hexafluoride. Although it has not yet been unequivocally demonstrated, there are indications that these complexes are formed *via* acid–base type reactions and both basic salts[5] and acid salts[6,7] of xenon hexafluoride have been isolated. This similarity in chemi-

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] D. F. Smith, "Noble Gas Compounds," H. H. Hyman, Ed., University of Chicago Press, Chicago, Ill., 1963, p. 295.

[3] R. E. Rundle, *J. Am. Chem. Soc.*, **85**, 112 (1963).

[4] K. S. Pitzer, *Science*, **139**, 414 (1963).

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[6] G. L. Gard and G. H. Cady, *Inorg. Chem.*, **3**, 1745 (1964).

[7] H. Selig, *Science*, **144**, 537 (1964).