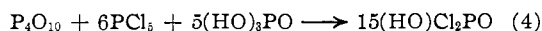
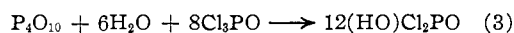


A quantitative measure of the yield of dichlorophosphoric acid was not made in any of these studies since appropriate physical methods were not available and the problem of separating dichlorophosphoric acid from the by-products of the reaction has not yet been solved. We have repeated these preparations and investigated several other preparations of dichlorophosphoric acid, using nuclear magnetic resonance to evaluate quantitatively the composition of the reaction products. Following Meerwein and Bodendorf,⁶ equimolar amounts of orthophosphoryl chloride dissolved in ether were combined with water at room temperature. Following Goubeau and Schulz,⁷ equimolar amounts of orthophosphoryl chloride and water were combined, taking care to keep the temperature in the range of -20 to -10° . In addition, we made dichlorophosphoric acid according to the two equations



The reactions described in equations 3 and 4 were carried out by heating to 230° in a sealed tube for 72 hr.

In all cases, it was found that $93 \pm 3\%$ of the total phosphorus occurred as the dichlorophosphoric acid, with the remaining $7 \pm 3\%$ being present as a mixture of condensed phosphates (primarily pyrophosphoryl chloride). In other words, the equilibrium shown in Fig. 1 apparently can be achieved by any of these preparation methods. This means that Grunze and Thilo⁸ were incorrect in saying that Goubeau and Schulz did not make dichlorophosphoric acid by their procedure. We did not test the procedure of Grunze and Thilo involving the hydrolysis of pyrophosphoryl chloride but see no reason why this also should not give almost pure dichlorophosphoric acid.

We found the density of the 93% dichlorophosphoric acid to be 1.77 g./cc. at 25° . (The other reported density⁸ is 1.6878.) Its vapor pressure is 17 mm. at the same temperature as compared to 40 mm. for $POCl_3$. There is a gradual increase in measured pressure, with time, due to evolution of HCl and concomitant formation of condensed phosphoric acids. When dichlorophosphoric acid is heated at atmospheric pressure, it loses HCl with increasing rapidity as the temperature is raised. When heated sufficiently long or sufficiently hot, all of the chlorine can be removed as HCl. Unlike orthophosphoryl chloride, dichlorophosphoric acid is miscible with water. In cold water, it hydrolyzes gently. It is soluble in alcohol and undergoes a reaction therein which probably results in the dialkyl ester of orthophosphoric acid. The odor of dichlorophosphoric acid is similar to that of orthophosphoryl chloride but is less penetrating.

The Orthophosphoric Acid-Triphenyl Orthophosphate System

In spite of the presence of side reactions, the $H_3PO_4-(C_6H_5O)_3PO$ system gave the kind of results to be expected for an uncharged molecule reorganizing with molecule-ions, all bearing approximately a single negative charge. Thus, after one month at 200° , the diphenyl phosphate was found to maximize at a value of $R = C_6H_5O/P = 2$ to give a value of *ca.* 70% of the total phosphorus minus the phosphorus in by-products, as compared to *ca.* 40% of the total phosphorus as monophenyl phosphate at $R = 1$ where the amount of the monophenyl ester reaches a maximum.

Acknowledgments.—We wish to thank Dr. Donald P. Ames and Mr. George Brautigam for the n.m.r. measurements reported herein.

ST. LOUIS, MISSOURI

[CONTRIBUTION FROM MONSANTO CHEMICAL COMPANY, RESEARCH DEPARTMENT, INORGANIC CHEMICALS DIVISION]

Principles of Phosphorus Chemistry. VIII. Reorganization of Triply Connected Monophosphorus Compounds

BY EKKEHARD FLUCK,¹ JOHN R. VAN WAZER AND LEO C. D. GROENWEGHE

RECEIVED MAY 6, 1959

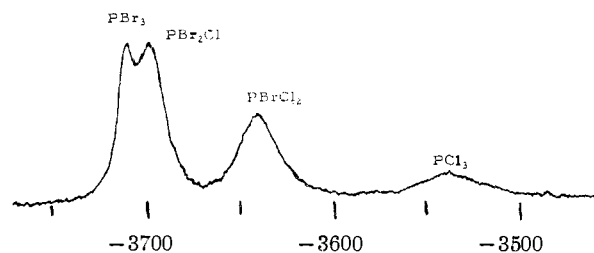
Various mixtures of phosphorus trichloride, phosphorus tribromide and triphenyl phosphite were prepared to study the equilibrium between the ten compounds expected from reorganization in this system. All ten compounds, based on triply connected phosphorus, were found, and equilibrium constants for their formation are presented. These equilibrium constants are compared with values calculated on the basis of completely random reorganization, and the system is shown to deviate from the completely random case. This deviation becomes less pronounced as the bromine increases from one to two bromines per phosphorus atom.

As part of a general study of the reorganization process in phosphorus-based compounds, some work has been carried out on the exchange of ligands between simple structures based on triply connected phosphorus. The purpose of this work was to discover whether the reorganization was approximately random and if it followed the same general principles² that apply to compounds based

on quadruply connected phosphorus. In this work, three related systems were investigated: $P(OC_6H_5)_3-PCl_3$, $P(OC_6H_5)_3-PBr_3$ and PBr_3-PCl_3 . These systems were chosen because the work on quadruply connected phosphorus compounds² indicated that reorganization would occur reasonably fast in them. This was found to be the case.

(1) On leave from Heidelberg University, Germany, during the academic year of 1957-1958.

(2) L. C. D. Groenweghe and J. H. Payne, *THIS JOURNAL*, **81**, 6357 (1959); J. R. Van Wazer and E. Fluck, *ibid.*, **81**, 6360 (1959); L. C. D. Groenweghe, J. H. Payne and J. R. Van Wazer, unpublished.



Chemical shift in c.p.s. (referred to 85% H_3PO_4).

Fig. 1.—Nuclear magnetic resonance spectrum of an equilibrium mixture of phosphorus tribromide and phosphorus trichloride.

Experimental Details

The triphenyl phosphite, $\text{P}(\text{OC}_6\text{H}_5)_3$, and the phosphorus tribromide, PBr_3 , were obtained from Eastman Organic Chemicals. The phosphorus trichloride, PCl_3 , was an analytical-reagent grade. Reorganization was carried out by mixing the desired proportions of these end members of the systems and sealing them in a test-tube of the proper size to be used in the nuclear magnetic resonance probe.

Reorganization of the two systems involving triphenyl phosphite was carried out at 180° . This temperature was chosen on the basis of preliminary experiments which indicated that only a small amount of reorganization occurred in about 0.5 hr. The samples were held for 66 hr. at this temperature. Since the same distribution of products was found after 12 hr. in several test samples, we concluded that the 66-hr. samples were all at equilibrium before cooling. When the samples were removed from the oven, they were cooled to room temperature within five minutes so as to retain the equilibrium corresponding to 180° . When the end members of the reorganizing series based on triphenyl phosphite were mixed and allowed to stand at room temperature, 12–15 hr. were needed to obtain a detectable amount of reorganization. Since nuclear magnetic resonance measurements were carried out on the cooled tubes well within this time, the results reported here should correspond to equilibrium at 180° .

The rate of reorganization in the all-halide system, $\text{PBr}_3\text{-PCl}_3$, is much faster than in the two systems involving triphenyl phosphite. Thus, at room temperature, barely detectable reorganization occurs in about 15 minutes. Measurements after one week and after two weeks at room temperature gave the same results and thus correspond to equilibrium values.

The nuclear magnetic resonance measurements were carried out in the manner previously described²; however, the correction for sweep linearity deviation was not applied. Since these measurements were made shortly after nuclear magnetic resonance work was started in this Laboratory, the data are not nearly as accurate as those reported in Papers IV and V of this series.³ In all of the two-component systems studied, two resonance peaks in addition to the peaks of the pure end-members of the series were observed. These peaks were attributed to the intermediate products to be expected from reorganization. Another resonance peak was found for the compound $\text{PClBr}(\text{OC}_6\text{H}_5)$, when equimolar amounts of PCl_3 , PBr_3 and $\text{P}(\text{OC}_6\text{H}_5)_3$ were combined and kept for 140 hr. at 180° . There were thus ten resonance peaks (see Fig. 4), seven being newly described. Assignments of the new peaks are unequivocal because (1) the peak corresponding to a given intermediate reaches a maximum at the concentration where this intermediate should predominate, and (2) for some of the compositions, the stoichiometry will allow no other assignments.

In the mixed-halide system, the general proofs presented above hold for the assignment of the resonance peak corresponding to PCl_2Br . However, the chemical shift between the peaks corresponding to PClBr_2 and PBr_3 is only ca. 10 c.p.s. so that these peaks are never completely resolved and were more difficult to assign. An example of a typical spectrum is shown in Fig. 1. The assignment of the PClBr_2 peak finally was made on the basis of two criteria. The first criterion was based on the fact that the PBr_3 peak would be increased by adding PBr_3 to the mixture. When this was done and quickly measured, the most negative peak of the spectrum in Fig. 1 increased. The second criterion is de-

pendent on the fact that the quadrupole broadening of the phosphorus resonance by chlorine is considerably greater than by bromine. As can be seen in Fig. 1, the broadness of the peaks continuously increases when going from left to right, and the resolved upper portion of the peak assigned to PBr_3 appears to be sharper than the top of the peak assigned to PClBr_2 .

Results

Experimental data for the $\text{P}(\text{OC}_6\text{H}_5)_3\text{-PCl}_3$ and the $\text{P}(\text{OC}_6\text{H}_5)_3\text{-PBr}_3$ systems are presented in Figs. 2 and 3. The dotted lines in these figures

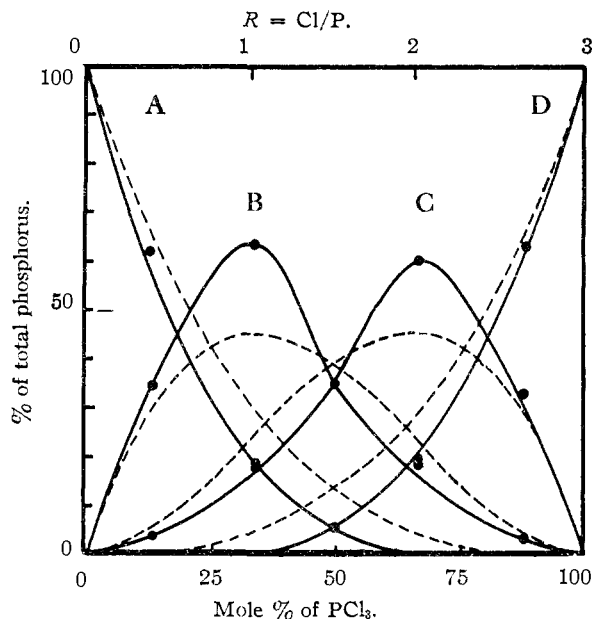
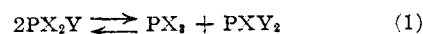


Fig. 2.—Equilibrium in the system $\text{P}(\text{OC}_6\text{H}_5)_3\text{-PCl}_3$ at 180° . The dotted curves represent the equilibrium values to be expected if the reorganization were completely random: A = $\text{P}(\text{OC}_6\text{H}_5)_3$; B = $\text{PCl}(\text{OC}_6\text{H}_5)_2$; C = $\text{PCl}_2(\text{OC}_6\text{H}_5)$; D = PCl_3 .

correspond to the distribution which would be expected on a purely random basis.^{2,3} It is apparent from these figures that the mixed compounds are present in larger amounts than corresponds to a completely random reorganization-process. Indeed, at a 1:1 ratio of halogen to phenoxy groups, the observed mole ratio of $\text{P}(\text{OC}_6\text{H}_5)_3\text{:PCl}(\text{OC}_6\text{H}_5)_2\text{:PCl}_2(\text{OC}_6\text{H}_5)\text{:PCl}_3$ is 1:7:7:1 instead of the 1:3:3:1 ratio corresponding to the completely random case. Likewise, the mole ratio of $\text{P}(\text{OC}_6\text{H}_5)_3\text{:PBr}(\text{OC}_6\text{H}_5)_2\text{:PBr}_2(\text{OC}_6\text{H}_5)\text{:PBr}_3$ is 1:6.8:5.5:1.7.

The experimental data can be summarized in terms of equilibrium constants. Equation 1, given below, is of the form used in the theoretical treatment previously published.³ Values of the corresponding equilibrium constant K_d are presented in Table I for the mixed halides in the three two-component systems studied, with X and Y being either Cl, Br or (OC_6H_5) .



$$K_d = \frac{[\text{PX}_3][\text{PXY}_2]}{[\text{PX}_2\text{Y}]^2} \quad (2)$$

(3) J. R. Parks and J. R. Van Wazer, *THIS JOURNAL*, **79**, 4890 (1957).

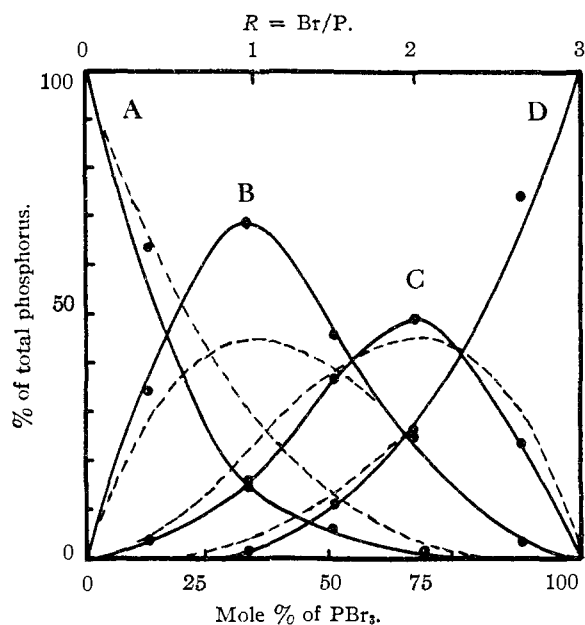


Fig. 3.—Equilibrium in the system $P(OC_6H_5)_3$ - PBr_3 at 180° . The dotted curves represent the equilibrium values to be expected if the reorganization were completely random: A = $P(OC_6H_5)_3$; B = $PBr(OC_6H_5)_2$; C = $PBr_2(OC_6H_5)$; D = PBr_3 .

The equilibrium constants represented by equation 2 can be converted into equilibrium constants K_f corresponding to formation from the unmixed or parent compounds. Values of K_f are also presented in Table I.

$$K_f = \frac{[PX_2Y]^3}{[PX_3]^2[PY_3]} = \frac{1}{(K_d \text{ for } PX_2Y)^2(K_d \text{ for } PXY_2)} \quad (3)$$

TABLE I
EQUILIBRIUM DATA

Compound	Temp., °C.	Equilibrium constants		Energy non-ideality ΔF (kcal./mole)
		K_d	K_f	
$PCl_2(OC_6H_5)_2$	180	0.13	460	-0.9
$PCl(OC_6H_5)_3$	180	.13	460	-.9
$PBr_2(OC_6H_5)_2$	180	.38	56	-.22
$PBr(OC_6H_5)_3$	180	.12	170	-.6
PCl_2Br	25	.2	40	-.8
$PClBr_2$	25	.7	10	+.20
Ideal randomness	Any	.33	27	.00
$PClBr(OC_6H_5)_2$	180	..	1,500	ca. -0.6
Ideal randomness	Any	..	216	0.000

As previously calculated,² the equilibrium constant K_d should exhibit a value of 0.33 for completely random reorganization. The value of K_f corresponding to this is 27. When the experimental value of K_f is greater than 27, the mixed compounds are more stable than the parent unmixed compounds; *i.e.*, the free energies of the mixed compounds are lower than the value obtained by summing the proper proportions of the free energies of the unmixed compounds. These differences in free energy calculated from equation 4 are shown in the last column of Table I. This column demonstrates that all of the mixed

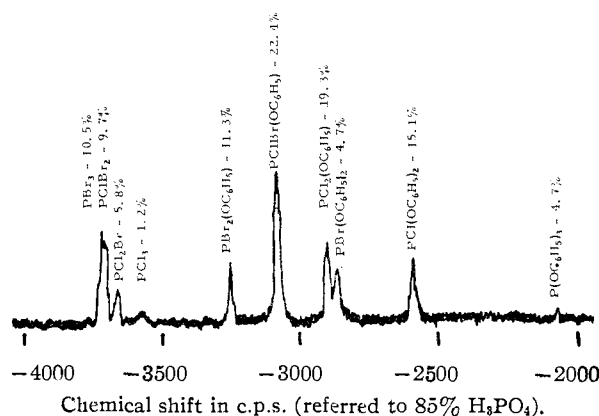


Fig. 4.—Nuclear magnetic resonance trace for an equimolar mixture of PCl_3 , PBr_3 and $P(OC_6H_5)_3$, equilibrated at 180° . Values following the chemical formulas are mole percentages.

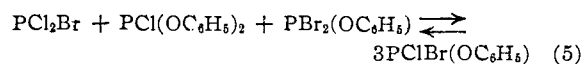
halides except $PClBr_2$ are more stable than would be predicted from simple statistical calculations.

$$\Delta F = -(RT/3) \ln (K_f/27) \quad (4)$$

Equilibrium in the $P(OC_6H_5)_3$ - PCl_3 system was previously studied⁴ by classical methods. However, this earlier work gave only a qualitative notion of the equilibria, since analysis for the intermediate reorganization products was carried out by distillation. Apparently some reorganization took place during distillation and, moreover, the separation was not clean. Although the two mixed halides, PCl_2Br and $PClBr_2$, have been made previously,⁵ the equilibrium in the all-halide system had not been measured.

The nuclear magnetic resonance spectrum obtained on an equilibrated, equimolar mixture of PCl_3 , PBr_3 and $P(OC_6H_5)_3$ is shown in Fig. 4. The assignment and mole percentage of the particular species are given above each resonance peak in this figure. These assignments agree with the observed chemical shifts and the mole percentages are obtained from the measured peak areas and the material balances based on P, Cl, Br and (OC_6H_5) . If the system corresponded to completely random reorganization, the three unmixed compounds of the PX_3 type should each be present to the amount of 3.7 mole % in the 1:1:1 mixture at equilibrium. Likewise, there should be 11.1 mole % of each of the six compounds of the type PX_2Y and 22.2 mole % of the compound $PXYZ$.

A large number of equations may be written to represent the formation of the completely mixed compound, $PClBr(OC_6H_5)_2$, from various combinations of the ten other compounds present in the system. However, for the 1:1:1 mixture, the equilibrium can best be calculated from the reaction

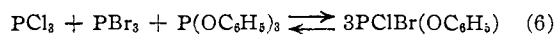


since these three compounds do not have overlapping peaks and are present in appreciable con-

(4) J. B. Conant, V. H. Wallingford and S. S. Gandhekar, *THIS JOURNAL*, **45**, 764 (1923).

(5) A. Renc, *Roczniki Chem.*, **14**, 69 (1934); **13**, 509 (1953); T. Mitobedzki and S. Krakowiecki, *ibid.*, **8**, 563 (1928).

centration, as indicated in Fig. 4. The formation constant for the completely mixed compounds from the end members according to the reaction



can then be calculated by the equation

$$K_f = K_5(K_f'K_f''K_f''')^{1/3} = 1.5 \times 10^3 \quad (7)$$

in which K_5 is the equilibrium constant for equation 5 and K_f' , K_f'' and K_f''' are the three formation constants for the reactants in equation 5 whose values are given in Table I. Because of accumulated errors, the value of the formation constant is considered rather inaccurate. It is given only to indicate that its order of magnitude is significantly greater than that calculated for a completely random system which would be 216.

Although there are not sufficient data on which to reach firm conclusions, it appears that deviations from ideal randomness are more pronounced in systems based on triply connected phosphorus than in equivalent systems based on quadruply connected phosphorus. This conclusion is in accord with the wide variations in chemical shifts observed in nuclear magnetic resonance studies on compounds based on triply connected phosphorus as compared to those based on quadruply connected phosphorus. These findings can be explained qualitatively by the difference between the way significant intramolecular electrical charge differences are avoided in compounds based on triply connected phosphorus as compared to compounds based on quadruply connected phosphorus.⁶

(6) J. R. Van Wazer, "Phosphorus and Its Compounds: Chemistry," Interscience Publishers, Inc., New York, N. Y., 1958, Chapter 2; J. R. Van Wazer, *THIS JOURNAL*, **78**, 5709 (1956).

When three ligands are attached to a phosphorus atom, avoidance of charge unbalance between them and the phosphorus is achieved by changing the bond angles and hence the type of hybridization; whereas feedback of the charge appears to be accomplished in compounds based on quadruply connected phosphorus by π -bonding, utilizing the d orbitals of the phosphorus.⁷

Although detailed rate measurements were not made, our studies indicate that exchange of ligands between molecules based on triply connected phosphorus proceeds at a considerably faster rate than exchange of the same ligands between molecules based on quadruply connected phosphorus. Presumably the exchange for the molecules based on triply connected phosphorus occurs *via* a Walden inversion which might be expected to be a lower energy process than the one involved in the exchange of ligands between molecules based on quadruply connected phosphorus. In this latter case, the activated complex may well involve the utilization of a d orbital of the phosphorus in its σ -bond base structure, so that the activated complex would be based on sp^3d hybridization of the phosphorus.

Acknowledgments.—We wish to thank Dr. Donald P. Ames for carrying out some nuclear magnetic resonance measurements reported herein and for his help in interpreting the nuclear magnetic resonance data. Mr. George Brautigam also made a number of the nuclear magnetic resonance determinations and measured some of the resulting resonance peak areas.

(7) H. H. Jaffé, *J. Inorg. Nuclear Chem.*, **4**, 372 (1957).

ST. LOUIS, MISSOURI

[CONTRIBUTION FROM MONSANTO CHEMICAL COMPANY, RESEARCH DEPARTMENT, INORGANIC CHEMICALS DIVISION]

Principles of Phosphorus Chemistry. IX. Reorganization of Triply and Quadruply Connected Monophosphorus Compounds¹

BY EINHARD SCHWARZMANN² AND JOHN R. VAN WAZER

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In simple reorganization between triply and quadruply connected monophosphorus compounds, eight molecular species are involved. In addition to the two dissociation constants of the mixed triply connected molecules and the two dissociation constants of the mixed quadruply connected molecules, a fifth equilibrium constant is needed to describe the system. The systems $\text{OPCl}_3\text{-PBr}_3$ and $\text{OPBr}_3\text{-PCl}_3$ are compared and found to have the same set of five equilibrium constants, as would be expected. Some preliminary data on the system $\text{OPCl}_3\text{-P}(\text{OC}_6\text{H}_5)_3$ also are given.

To round out the work reported in the previous four papers³ of this series, a study was made of reorganization between triply and quadruply connected compounds based on a single phosphorus atom. The major amount of work was done on the systems $\text{OPCl}_3\text{-PBr}_3$ and $\text{OPBr}_3\text{-PCl}_3$. Less precise measurements were made on the $\text{OPCl}_3\text{-P}(\text{OC}_6\text{H}_5)_3$ system.

(1) A preliminary investigation of this subject was made by Dr. Ekkehard Fluck shortly before he left our laboratory to return to Heidelberg University.

(2) On leave of absence during the 1958-1959 academic year from Göttingen University, Germany.

(3) L. C. D. Groenweghe and J. H. Payne, Jr., *THIS JOURNAL*, **81**, 6357 (1959); J. R. Van Wazer, and E. Fluck *ibid.*, **81**, 6360 (1959); L. C. D. Groenweghe, J. H. Payne and J. R. Van Wazer, unpublished.

Experimental Results

The reagents and method of study were the same as those described in preceding papers of this series.³ The reorganization between $\text{OPCl}_3\text{-PBr}_3$ was carried out at temperatures of 200 and 110°. Measurements on the 200° samples were made after eight weeks, but trial experiments indicated that equilibrium was reached in several days. The measurements on the 110° samples were made after four weeks. It is interesting to note that, after two months at 25°, essentially no reaction was found. The system $\text{OPBr}_3\text{-PCl}_3$ was measured after one week at 200°. All of the tubes contained clear colored liquids at the end of the heating period, and there was no indication of side reactions.

The system $\text{OPCl}_3\text{-P}(\text{OC}_6\text{H}_5)_3$ was measured after one week at 200°, and another set of tubes was heated to 300° for several weeks. At 200°, no decomposition was observed. However, the liquids in the tubes stored at 300° exhibited a licorice-brown color, and the n.m.r. measurements gave