In summary, it appears that the reaction schemes occurring in biology are dependent on employment of an element, for which d-orbitals are sufficiently available to play a role in the σ-bond structure of activated complexes but do not enter into the σ-bond structure of the common compounds. Primarily because of slow kinetics in simple aqueous solutions, but also because of a generally moderate tendency toward hydrolysis, phosphorus is the Second-Row element of outstanding biochemical activity.

Acknowledgments.—We wish to thank Dr. Editha Karl-Kroupa for her guidance in carrying out the chromatographic work, and Messrs. Lee Loveless and Thomas Kichline who gave us helpful advice.

ST. LOUIS, MO.

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

Principles of Phosphorus Chemistry. IV. The System of Fluorophosphoric Acids

BY DONALD P. AMES, SHIGERU OHASHI,[1] CLAYTON F. CALLIS AND JOHN R. VAN WAZER

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In the single-phase liquid system H_2O–HF–P_2O_5, the nine structural entities herein listed were quantitatively determined from phosphorus and fluorine nuclear magnetic resonance spectra: mono-, di- and hexafluorophosphoric acids, orthophosphoric acid, end- and middle-phosphate structure units, free water, free hydrofluoric acid, and a new structure unit containing one fluorine per phosphorus. This new structure unit is believed to be a monofluorophosphate end group. Lines of equal concentration are shown for the nine structural entities in the single-phase region of a series of H_2O–HF–P_2O_5 triangular diagrams in which the two-phase area covers the region corresponding to more than *ca.* 55 mole % P_2O_5. Four equilibrium constants were calculated for the system.

The ease of transformation from one fluorophosphoric acid to another or into orthophosphoric acid in the presence of HF or H_2O is well-known.[2] However, the equilibria involved have not been investigated quantitatively except for the reaction[3] between monofluorophosphoric acid and water to give orthophosphoric acid and hydrogen fluoride.

This paper describes a study in which the relative proportions of the various molecular constituents in the system H_2O–HF–P_2O_5 at equilibrium were determined by nuclear magnetic resonance spectroscopy. This relatively new physical technique is particularly suited to the determination of equilibrium composition diagrams in liquid systems where the molecular species contain atoms exhibiting nuclear spin. The system involving fluorophosphoric acids is particularly adaptable to the n.m.r. technique, since naturally occurring hydrogen, fluorine and phosphorus have the optimum nuclear properties, *i.e.*, a predominant isotope with large magnetic moment and zero quadrupole moment.

Experimental

Samples Studied.—Approximately 125 separate compositions, scattered throughout the homogeneous region shown in Figs. 2–10, were investigated in this study. The majority of these samples were made from eight concentrated preparations which were diluted with water. In a few cases, P_2O_5 and HF were added to the original preparation. The original preparations were obtained from Dr. Wayne E. White of the Ozark Mahoning Company, who simply combined phosphorus pentoxide and anhydrous HF to make all of them except the anhydrous difluorophosphoric acid, which was distilled. The original sample of difluorophosphoric acid must have contained some paramagnetic impurities, since the nuclear magnetic resonance peaks of this sample and of mixtures made by diluting it with water were exceptionally broad. A duplicate sample obtained from Dr. White exhibited sharp resonance peaks.

The various compositions studied were equilibrated at a temperature of 50° for more than 20 hr. in polyethylene bottles. Some of the tubes were stored thereafter for 48 hr. more at 50° with no change in their molecular composition. Further proof that equilibrium was reached was obtained by making samples having the same proximate analysis from different starting materials. In such cases, the same molecular composition was found.

Nuclear Magnetic Resonance Measurements.—All measurements were made with a Varian Model V-4300B nuclear induction magnetic resonance spectrometer utilizing a Varian magnet, Model V-4012-HR. The P^{31} spectra were obtained with a 16.2 mc. radiofrequency oscillator using a field of 9395 gauss. The F^{19} spectra were obtained with a 40.0 mc. radiofrequency oscillator using a field of 9985 gauss. The 40 mc. oscillator also was used to obtain hydrogen spectra at a field of 9395 gauss.

The samples were measured in 15 mm. o.d. polyethylene test-tubes containing 3 to 5 ml. of liquid. The tubes were sealed with a rubber stopper protected from the vapors with a layer of Saran Wrap®, and the stopper was affixed tightly with plastic pressure-sensitive tape. Referencing was carried out by a modification of the concentric-tube technique,[4] in which a small polyethylene tube filled with the reference material was inserted through a single-hole stopper into the sample under investigation. For the phosphorus spectra, 85% phosphoric acid was used as reference; whereas for the fluorine spectra 100% trifluoroacetic acid (Eastman reagent) was employed. The referencing was carried out by the side-band technique.[5] The side-band frequencies were counted with a Hewlett-Packard electronic counter, Model 524B. With either the fluorine or phosphorus spectra, no anomalies[6] were noted when the concentric-tube technique of referencing was employed. As expected, the hydrogen spectra were of little value in investigating the system studied, since the acidic hydrogens of the HF and the various phosphoric acids exchange with each other and with the water present so that only a single resonance peak is observed.

Both the phosphorus and fluorine spectra were obtained by utilizing the "intermediate-passage" absorption-mode

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(1) On leave of absence from Kanazawa University, in Japan, during the 1957–1958 academic year.

(2) W. Lange, "Fluorine Chemistry," Vol. I, Edited by J. H. Simons, Academic Press, Inc., New York, N. Y., 1950, Chap. 3, pp. 125–188; John R. Van Wazer, "Phosphorus and Its Compounds. I. Chemistry," Interscience Publishers, Inc., New York, N. Y., 1958, Chap. 13, pp. 801–820.

(3) W. Lange, *Ber.*, **62B**, 1084 (1929); *Z. anorg. allgem. Chem.*, **214**, 44 (1933).

(4) J. R. Zimmerman and M. R. Foster, *J. Phys. Chem.*, **61**, 282 (1957).

(5) J. T. Arnold and M. E. Packard, *J. Chem. Phys.*, **19**, 1608 (1951).

(6) C. A. Reilly, H. M. McConnell and R. G. Meisenheimer, *Phys. Rev.*, **98**, 264 (1955).

presentation. The areas of the resulting resonance peaks were measured by weighing traces made on a tracing paper of uniform weight. Replicate F^{19} resonance area measurements showed a standard deviation of 2.4% of the peak area on resonance peaks exhibiting areas which were in the range of 15 to 30% of the total fluorine; whereas, replicate P^{31} resonance area measurements showed a standard deviation of 5.0% for the same range. As the intensity of the measured peak became lesser or greater, the standard deviation, respectively, increased or decreased, as anticipated. Other work[7] has shown that the relative areas of n.m.r. peaks give an accurate measure of the relative amounts of the various constituents represented by the peaks when the nuclear magnetic spectrometer is properly adjusted.

In the H_2O–HF–P_2O_5 system studied, F^{19} resonances were observed for hydrofluoric acid, HF; monofluorophosphoric acid, $(HO)_2(O)PF$; difluorophosphoric acid, $(HO)(O)PF_2$; hexafluorophosphoric acid, HPF_6; and a new species which was shown to be a building unit for making condensed fluorophosphoric acids and is believed to be the fluorophosphate end group, $(HO)(O)P(F)O_{1/2}-$. Except for the hydrofluoric acid, two resonance peaks of equal size appeared in the F^{19} spectra of each of these species from the spin-spin coupling between the phosphorus and fluorine atoms. For both the phosphorus and fluorine spectra, the observed peaks were very close to the resonance values previously reported in the literature.[8] The observed spin-spin splittings were always identical to the literature values, within experimental error; but slight changes in the chemical-shift values were noted, with the resonances appearing at slightly lower fields as the water concentration increased. This change in the chemical shift is at least partially attributable to increased ionization with greater dilution. Work on this is continuing in our Laboratory.

The three fluorophosphoric acids and the supposed fluorophosphate end group gave P^{31} resonances. In addition, phosphorus resonance peaks were observed for orthophosphoric acid, $(HO)_3PO$; the phosphate end group, $(HO)_2P(O)O_{1/2}-$; and the phosphate middle group, $-O_{1/2}(O)P(OH)O_{1/2}-$. Spin–spin multiplets were seen for the fluorophosphates. The monofluorophosphate ion gives a 1–1 doublet, the difluorophosphate ion a 1–2–1 triplet, and the hexafluorophosphate ion a 1–6–15–20–15–6–1 septuplet, as previously reported.[8,9]

Paper Chromatographic Analyses.—The chromatographic procedures[10] generally employed in this Laboratory were used to study certain of the samples. The phosphorus content of the chromatographic spots was measured according to the usual technique.[10] Qualitative analyses for fluorine in the various chromatographic spots were made by the zirconium-alizarin spot test.[11] The quantitative analyses for fluorine in the chromatographic spots were carried out by the Willard–Winter micro technique.[12]

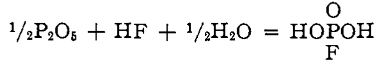
The samples were prepared for chromatographic analyses by cooling them to 0°, adding ice, and then neutralizing them to *p*H 7 with ice-cold sodium hydroxide (*ca.* 2 *N*). This procedure reduced hydrolysis to negligible amounts as evidenced by comparing the P^{31} spectra before and after this treatment.

Proximate Analyses and Handling of Data.—The proximate composition of the various samples was determined by two independent procedures, and one partially independent technique. First, the compositions of the eight original preparations were known from the amounts of anhydrous hydrogen fluoride and phosphorus pentoxide employed in making them. The compositions of the various samples obtained by diluting these preparations were also known, since the dilutions were carried out quantitatively. Secondly, quantitative analyses were made on the eight original preparations and several of the diluted samples. The third method of assaying depended on interpretation of the n.m.r. data, as indicated in following paragraphs.

From the n.m.r. work, proximate analyses in terms of phosphorus pentoxide, hydrogen fluoride and water of composition are obtained. Since the water of composition is equal to or less than the total water (the H_2O of the proximate analysis), these n.m.r. values can be corrected so that one of the three proximate composition parameters (HF, H_2O and P_2O_5) agrees with the value obtained analytically. This correction is carried out by adding an adjustable constant, the "free water" to the water of composition. As can be seen from the Supplementary Tables[13] available from the American Documentation Institute, the agreement between the proximate analyses obtained by nuclear magnetic resonance and by quantitative analysis is satisfactory. Since the fluorine n.m.r. data are more accurate than the phosphorus data, the best results are found when the proximate analysis for HF as obtained by nuclear magnetic resonance is equated to the HF value obtained by quantitative, wet-chemical analyses. This was done to get the values shown in the Supplementary Tables.

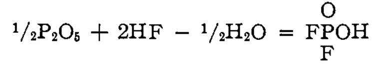
The steps taken in determining the proximate composition from the n.m.r. data are as follows. First the F^{19} and P^{31} resonance lines in each spectrum are assigned to the various fluorine or phosphorus compounds, using measured resonances[8] as the basis of the assignment. Then the area percentage of each resonance peak is determined, and the relative areas for each compound are found by adding the areas of the spin-spin multiplets attributable to the compound. This gives the percentages of the total fluorine and of the total phosphorus present in each compound. The fluorine spectrum is approximately twice as accurate as the phosphorus spectrum because (1) the higher frequency (40 mc.) used for fluorine gives higher signal to noise ratio, and (2) the fluorine peaks are generally fewer than the phosphorus peaks since the highest spin-spin multiplet for any fluorophosphoric acid is a doublet as compared to, say, the septuplet for the phosphorus spectrum of the hexafluorophosphate. This means that the most accurate results are obtained by using the fluorine spectrum to get the relative proportions of the fluorine-containing acids and utilizing the phosphorus spectrum only to determine the amount of the fluorine-free phosphorus compounds with respect to the total amount of fluorine-containing compounds. This is done by multiplying the mole percentages of the fluorine-free phosphoric acids by a factor obtained by dividing the sum of the mole percentages of the fluorophosphoric acids from the F^{19} spectra by the sum of the same mole percentages obtained from the P^{31} spectra. After normalizing, so as to make the total moles of compounds based on phosphorus and fluorine equal to 100 mole %, the amount of total P_2O_5, total HF and total water of composition is obtained from the stoichiometry of the equations

Monofluorophosphoric acid



$$\frac{1}{2}P_2O_5 + HF + \frac{1}{2}H_2O = HO\overset{O}{\underset{F}{P}}OH \qquad (1)$$

Difluorophosphoric acid

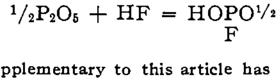


$$\frac{1}{2}P_2O_5 + 2HF - \frac{1}{2}H_2O = F\overset{O}{\underset{F}{P}}OH \qquad (2)$$

Hexafluorophosphoric acid

$$\frac{1}{2}P_2O_5 + 6HF - \frac{5}{2}H_2O = HPF_6 \qquad (3)$$

Monofluorophosphate end groups[14]



$$\frac{1}{2}P_2O_5 + HF = HO\overset{O}{\underset{F}{P}}O^{1/2-} \qquad (4)$$

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[7] R. B. Williams, *Ann. N. Y. Acad. Sci.*, **70**, 890 (1958); *Spectrochim. Acta*, **14**, 24 (1959); N. F. Chamberlain, *Anal. Chem.*, **31**, 56 (1959); D. P. Ames and C. F. Callis, unpublished work.

[8] H. S. Gutowsky, D. W. McCall and C. P. Slichter, *J. Chem. Phys.*, **21**, 279 (1953); H. S. Gutowsky and D. W. McCall, *ibid.*, **22**, 162 (1954); W. E. Quinn and R. M. Brown, *ibid.*, **21**, 1605 (1953).

[9] For pictures of these spectra, see J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1958, pp. 807, 812.

[10] E. Karl-Kroupa, *Anal. Chem.*, **28**, 1091 (1956). For the three well-known fluorophosphates, see L. Kolditz and A. Feltz, *Z. anorg. allgem. Chem.*, **293**, 155 (1957).

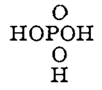
[11] F. Feigl, "Quantitative Analyse mit Hilfe von Tüpfelreaktionen," Akademische Verlagsgesellschaft, Leipzig, 1938, pp. 153, 292, 295.

[12] H. H. Willard and O. B. Winter, *Ind. Eng. Chem., Anal. Ed.*, **5**, 7 (1933).

[13] Material supplementary to this article has been deposited as Document number 5898 with the ADI Auxiliary Publication Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $3.75 for photoprints, or $2.00 for 35 mm. microfilm in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

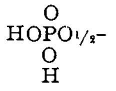
[14] If the monofluorophosphate end group were in fact a fluorophosphate middle group, the only proximate-analysis values which would be

Orthophosphoric acid



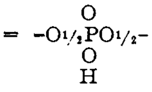
$$\tfrac{1}{2}P_2O_5 + \tfrac{3}{2}H_2O = HO\underset{\underset{\displaystyle H}{\displaystyle O}}{\overset{\displaystyle O}{P}}OH \qquad (5)$$

Phosphate end groups



$$\tfrac{1}{2}P_2O_5 + H_2O = HO\underset{\underset{\displaystyle H}{\displaystyle O}}{\overset{\displaystyle O}{P}}O_{1/2}- \qquad (6)$$

Phosphate middle groups



$$\tfrac{1}{2}P_2O_5 + \tfrac{1}{2}H_2O = -O_{1/2}\underset{\underset{\displaystyle H}{\displaystyle O}}{\overset{\displaystyle O}{P}}O_{1/2}- \qquad (7)$$

In the Supplementary Tables,[13] the values labeled "Proximate Composition from Nuclear Magnetic Resonance" were obtained by adding that value for the "free water" to the water of composition which makes the mole percentage of HF in the proximate composition agree with the analytically determined mole percentage of HF. The free water shown in the last column of the Supplementary Table was calculated by subtracting the water of composition obtained from the n.m.r. data based on fluorine from the total water as calculated from the proximate wet-chemical analyses.

Results and Conclusions

Composition Diagrams.—In Fig. 1, the fluorine and phosphorus nuclear magnetic resonance spectra are shown for a typical sample. Although the phosphorus spectrum presented in this figure is quite complicated, some spectra were found to exhibit as many as twelve resonance peaks.

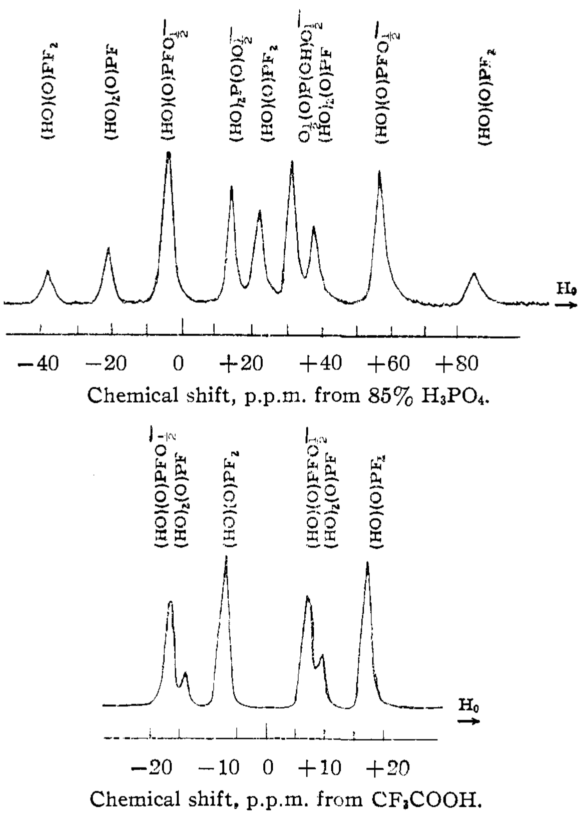


Fig. 1.—F^{19} (bottom) and P^{31} (top) nuclear magnetic resonance spectra of a typical sample (sample number 123 in the Supplementary Tables[13]).

The experimental results are given in Figs. 2 through 10, which are all triangular diagrams covering the H_2O–HF–P_2O_5 system. There is a separate diagram for each of the nine molecular species determined. In these diagrams, lines of constant molecular composition are shown for the region in which a single phase was found. Since

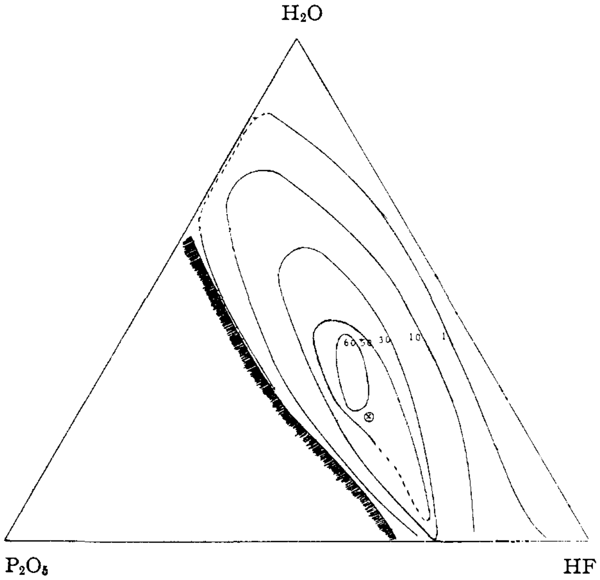


Fig. 2.—Mole percentages of monofluorophosphoric acid at equilibrium in the H_2O–HF–P_2O_5 system. Dotted lines are estimated and the ⊗ denotes the composition of 100% monofluorophosphoric acid. The region to the right of the feathered line is a homogeneous liquid.

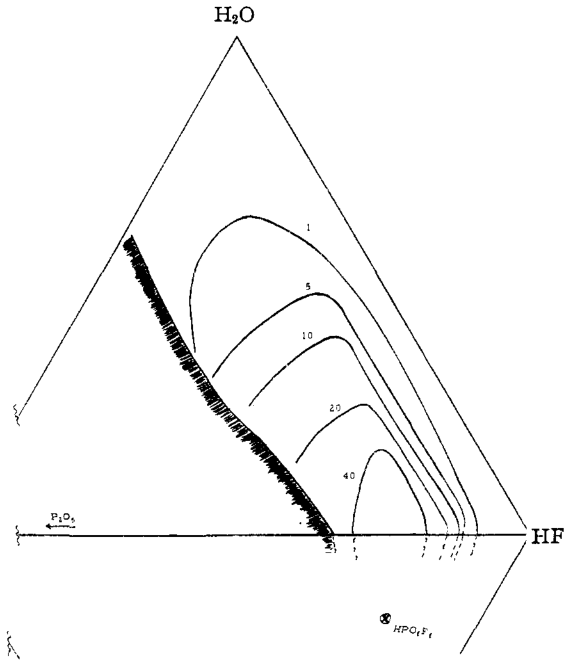


Fig. 3.—Mole percentages of difluorophosphoric acid at equilibrium in the H_2O–HF–P_2O_5 system. The ⊗ denotes the composition of 100% difluorophosphoric acid. The region to the right of the feathered line is a homogeneous liquid.

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affected by this change would be the water of composition and hence the total water by nuclear magnetic resonance.

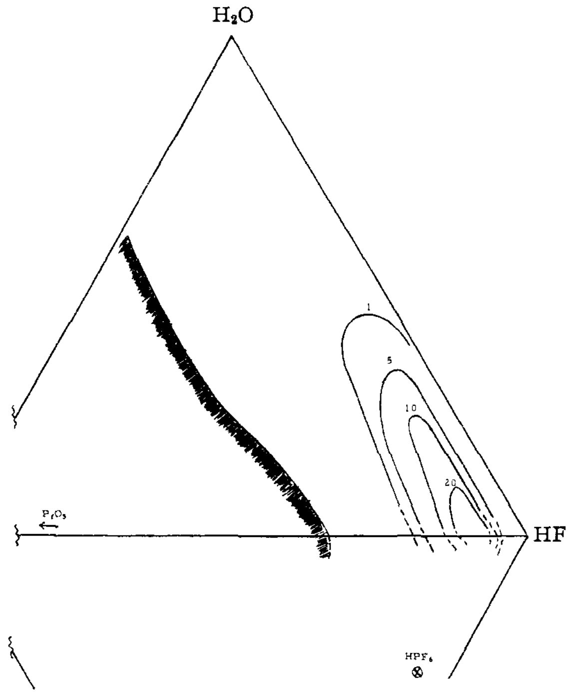


Fig. 4.—Mole percentages of hexafluorophosphoric acid in equilibrium in the H_2O–HF–P_2O_5 system. The ⊗ denotes the composition of 100% hexafluorophosphoric acid. The region to the right of the feathered line is a homogeneous liquid.

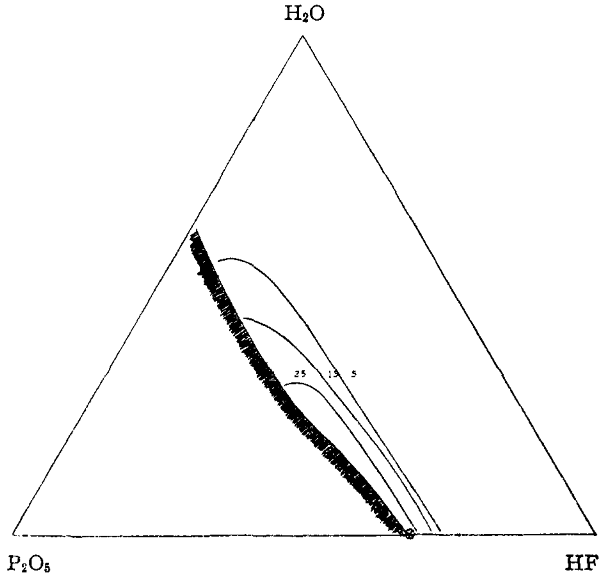


Fig. 5.—Mole percentages of fluorophosphate end group at equilibrium in the H_2O–HF–P_2O_5 system. The ⊗ denotes 100% difluoropyrophosphoric acid (all fluorophosphate end groups). The region to the right of the feathered line is a homogeneous liquid.

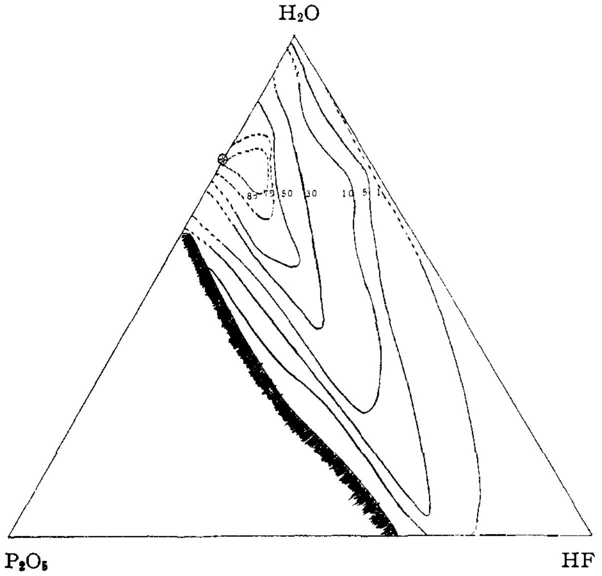


Fig. 6.—Mole percentages of orthophosphoric acid in equilibrium in the H_2O–HF–P_2O_5 system. Dotted lines are estimates and the ⊗ denotes the composition of 100% orthophosphoric acid. The region to the right of the feathered line is a homogeneous liquid.

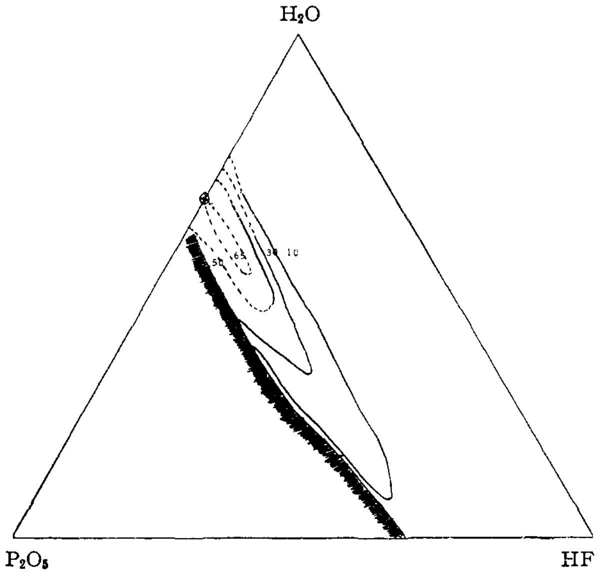


Fig. 7.—Mole percentages of phosphate end groups at equilibrium in the H_2O–HF–P_2O_5 system. Dotted lines are estimated and the ⊗ denotes the composition of 100% pyrophosphoric acid (all phosphate end groups). The region to the right of the feathered line is a homogeneous liquid.

two of the species, difluorophosphoric acid and hexafluorophosphoric acid, do not lie within the simple triangular diagram, Figs. 3 and 4 have been extended into the range of negative water so that the compositions of the difluorophosphoric and hexafluorophosphoric acids can be presented in terms of negative water according to equations 2 and 3.

It is interesting to note that the maximum concentration of all or nearly all of the species, except free water and free hydrogen fluoride, does not appear at the composition corresponding to the empirical formula of that species. This is well-illustrated by Fig. 2. Previous work[15] on orthophosphoric acid shows that the liquid corresponding to 100% H_3PO_4 is a mixture of free water,

[15] A. L. Huhti and P. A. Gartaganis, *Can. J. Chem.*, **34**, 785 (1956).

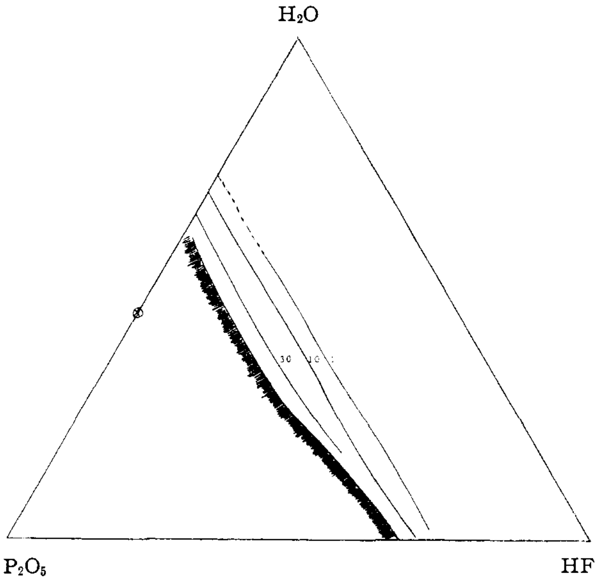


Fig. 8.—Mole percentage of phosphate middle groups at equilibrium in the H_2O–HF–P_2O_5 system. The dotted line is estimated and the ⊗ corresponds to 100% metaphosphoric acid (all phosphate middle groups). The region to the right of the feathered line is a homogeneous liquid.

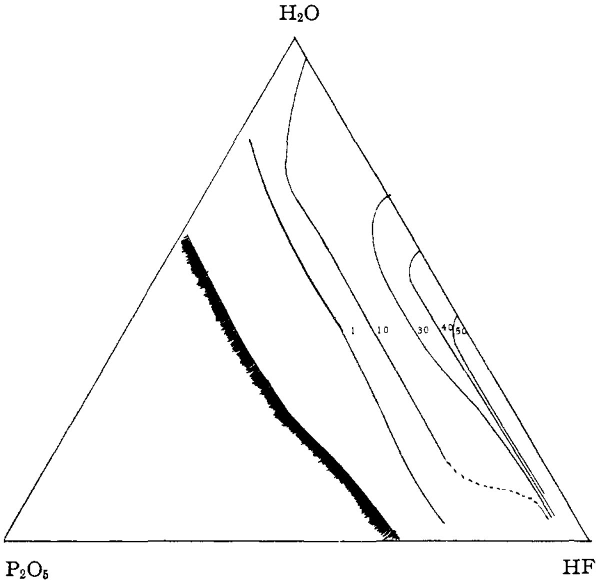


Fig. 9.—Mole percentages of free hydrogen fluoride dissolved in the H_2O–HF–P_2O_5 system at equilibrium. The dotted line is estimated and the region to the right of the feathered line is a homogeneous liquid.

orthophosphoric acid, pyrophosphoric acid and traces of higher homologs and that the liquids having the exact composition of the higher homologs of orthophosphoric acid (pyro-, tripolyphosphoric acid, etc.) are also mixtures. Values obtained in this previous work are presented on the H_2O–P_2O_5 axis in Figs. 6, 7, 8 and 10. Apparently the liquids corresponding to the various fluorophosphoric acids are also equilibrium mixtures so that a pure crystalline fluorophosphoric acid will melt to give an equilibrium liquid of a different composition.

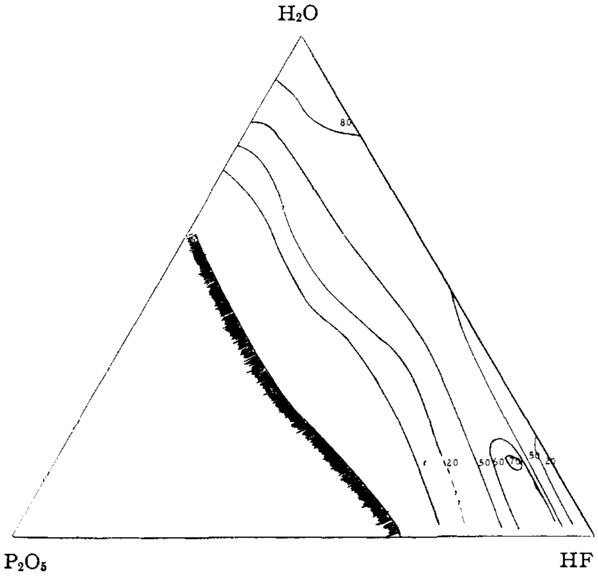


Fig. 10.—Mole percentages of free water at equilibrium in the H_2O–HF–P_2O_5 system. Values are approximate and the region to the right of the feathered line is a homogeneous liquid.

In Figs. 2 through 10, the boundary between the homogeneous liquid phase and systems containing solid materials is shown. Although they were not analyzed, it is presumed that these solids consisted of a mixture of compounds based on a number of phosphorus atoms. Throughout the major part of the area in which solid materials are to be found, the observed insolubility probably is attributable to cross linking.

The data depicted in Figs. 2 through 10 show that certain species are not found together in appreciable concentrations. This is shown in Table I where the X indicates mutual coexistence, and the 0 indicates undetectable amounts of one constituent when the other constituent was observed. From this table, it is apparent that when the supposed fluorophosphate end units, the phosphate end units and the phosphate middle units are present, the amount of free water, free hydrogen fluoride and hexafluorophosphoric acid is vanishingly small. Logically one would not expect to find free water or free hydrogen fluoride with an appreciable amount of condensed phosphate species, whether or not these species contain fluorine. Indeed, the only detectable amounts of free water with phosphate end groups occur near 75 mole % of H_2O on the H_2O–P_2O_5 axis. This indicates that the hydrogen fluoride reinforces the hydrolyzing activity of the water—a conclusion which is opposite to that which would be reached on the classical idea that "hydration" of hydrogen fluoride or its ions would tie up some of the "free water."

An interesting check on the accuracy of the nuclear magnetic resonance data was obtained by running Sample 127[13] by paper chromatography.[10] The results obtained by the two methods are given in the listing shown, in which the paper chromatographic values are italicized: percentage of phosphorus as orthophosphoric acid, 13, *11;*

Table I

Areas of Mutual Coexistence in the H_2O–HF–P_2O_5 System[a]

	Free water	Free hydrofluoric acid	Phosphate middle group	Phosphate end group	Orthophosphate	Monofluorophosphate end group	Hexafluorophosphate	Difluorophosphate
Monofluorophosphate	X	X	X	X	X	X	X	X
Difluorophosphate	X	X	X	X	X	X	X	
Hexafluorophosphate	X	X	O	O	X	O		
Monofluorophosphate end groups	O	O	X	X	X			
Orthophosphate	X	X	X	X				
Phosphate end groups	O	O	X					
Phosphate middle groups	O	O						
Free hydrofluoric acid	X							

[a] X = mutual coexistence; O = species undetectable in presence of other constituent.

Table II

Equilibrium Constants for Reactions in the H_2O-HF-P_2O_5 System

Equilibrium eq. in text	No. of compn. used in determining constant	Compn. range, mole % P_2O_5	Compn. range, mole % HF	Compn. range, mole % H_2O	Equilibrium constant Av. value	Equilibrium constant Range of calcd. values	Stand. dev.
8	11	5–15	5–35	65–85	1.2	0.3–2.8	0.7
9	8	10–20	20–45	40–60	20	5.6–51	16
10	12	10–20	55–75	10–35	10^7	10^4–10^8	Large
11	13	30–35	10–45	25–55	12	6.1–22	6

monofluorophosphoric acid, 24, *20;* difluorophosphoric acid, 6, *6;* condensed species, 57, *63.*

Equilibrium Constants.—From the data in this paper, it is possible to compute a number of equilibrium constants. Since there are nine chemical species (where structure building blocks are considered as independent species), there should be eight independent equations to completely define the equilibria involved in the system. Unfortunately we were not able to obtain equilibrium constants corresponding to all of these eight equations since, as previously noted, free hydrogen fluoride and free water are not present in measurable concentrations when the concentrations of the condensed phosphates (structure-building units) are high or *vice versa.*

Equilibria between orthophosphoric acid, the three fluorophosphoric acids, hydrogen fluoride and water are the most accurately defined by our experimental data. These equilibria are:

$$H_3PO_4 + HF = H_2PO_3F + H_2O \quad (8)$$

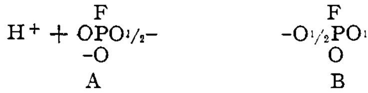
$$2H_3PO_4 + 3HF = H_2PO_3F + HPO_2F_2 + 3H_2O \quad (9)$$

$$3H_3PO_4 + 9HF = H_2PO_3F + HPO_2F_2 + HPF_6 + 7H_2O \quad (10)$$

Equilibrium constants for these relationships were calculated for the various individual samples described in the Supplementary Tables,[13] and from the smoothed values presented in Figs. 2 through 10. Since the constants obtained in the latter manner were based on averaged data, they were found to vary the least—as would be expected. The equilibrium constants are summarized in Table II from a series of calculations given in the Supplementary Tables. A value is also given in Table II for equation (11), which involves the structure units used in building condensed acids.

$$H_3PO_4 + {-O_{1/2}PO_2HO_{1/2}-} + H_2PO_3F + HPO_2FO_{1/2}{-} = HPO_2F_2 + 3(H_2PO_3O_{1/2}-) \quad (11)$$

Condensed Fluorophosphates.—In the composition region where the n.m.r. peaks[16] for phosphate end groups and middle groups were observed, a new resonance doublet was found in the P^{31} spectra, as previously noted. Since the F^{19} spectra also showed a doublet, we conclude that there is a fluorophosphate structure-building unit in which there is a single fluorine per phosphorus. This could be either a monofluorophosphate end group as shown in formula 12-A or a fluorophosphate middle group as shown in formula 12-B.



$$H^+ + \overset{F}{\underset{-O}{OPO_{1/2}-}} \qquad \overset{F}{\underset{O}{-O_{1/2}PO_{1/2}-}}$$

A B (12)

Since the only new resonance peaks which appeared in either the fluorine or the phosphorus spectra were the doublet corresponding to this particular building block, we also must conclude that the building block in question is particularly favored so that only one of the three possible fluorophosphate building units (the fluorophosphate middle group, the monofluorophosphate end group and the difluorophosphate end group) can exist to any extent in the H_2O–HF–P_2O_5 system. The spin-coupling constant for the new species is 944 ± 2 c.p.s. The chemical shifts vary somewhat with the over-all composition. In the P^{31} spectrum, they are -4.3 ± 1 and $+54 \pm 1$ p.p.m. relative to 85% H_3PO_4. In the F^{19} spectrum, the shifts relative to 100% trifluoroacetic acid are -16.5 ± 1 and $+7.1 \pm 1$ p.p.m. of the applied field at 40 megacycles.

Paper chromatography of Sample 127,[13] which was high in the new species, showed that the fluorine is distributed among all the condensed structures. This proves that the fluorophosphate

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[16] J. R. Van Wazer, C. F. Callis and J. N. Shoolery, This Journal, **77**, 4945 (1955). Also see J. R. Van Wazer, C. F. Callis, J. N. Shoolery and R. C. Jones, *ibid.*, **78**, 5715 (1956).

Table III

Quantitative Paper Chromatograhy of a Liquid (Sample 127) Based on 34.1 Mole % P_2O_5, 36.0 Mole % HF, and 29.9 Mole % H_2O

Species	Mole %	
	P_2O_5	HF
Monofluorophosphoric acid	5.7	7.8
Difluorophosphoric acid	1.9	11.3
Orthophosphoric acid	1.7	0.0
Spot A (like pyrophosphoric acid)	9.5	4.7
Spot B (like tripolyphosphoric acid)	6.5	4.9
Spot C (like unresolved tetra- and pentapolyphosphoric acids)	5.7	4.6
Spot D (like a polyphosphoric acid mixture for which $6 \leqslant n \leqslant 10$)	3.1	2.7
Totals	34.1	36.0

i.e., the tripolyphosphate molecule–ion built from two fluorine-free end groups and a monofluorophosphate middle group has the same R_f value in the Ebel acid solvent as does the fluorine-free pyrophosphate ion. The first of these two alternatives seems the most probable, since the complicated variety of mixed species which would be expected from a random build-up involving fluorophosphate middle groups and fluorine-free middle groups ought to lead to a band of partially coalesced chromatographic spots rather than the relatively clear-cut spots which were observed. However, rough calculations based on the meager quantitative paper chromatographic results shown in Table III can be interpreted to indicate that the fluorine is present in middle groups, since the structure exhibiting the newly discovered nuclear magnetic resonance peaks is truly a building unit, which can combine with the usual fluorine-free phosphate building units to make complex molecule–ions.

Table IV

Composition of the Commercial Fluorophosphates

Sample	Composition in mole %		
	Fluorine species only From F^{19} spectra	Phosphorus species only From P^{31} spectra	From combination of both F^{19} and P^{31} spectra
Potassium difluorophosphate			
difluorophosphate	78.5	80.5	
monofluorophosphate	21.5	19.5	
Sodium monofluorophosphate			
monofluorophosphate	95.2	Only monofluorophosphate detected	
hydrofluoric acid	4.8		
Potassium hexafluorophosphate	Only hexafluorophosphate detected		
Difluorophosphoric acid		Result obscured by peak broadening from paramagnetic impurities. The only resonance discernible other than that of difluorophosphate is that for small amount of monofluorophosphate	
difluorophosphate	96.5		
monofluorophosphate	3.5		
Hexafluorophosphoric acid			
hexafluorophosphate			25
difluorophosphate			1
monofluorophosphate			1
hydrofluoric acid			7
"free" water			66
Monofluorophosphoric acid			
monofluorophosphate			62
difluorophosphate			12
orthophosphate			15
end-group phosphate			7
monofluorophosphate end group			4
"free" water			0

Since the chromatograms showed only normally sharp spots at the compositions expected for the known fluorine-free condensed phosphates and since the nuclear magnetic resonance data showed only one fluorine-containing building unit having one fluorine atom per phosphorus atom, we must arrive at either one or the other of the following two conclusions. (1) If monofluorophosphate end groups are present, molecule–ions containing these end groups exhibit essentially the same R_f value as the same size fluorine-free molecule ions. (2) If fluorophosphate middle groups are present, a given molecule–ion must exhibit about the same R_f value as the next shorter fluorine-free chain; four calculated values of the ratio of monofluorophosphate end groups (assuming this is the species) to fluorine-free end groups increased greatly with increasing chain length; whereas, the same number of calculated values of the ratio of fluorophosphate middle groups (assuming these to exist) to regular middle groups gave approximately constancy as expected for a random sorting process.

From a theoretical viewpoint, the monofluorophosphate end group is expected to be much more stable in the presence of fluorine-free phosphoric acids than a fluorophosphate middle group would be. This is because the monofluorophosphate end group can dissociate to give a hydrogen ion; whereas, the fluorophosphate middle group does not ionize. If it were present in a system where ionization were taking place either completely or partially, the fluorophosphate middle group would represent an uncharged segment, which would not be expected on the basis of the most uniform distribution of the counterions. Thus, a tripolyphosphate composed of two fluorine-free end groups and a fluorophosphate middle group would exhibit a very unequal charge distribution—negative charges on both ends with none in the middle of the molecule-ion. Reorganization should not allow this state of affairs to persist.

To summarize, it seems logical to assume that the new structure building unit is a monofluorophosphate end group (see formula 12-A), although there is no definite proof for this idea. If this assumption is in error, the over-all picture of the H_2O–HF–P_2O_5 system presented herein is essentially unaltered. By this argument, neither difluorophosphate end groups, fluorophosphate middle groups or branching points are to be expected in appreciable amounts in the H_2O–HF–P_2O_5 system.

Commercial Fluorophosphates.—In order to inform other investigators about the purity of commercial fluorophosphates, we are reporting some values obtained on commercial samples during the course of this work. The analyses reported here were carried out by the nuclear magnetic resonance technique on stock samples obtained from the Ozark–Mahoning Company of Tulsa, Oklahoma. The data are presented in Table IV. It is interesting to note that qualitative paper chromatographic studies agree with the results presented in this table.

Acknowledgments.—We thank Dr. Wayne E. White of the Ozark–Mahoning Company at Tulsa, Oklahoma, for preparing the chemicals used in this work, and Mr. Albert B. Finley at Monsanto, Tennessee, for quantitative fluorine and phosphorus analyses. Mr. George F. Brautigam made some of the nuclear magnetic resonance measurements and helped to analyze the resulting traces.

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

Principles of Phosphorus Chemistry. V. Reorganization of Quadruply Connected Monophosphorus Compounds. Part A. The Phosphoryl and Thiophosphoryl Halides

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Reorganization to form the mixed halides in the two systems $POCl_3$–$POBr_3$ and $PSCl_3$–$PSBr_3$ was quantitatively investigated by means of nuclear magnetic resonance (n.m.r.). The behavior of both systems approached that calculated for a completely random reorganization with equilibrium being achieved in less than one week at 130°. The mixed halides, $POClBr_2$, $POCl_2Br$, $PSClBr_2$ and $PSCl_2Br$ can be made in yields of over 40% by heating mixtures of $POCl_3$ and $POBr_3$ or of $PSCl_3$ and $PSBr_3$ for a few hours at temperatures of above 200°. It is shown that, under suitable conditions, the percentage of the total phosphorus present as a given compound in a mixture can be determined by n.m.r. to within better than ±1 mole %.

Structural reorganization based on exchange of ligands attached to the phosphorus atom is a common phenomenon in the chemistry of phosphorus compounds. In many respects, compounds based on sp^3 hybrids of phosphorus are similar to organic compounds based on sp^2 hybrids of carbon. This similarity may, at least in part, be attributed to π-bonding, a subject which was discussed in the first paper[1] of this series. The similarity is exemplified by the reorganization process, since many compounds based on a single phosphorus atom undergo reorganization about as rapidly as do organic esters and the reorganization of organic polyesters finds many parallels in phosphorus chemistry.[2]

In a number of forthcoming papers in this series, we shall attempt to outline the principles involved in reorganization of phosphorus compounds and to describe a sufficient number of examples to prove how general this behavior is. The present paper is concerned with reorganization equilibrium in two related systems based on a single phosphorus atom per molecule: $POCl_3$–$POBr_3$ and $PSCl_3$–$PSBr_3$.

Experimental Section

The phosphorus oxychloride $POCl_3$ used in these experiments was redistilled from the Monsanto commercial-grade product. The phosphorus oxybromide $POBr_3$ was purchased. Nuclear magnetic resonance measurements showed that this sample contained about 5% of the phosphorus as phosphorus tribromide. Since this was a relatively small amount of impurity which could be accounted for in our studies, the sample was used without further purification.[3]

The thiophosphoryl chloride was made from phosphorus trichloride and sulfur according to the method of Inorganic Syntheses.[4] The thiophosphoryl bromide also was prepared according to the method of Booth and Seabright.[5] The product had a sharp melting point at 38°.

Reorganization was carried out by weighing the desired proportions of the trichloride and tribromide and sealing them in a thick-walled Pyrex tube which was held in an oven at 130° after thorough mixing. It was found that in an hour's time, the phosphoryl halide system reorganized so as to give about 5% of the amount of mixed oxyhalides expected at equilibrium, whereas, in the thiophosphoryl halide system, only a trace of the mixed halides was found.

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(1) J. R. Van Wazer, THIS JOURNAL, **78**, 5709 (1956).

(2) J. R. Parks and J. R. Van Wazer, *ibid.*, **79**, 4890 (1957).

(3) This small amount of PBr_3 has been weighed as $POBr_3$ and has only a slightly smaller molecular weight. It reorganizes with the chlorine-containing molecules to give an equilibrium similar to the quadruply connected molecules, making practically the desired ratio of Cl:Br atoms available for the study.

(4) T. Moeller, H. J. Birch and N. C. Nielsen, "Inorganic Syntheses," Vol. IV, McGraw-Hill Book Co., New York, N. Y., 1953, p. 71.

(5) H. S. Booth and C. A. Seabright, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., New York, N. Y., 1946, p. 153.