Principles of Phosphorus Chemistry. XIV.
Interchanges in Esters of Monophosphorus Acids[1]

By KURT MOEDRITZER,[2] GRAHAM M. BURCH,[3] JOHN R. VAN WAZER, AND HEINZ K. HOFMEISTER[4]

Redistribution of methyl and ethyl groups has been studied by gas chromatography for trialkyl and dialkyl phosphites and trialkyl phosphates. Essentially random-interchange equilibria were found for these three systems: $P(OCH_3)_3$ *vs.* $P(OC_2H_5)_3$, $HPO(OCH_3)_2$ *vs.* $HPO(OC_2H_5)_2$, and $OP(OCH_3)_3$ *vs.* $OP(OC_2H_5)_3$. The time for attainment of equilibrium in the trialkyl phosphite system at room temperature ranges from months with no catalyst to minutes with an acid catalyst. P^{31} and H^1 nuclear magnetic resonance were used to study exchange of substituents on phosphorus in the systems: $P(SCH_3)_3$ *vs.* $P(SC_4H_9)_3$ and $P(SC_4H_9)_3$ *vs.* PCl_3. The equilibrium constants were found to be very close to those for the equivalent compounds in which oxygen atoms occur in place of all of the sulfur atoms. Attempts to cause an RO group to exchange for an RS group were consistently unsuccessful.

As shown by previous papers in this series,[5] structural reorganization (*i.e.*, scrambling reactions involving large as well as the more usual small molecules) plays an important role in phosphorus chemistry. Deviations from random scrambling of the substituents are probably primarily due to the enthalpy contribution to the free energy of reorganization, and such contributions are generally less than 1–2 kcal./mole.[6] However, these small differences in the enthalpy of reorganization cause extreme variations in the various kinds and sizes of molecular species found in families of phosphorus-based compounds at equilibrium.[5–7] The fact that the end and middle groups in the completely esterified polyphosphoric acids are present to considerably greater amounts than would be predicted from random sorting of methoxyl and oxyphosphoryl groups[8] prompted the investigation of exchange of alkoxyl groups on the orthophosphate esters to see if this exchange were random. Likewise, the presence of end groups in the completely esterified, completely sulfur-substituted polythiophosphoric acids in amounts considerably less than predicted by random sorting[9] focused attention on ester interchange between orthothio acids. Previous work on the nonrandom exchange of oxygen and sulfur in the isolated position on the quadruply-connected phosphorus[10] also indicated need for investigating the equilibria involved in interchange of alkoxy for alkyl mercapto groups. These and related studies are described herein.

Experimental

Known Compounds.—The phosphites used in this study were redistilled from commercial products purchased from Virginia-Carolina Chemical Company. The triethyl phosphate came from Eastman Organic Chemical Company and the trimethyl phosphate from Aldrich Chemical Company. Both were redistilled.

The tributyl and trimethyl thiophosphites, $P(SR)_3$, were prepared according to the literature[11] and carefully redistilled. Dimethyl methylphosphonate, $CH_3P(O)(OCH_3)_2$, was made by the rearrangement of refluxing trimethyl phosphite, employing a trace amount of dimethyl sulfate as catalyst. The PCl_3 was a high-purity redistilled Monsanto product.

New Compounds.—Substances which have not been previously described in the literature were prepared either as reagents for scrambling reactions or as standards for elucidation of nuclear magnetic resonance (n.m.r.) chemical shifts. These compounds are listed in Table I, where their synthesis is reported in condensed form and certain physical properties[12] useful for characterization are presented. The existence and purity of these compounds were adequately demonstrated by physical methods. Thus, for example, S-butyl methylphosphonochloridothioate, compound I, exhibited an H^1 n.m.r. spectrum in which one quarter of the total hydrogen was present as a methyl group, the chemical shift of which showed it was bonded directly to the phosphorus. The remaining hydrogens gave the pattern corresponding to a butyl group bonded to a sulfur atom. Since there was a single resonance in the P^{31} n.m.r. spectrum having a chemical shift in the range[13] to be expected for this type of compound and H^1 n.m.r. gave no evidence of hydrogen-containing impurities, we conclude that this preparation met the usual standards of purity. It definitely had less than 3% of either the total phosphorus or the total hydrogen present in the form of other structures.

For all compounds except IV, the n.m.r. spectra were readily interpretable. For IV, however, three sharp n.m.r. peaks were observed in the H^1 spectra, even under the optimum conditions of a 50 c.p.s. sweep width and unusually high resolution with the Varian A-60 spectrometer. As shown in Fig. 1, dilution with about three parts of carbon tetrachloride caused this unexpected three-peak spectrum to split into the expected pair of equal-area doublets. It is believed that such exact superposition of two peaks has not been previously reported. Except for the

(1) Presented in part at the 141st National Meeting of the American Chemical Society, Washington, D. C., March 22, 1962. Previous papers in this series have appeared in *J. Am. Chem. Soc.*

(2) On leave of absence from the Inorganic Chemicals Division of Monsanto, July 1961–July 1962.

(3) Visiting from England, October, 1961–October, 1962.

(4) On leave of absence from Göttingen University, Germany, July, 1961–July, 1962.

(5) See paper IV, *J. Am. Chem. Soc.*, **81**, 6360 (1959), through paper XIII, *ibid.*, **84**, 3052 (1962).

(6) J. R. Van Wazer, *Am. Scientist*, **50**, 450 (1962).

(7) J. R. Van Wazer and C. F. Callis, "Inorganic Polymers," F. G. A. Stone and W. A. G. Graham, Ed., Academic Press, New York, N. Y., 1962, pp. 28–97.

(8) E. Schwarzmann and J. R. Van Wazer, *J. Am. Chem. Soc.*, **83**, 365 (1961).

(9) L. Maier and J. R. Van Wazer, *ibid.*, **84**, 3054 (1962); also see Fig. 18 on p. 469 of ref. 6.

(10) L. C. D. Groenweghe and J. H. Payne, *J. Am. Chem. Soc.*, **83**, 1811 (1961).

(11) A. Lippert and E. E. Reid, *ibid.*, **60**, 2370 (1938).

(12) L. C. Thomas and R. A. Chittenden, *Chem. Ind.* (London), 1913 (1961), have given a description of the ultraviolet spectrum of the thiophosphoryl moiety.

(13) V. Mark, J. R. Van Wazer, and M. M. Crutchfield, "Progress in Phosphorus Chemistry," M. Grayson and E. J. Griffith, Ed., to be published in 1963.

TABLE I

NEW COMPOUNDS

No.	Formula	Synthesis[a]	Yield, % based on P	Impurity,[b] %	B.p., °C. (mm.)	n^{25}D	P^{31} chem. shift,[c] p.p.m.	H¹ n.m.r. of CH₃[d] Chem. shift, p.p.m.	J_{H-P}, c.p.s.	Other H¹ n.m.r.[e]	Prominent ultraviolet bands
I	$CH_3P(O)(SC_4H_9)Cl$	$C_4H_9SH + (C_2H_5)_3N$ to $CH_3P(O)Cl_2$ in CH_2Cl_2; filt.; ether extract; vac. distil	37	<3	69.5-70 (0.25)	1.4997	-60.6	-2.30	14.3	³/₄ of H as n-butyl	Phosphoryl
II	$CH_3P(O)(SC_4H_9)_2$	Rearr. of VI with CH₃I at 120°. After 4 hr., ultra-violet band for C–O gone, phosphoryl band at max. Then vac. distil	80+	ca. 3	46-48 (0.02)	1.4778	-53.3	-2.00	13.0	Same as VI	Phosphoryl at 8.4 μ
III	$CH_3P(O)(OCH_3)(SC_4H_9)$	$CH_3OH + (C_2H_5)_3N$ to I in ether; filt.; evap.; vac. distil	58	<3	46-48 (0.02)	1.4778	-53.3	CH_3O, -3.63 CH_3P, -1.72 ($CH_3O = CH_3P$ in area)	12.5 15.5	1 n-butyl per CH₃O or CH₃P	Phosphoryl at 8.15 μ
IV	$CH_3P(S)(SCH_3)Cl$	Distil fraction from prep. of V	12	3-6 of V only	58-62 (0.40)	1.6038	-94.8	See Fig. 1 CH_3S, -2.55 CH_3P, -2.59	18.5 13.5	...	No phosphoryl; thiophosphoryl[f] at 13.0 and 15.5 μ
V	$CH_3P(S)(SCH_3)_2$	$CH_3CH + (C_2H_5)_3N$ in pentane to $CH_3P(S)Cl_2$ in pentane; filt.; evap.; vac. distil	29	3-6 of IV only	91-94 (0.40)	1.6331	-82.6	CH_3S, -2.35 CH_3P, -2.28 ($CH_3S = 2$ CH₃P in area)	15.9 12.9	...	No phosphoryl; thiophosphoryl[f] at 13.3 and 15.8 μ
VI	$(CH_3O)P(SC_4H_9)_2$	$CH_3OH + (C_2H_5)_3N$ to FCl_3 in pentane; then $C_4H_9SH + (C_2H_5N)$; repeated in reverse order; filt.; evap.; vac. distil .nixel preps.	38	ca. 4 of $P(SC_4H_9)_3$	94-95 (0.15)	1.5152	-162.1	-3.46	8.5	⁶/₇ of H as n-butyl	No phosphoryl or thiophosphoryl

[a] Original reactions at 0° unless specified. All major steps noted. [b] Calculated from n.m.r. spectra on basis of % of total H or total P. [c] Referenced to 85% H_3PO_4 in p.p.m. of the magnetic field. [d] Referenced to tetramethylsilane. [e] Fraction of total hydrogen corresponding to characteristic n-butyl spectrum. [f] See ref. 13.
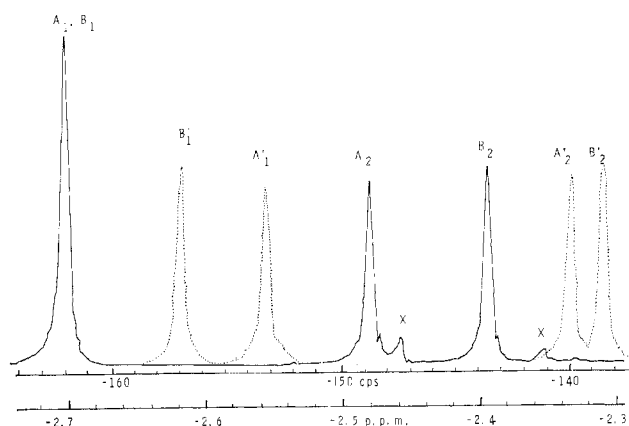
Fig. 1.—Proton n.m.r. spectrum of $CH_3P(S)(SCH_3)Cl$ in undiluted form (solid line) and diluted with three parts of carbon tetrachloride (dotted line). Peaks A_1 and A_2 correspond to the doublet of the CH_3P group and B_1 and B_2 to the CH_3S group when undiluted. Peaks A_1' and A_2' correspond to the CH_3P and B_1' and B_2' to the CH_3S when diluted. Peak X represents the impurity $CH_3P(S)(SCH_3)_2$. The other two resonances corresponding to this compound are off-scale upfield.

finding that the H^1 n.m.r. doublet corresponding to the CH_3P group shifts upfield at a greater rate with dilution than does the CH_3SP doublet, this spectrum would have become one of the few mysteries in n.m.r. structure work, assuming that the chemical structure had been proven by other means.

Analytical Techniques.—Gas chromatography was used for the esters of the oxyacids of phosphorus and P^{31} n.m.r., with checking by H^1 n.m.r., for the sulfur-containing esters. The gas chromatography was done with a Perkin-Elmer vapor fractometer, Model 154D, having a thermistor-bead thermal-conductivity detector and a digital-integrator print-out. A 3-m. column was filled with 10% Tween 80 on C-22 firebrick for all studies. For the trialkyl phosphites, the column temperature was 114°; for the dialkyl phosphites, it was 135°; and for the trialkyl phosphates, 150°; 2–4 μl. samples were employed.

When mixtures of freshly distilled trimethyl phosphite and triethyl phosphite were kept at room temperature for several days or less and then analyzed, only two sharp chromatographic peaks were obtained, the retention times of which agreed with those of the pure starting materials. The ratio of the areas of these two peaks equaled the mole ratio of the starting mixture within several per cent and did not change when the column temperature was raised to 200° from the lowest possible temperature (about 114°) for optimum resolution. The error in this determination has three possible sources: faulty preparation of the mixture, detector response, and the digital integrator. As described elsewhere,[14] mathematical analysis of this error (using a regression technique with an IBM-704 computer) showed that it could be attributed to a decrease in detector sensitivity by a factor of 0.97 for the triethyl phosphite as compared to the trimethyl or the mixed methyl ethyl phosphites. In all cases, the detector response was found to be linear. In the case of the dialkyl phosphites and trialkyl phosphates, fresh unheated mixtures of the end-member compounds again gave pairs of sharp chromatographic peaks, the areas of which were proportional to the amount of the two compounds mixed together.

The H^1 n.m.r. data were obtained with a Varian A-60 spectrometer running at a frequency of 60 Mc., generally using the smallest available sweep width (50 c.p.s. for the entire scale) and a sweep time of 250 sec. The P^{31} n.m.r. studies on a Varian HR-60 high-resolution spectrometer utilized a V-4311 radiofrequency probe operating at 24.288 Mc. Measurements were all made in 5-mm. precision tubes and negative shifts were measured downfield. In the case of the H^1 spectra, referencing was done by adding a drop of the standard, tetramethylsilane,

(14) L. C. D. Groenweghe and J. R. Van Wazer, *Anal. Chem.*, in press.

to the test sample; for the P^{31} spectra, the reference standard, 85% H_3PO_4, was enclosed in a sealed thin-walled capillary (melting-point tube) which was inserted into the 5-mm. sample tube. In all cases, care was taken to avoid magnetic saturation so that peak areas were exactly proportional to the amount of the resonating nuclei. Integration of the resonance peaks was carried out by reproducing the n.m.r. traces on a Xerox copier and accurately cutting out and weighing the peaks. However, in some cases, the electronic integrator on the A-60 spectrometer was used. The integration error is *mainly* due to faulty establishment of the base line.[14]

Scrambling Reactions.—The redistribution studies were carried out by sealing various proportions of the two reagents (unmixed esters) in glass tubes (7-mm. or thick-walled 15-mm. o.d.) and heating the tubes for the specified lengths of time at the selected temperature. These times were chosen to be considerably longer than the period needed for equilibration in order that there would be no questions as to whether equilibrium were reached.

Pilot studies to estimate the minimum time for equilibration were run on all of the systems investigated. In these runs, only the equilibration time was of interest so that a sequence of output graphs from n.m.r. or gas chromatography were generally intercompared by superposition only, without measuring and normalizing the individual peak area. In addition, some of the room-temperature pilot runs with the esters of oxyacids were done in screw-cap vials and, with the sulfur-containing compounds, in 5-mm. sealed tubes which could be re-examined by n.m.r. without opening.

A number of different proportions of a given pair of unmixed esters were studied so that tentative assignment of a particular gas-chromatographic or n.m.r. peak could be verified by a material balance (see the composition ratios from reactants and from products in Tables II–VI). The tentative assignments in gas chromatography were made by extrapolation of the retention times of the unmixed esters. The over-all stoichiometry of a mixture made, say, from $P(OR)_3$ and $P(OR')_3$ is expressed in terms of a composition ratio or R-value[6,7] $\equiv (RO)/P$ mole ratio.

Results and Conclusions

Trialkyl Phosphites.—Addition of trace amounts (*ca.* 0.01% by wt.) of dry HCl to the mixture of trialkyl phosphites at room temperature or heating in closed tubes at 120° led to equilibrium in the exchange of alkyl groups in about 10–15 hr. The catalyzed equilibrium data reported here were obtained after 20 hr. or more at 120°. Higher temperatures were not used because Arbuzov rearrangement of the methyl group occurs rapidly above *ca.* 150°. Base catalysis by sodium methoxide was not observed. It is interesting to note that mixtures of unpurified commercial trialkyl phosphites reach reorganization equilibrium in several days at room temperature due to catalysis, presumably by acidic impurities.

Equilibrium data for the system $P(OCH_3)_3$–$P(OC_2H_5)_3$ are presented in Table II, where the experimental results are compared to values calculated from the equilibrium constants given below. As can be seen, the agreement between the individual experimental values and the calculated values is quite good.

$$K_1 = [P(OCH_3)_3][P(OCH_3)(OC_2H_5)_2]/$$
$$[P(OCH_3)_2(OC_2H_5)]^2 = 0.394 \quad (1)$$

$$K_2 = [P(OC_2H_5)_3][P(OCH_3)_2(OC_2H_5)]/$$
$$[P(OCH_3)(OC_2H_5)_2]^2 = 0.367 \quad (2)$$

For these equilibrium constants, the standard devia-

TABLE II

EQUILIBRIUM DATA ON THE TRIALKYL PHOSPHITES

—CH₃O/P ratio from—		% of total phosphorus			
Reactants	Products	$P(OCH_3)_3$	$P(OCH_3)_2$-(OC_2H_5)	$P(OCH_3)$-$(OC_2H_5)_2$	$P(OC_2H_5)_3$
0.30	0.29	5.8	1.7	3.7	88.9
	.31	4.7	2.7	7.2	85.4
		(0.1)ᵃ	(3.0)	(23.6)	(73.3)
.60	.64	0.9	9.5	37.4	52.2
	.60	11.1	4.6	9.8	74.2
		(1.0)	(10.1)	(36.6)	(52.2)
.90	.89	11.7	10.7	25.1	52.5
	.91	9.4	12.0	30.8	47.6
		(3.3)	(19.2)	(40.8)	(35.7)
1.20	1.20	14.5	17.8	34.0	33.8
	1.21	12.4	20.2	37.9	29.6
	1.24	10.0	24.9	38.6	26.6
		(7.3)	(28.6)	(41.0)	(23.2)
1.50	1.55	14.5	35.7	37.4	12.5
	1.48	18.5	25.9	37.1	18.8
	1.50	11.0	36.9	40.2	11.9
		(13.7)	(36.6)	(35.9)	(13.9)
1.80	1.85	24.9	39.4	30.1	5.6
	1.81	23.6	39.4	29.5	7.5
		(21.8)	(41.7)	(28.0)	(7.4)
2.10	2.09	32.3	45.2	20.6	1.9
	2.08	33.1	43.2	21.0	2.7
		(35.4)	(42.6)	(18.8)	(3.3)
2.40	2.39	50.3	39.1	10.0	0.6
	2.43	51.6	40.0	7.9	0.6
	2.42	56.5	29.9	11.9	1.6
		(51.9)	(37.3)	(9.8)	(1.0)

ᵃ Amounts in parentheses are calculated from $K_1 = 0.394$ and $K_2 = 0.367$, using the CH_3O/P ratio from the reactants.

Fig. 2.—Semilog plot of the diminution of the relative concentrations of $P(OCH_3)_3$ (O) and $P(OC_2H_5)_3$ (△) as a function of time: curve 1 (upper time scale) without catalyst; curve 2 (lower time scale) acid catalyst.

tions, s, based on the stoichiometry[14] are 0.019 and 0.020, respectively. The deviations computed from the weighted distributions of the equilibrium constants[14] are 0.12 and 0.12, respectively. This means that the neglect of activity coefficients in computing the constants is experimentally detectable (see Table II).

If the correction by a factor of 0.97 due to detector sensitivity (see Experimental section and ref. 14) had not been employed, the equilibrium constants would turn out to be $K_1 = 0.40$ and $K_2 = 0.11$, with standard deviations, based on stoichiometry, of 0.03 and 0.01, respectively, and, based on the equilibrium constants, of 0.14 and 0.28. The detector-sensitivity correction is seen to bring the computed values of K_1 and K_2 closer to the random-sorting value of 0.333 and to reduce the standard deviation.

As shown in Fig. 2, when equimolar amounts of triethyl and trimethyl phosphites were combined, the diminution in the amounts of these species and the increase in the amounts of the mixed esters could be empirically fitted to first-order kinetics. At 25°, with no catalyst, the pseudo-first-order rate constants were about 0.0001 hr.⁻¹; with catalytic amounts (>0.1%) of HCl, these constants increased to 0.2 hr.⁻¹.

Some preliminary experiments were carried out by P³¹ n.m.r. on the system $P(OC_6H_5)_3$ *vs.* $P(OC_4H_9)_3$. Although methyl and ethyl groups in trialkyl phosphites exchange readily at 120°, no sign of redistribution of phenyl and *n*-butyl groups was observed after 2 days at 170°. After several days at 200°, it was found that
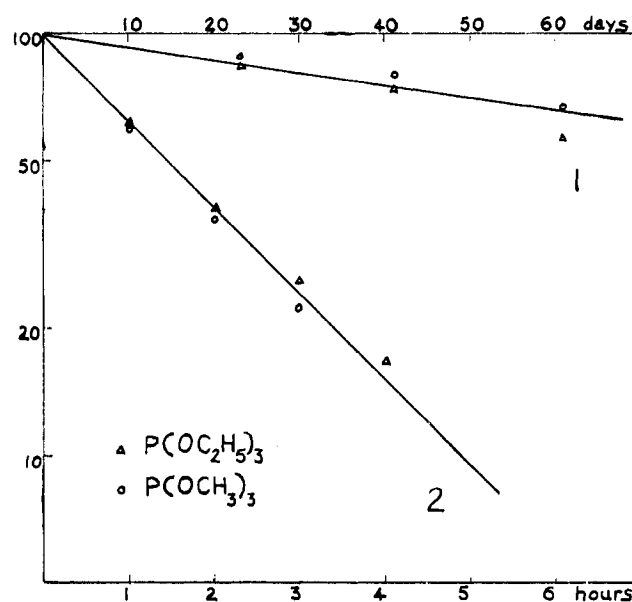
Arbuzov rearrangement of the butyl group obscured the redistribution reaction.

Dialkyl Phosphites.—When our work was nearly complete, a paper appeared describing application of gas chromatography to the investigation of ester interchange in dialkyl phosphites.[15] However, in that study, equilibrium was not measured.

For the freshly distilled pure dialkyl phosphites, it was found that there was less than 5% reorganization after 3 months at room temperature. However, in closed tubes, at 150° with no catalyst, test experiments showed that equilibrium was achieved in less than 12 hr. Acid but not base catalysis was found. The equilibrium data reported here correspond to 17 hr. with no catalyst at 150°.

The data for the system $HP(O)(OCH_3)_2$ *vs.* $HP(O)(OC_2H_5)_2$ are given in Table III, where the experimental values are again compared with calculated values, obtained from the equilibrium constant

$$K = [HPO(OCH_3)_2][HPO(OC_2H_5)_2]/[HPO(OCH_3)(OC_2H_5)]^2 = 0.286 \quad (3)$$

$$s = 0.024$$

This constant is close to the ideal random value of 0.2500.

In dialkyl phosphites, the lone hydrogen is bonded to the phosphorus atom as evidenced by n.m.r. spin–spin splitting.[16] It should be noted that the hydrogen does not exchange with the alkoxyl groups under the conditions employed here (150°), although it does ex-

(15) A. DeRose, W. Gerrard, and E. F. Mooney, *Chem. Ind.* (London), 1449 (1961).

(16) C. F. Callis, J. R. Van Wazer, J. N. Shoolery, and W. A. Anderson, *J. Am. Chem. Soc.*, **79**, 2720 (1957). Despite the comments of B. A. Arbuzov, "Khimiya i Primenenie Fosfororganicheskikh Soedinenii," Acad. Sci. U.S.S.R. Publ. House, Moscow, 1962, Chapter 2, there is no question concerning the fact that this hydrogen is bonded to the phosphorus since unequivocal n.m.r. proof has now been obtained in many laboratories.

TABLE III
EQUILIBRIUM DATA ON THE DIALKYL PHOSPHITES

CH₃O/P ratio from		% of total phosphorus		
Reactants	Products	HPO(OCH₃)₂	HP(OCH₃)(OC₂H₅)	HPO(OC₂H₅)₂
0.29	0.27	1.2	24.8	74.0
		(2.2)ᵃ	(23.5)	(74.3)
.57	.62	11.9	38.2	49.9
		(9.3)	(40.5)	(50.2)
1.00	.97	24.3	49.7	26.0
		(25.1)	(48.4)	(26.5)
1.33	1.27	40.0	47.2	12.8
		(42.9)	(44.2)	(12.9)
1.67	1.67	68.1	30.6	1.3
		(70.1)	(27.1)	(2.8)

ᵃ Amounts in parentheses are computed from the equilibrium constants given in the text, using the mean of the CH₃O/P ratios from the reactants and the products.

change[17] at room temperature with the hydrogen of water. This represents a case where the reaction mechanisms permit interchange of hydrogens with each other and of alkoxyl groups with each other at lower temperatures than would be needed for redistribution of hydrogens with alkoxyl groups or for the alternate process of formation of alcohols plus P–P-bridged solids.

Trialkyl Phosphates.—For the mixtures of trialkyl phosphates with or without HCl as catalyst, no reorganization was found after 3 months at room temperature. With trace amounts of NaOCH₃, reorganization equilibrium was achieved after 6 days in closed tubes at 120°. Under the same conditions with no catalyst, there was no sign of reorganization. At 200° in closed tubes with no catalyst, reorganization equilibrium was achieved within about 7 days. The equilibrium data reported here correspond to 14 days at 200°. Because of the high temperatures involved, gas pressures resulting from formation of volatile by-products (methyl ether, ethylene, etc.) were noted in the sealed tubes. However, such side reactions were small and did not affect the material balances within the reported experimental errors.

The experimental data are presented in Table IV. The parenthetical values in this table are computed from the equilibrium constants given in eq. 4 and 5.

$$K_1 = [OP(OCH_3)_3][OP(OCH_3)(OC_2H_5)_2]/$$
$$[OP(OCH_3)_2(OC_2H_5)]^2 = 0.224 \quad (4)$$

$$s_1 = 0.028$$

$$K_2 = [OP(OCH_3)_2(OC_2H_5)][OP(OC_2H_5)_3]/$$
$$[OP(OCH_3)(OC_2H_5)_2]^2 = 0.348 \quad (5)$$

$$s_2 = 0.037$$

These constants are not far from the ideally random case for which $K_1 = K_2 = 0.3333$. A preliminary study of the system OP(OCH₃)₃ *vs.* OP(OC₆H₅)₃ by P³¹ n.m.r.[18] showed that exchange of methyl and phenyl groups is considerably slower than that of methyl and ethyl groups, as was the case for the phosphite system.

(17) Z. Luz and B. Silver, *J. Am. Chem. Soc.*, **83**, 4518 (1961).
(18) The P³¹ chemical shift for OP(OCH₃)₂(OC₆H₅) is +5 p.p.m. and for OP(OCH₃)(OC₆H₅)₂ is +11 p.p.m. relative to 85% H₃PO₄ with positive shifts being upfield.

TABLE IV
EQUILIBRIUM DATA ON THE TRIALKYL PHOSPHATES

CH₃O/P ratio from		% of total phosphorus			
Reactants	Products	OP(OCH₃)₃	OP(OCH₃)₂(OC₂H₅)	OP(OCH₃)(OC₂H₅)₂	OP(OC₂H₅)₃
0.38	0.32	Trace	2.3	26.8	70.9
		(0.1)ᵃ	(3.5)	(26.4)	(70.0)
1.00	0.92	3.1	19.7	43.5	33.7
		(2.4)	(21.7)	(43.9)	(31.0)
1.50	1.40	6.4	39.8	40.2	13.6
		(9.2)	(39.5)	(38.3)	(13.0)
2.00	1.95	27.8	46.1	19.4	6.7
		(25.7)	(49.5)	(21.5)	(3.3)
2.63	2.59	63.0	33.2	3.8	Trace
		(63.9)	(32.3)	(3.7)	(0.1)

ᵃ Amounts in parentheses are computed from the equilibrium constants given in the text, using the mean of the CH₃O/P ratios from the reactants and the products.

Trialkyl Thiophosphites.—In the usual mannner various mixtures of the two starting materials, P(SCH₃)₃ and P[S(*n*-C₄H₉)]₃, were heated in the presence of a trace of HCl at 120° for 3 days, since preliminary experiments indicated that equilibrium was achieved in less than this time. The data are presented in Table V and the equilibrium constants for this system are given in eq. 6 and 7.

$$K_1 = [(C_4H_9S)_2P(SCH_3)][P(SCH_3)_3]/$$
$$[(C_4H_9S)P(SCH_3)_2]^2 = 0.335 \quad (6)$$

$$s_1 = 0.005$$

$$K_2 = [(C_4H_9S)_3P][(C_4H_9S)P(SCH_3)_2]/$$
$$[(C_4H_9S)_2P(SCH_3)]^2 = 0.322 \quad (7)$$

$$s_2 = 0.004$$

TABLE V
EQUILIBRIUM DATA ON THE TRIALKYL THIOPHOSPHITES

CH₃S/P ratio from		% of total P			
Reactants	Products	P(SCH₃)₃	P(SCH₃)₂(SC₄H₉)	P(SCH₃)(SC₄H₉)₂	P(SC₄H₉)₃
0.50	0.50	0.6	6.9	34.4	58.1
		(0.5)ᵃ	(7.0)	(34.7)	(57.9)
0.98	0.99	3.3	22.2	44.5	30.0
		(3.5)	(21.8)	(44.4)	(30.3)
1.50	1.49	12.1	37.5	37.8	12.7
		(12.2)	(37.7)	(37.6)	(12.5)
1.99	2.02	29.9	45.0	21.8	3.3
		(29.6)	(44.9)	(21.9)	(3.6)
2.49	2.51	57.9	35.1	7.0	0
		(57.7)	(35.0)	(6.8)	(0.4)

ᵃ Amounts in parentheses are computed from the equilibrium constants given in the text, using the mean of the CH₃O/P ratios from the reactants and the products.

As was found to be the case for the sulfur-free trialkyl phosphites, this system is essentially random.

Alkoxyl–Mercapto Interchange.—Considerable effort was expended in attempting to exchange an alkoxyl for an alkyl mercapto group on triply connected phosphorus but to no avail. Studies on the systems P(SC₄H₉)₃ *vs.* P(OC₄H₉)₃, P(SC₄H₉)₃ *vs.* P(OC₆H₅)₃, and P(SC₄H₉)₃ *vs.* P(OCH₃)₃ showed that at temperatures where ester interchange was found with either trialkyl phosphites or trialkyl trithiophosphites, there was no exchange of SR for OR groups, either with or without a per cent or so of potentially catalytic additives (AlCl₃,

HCl, NaOCH$_3$). At very much longer heating times or appreciably higher temperatures, including those conditions sufficiently extreme to give blackish tars, brown sludges, and some red to brown solids, there was no evidence of the formation of phosphites having both alkyl mercapto and alkoxyl groups in the molecule. Indeed, the major interpretable chemical finding was the well known rearrangement of P(OR)$_3$, where R = CH$_3$ or C$_4$H$_9$, to RP(O)(OR)$_2$.

During a period in this study, it appeared that the rearranged product might be exchanging an OR for an SR group of the thiophosphite, so the systems P(SC$_4$-H$_9$)$_3$ *vs.* CH$_3$P(O)(OCH$_3$)$_2$ and P(SCH$_3$)$_3$ *vs.* CH$_3$P(O)-(OCH$_3$)$_2$ were investigated. Again, extensive decomposition to give sludges was the first reaction to occur as either the time or temperature of heating was increased. Even under these conditions, there was no acceptable n.m.r. evidence for interchange of alkyl mercapto and alkoxyl groups.

As part of this investigation, the thermal decomposition of pure P[S(*n*-C$_4$H$_9$)]$_3$ was studied. At 210°, this compound was found to disappear at a rate corresponding to a half-life of about 80 hr. As the n.m.r. peak at −118 p.p.m. corresponding to the pure compound diminished, an insoluble yellow precipitate was seen to build up; while, in the liquid phase, one other P^{31} resonance, at −93 p.p.m., was seen to appear and then increase in magnitude. This resonance was assigned to the compound SP(SC$_4$H$_9$)$_3$. A preparation of this compound from pure tributyl trithiophosphite and sulfur confirmed this assignment, both by P^{31} and H^1 n.m.r. peak positions and by similarity of the H^1 n.m.r. fine structure. The insoluble yellow precipitate was amorphous to X-rays and fully insoluble in common organic solvents. It was therefore concluded that the material is probably a three-dimensional polymer. The precipitate was found to have 22.5% P and 27.3% S by elemental analysis. The remainder was shown to contain organic matter since charring and some gasification occurred upon deflagration. The material balance indicates that the empirical equation for the decomposition of tri-*n*-butyl thiophosphite is

2P(SC$_4$H$_9$)$_3$ ⟶ SP(SC$_4$H$_9$)$_3$ +

$$[PS(C_4H_9)] \downarrow + (C_4H_9)_2S \quad (8)$$
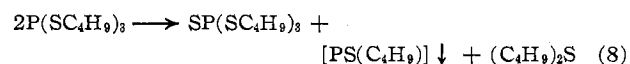
where [PS(C$_4$H$_9$)] is a network polymer containing P–P bonds.

Alkyl Thiophosphochlorodites.—In the system P-(SC$_4$H$_9$)$_3$ *vs.* PCl$_3$, significant interchange is evident after a period of 24 hr. at 120° and equilibration was achieved after 48 hr. at 120°. Equilibrium data obtained after 4 days at 120° are reported in Table VI, where the experimental results are compared with values computed from the equilibrium constants shown in eq. 9 and 10.

$$K_1 = [\text{PCl}_3][(C_4H_9S)_2PCl]/[(C_4H_9S)PCl_2]^2 = 0.157 \quad (9)$$

$$s_1 = 0.05$$

$$K_2 = [(C_4H_9S)PCl_2][(C_4H_9S)_3P]/$$
$$[(C_4H_9S)_2PCl]^2 = 0.302 \quad (10)$$

$$s_2 = 0.008$$

TABLE VI

EQUILIBRIUM DATA ON THE BUTYLMERCAPTO CHLOROPHOSPHITES

C$_4$H$_9$S/P ratio from—		————% of total phosphorus————			
Reactants	Products	P(SC$_4$H$_9$)$_3$	P(SC$_4$H$_9$)$_2$-Cl	P(SC$_4$H$_9$)-Cl$_2$	PCl$_3$
0.51	0.53	0	5.9	40.9	53.2
		(0.0)[a]	(4.6)	(42.8)	(52.6)
1.00	1.03	0	22.4	58.5	19.0
		(0.2)	(21.5)	(57.8)	(20.5)
1.50	1.50	0	54.4	40.7	4.9
		(1.7)	(51.2)	(42.5)	(4.6)
2.00	1.99	12.3	74.1	13.6	0
		(12.6)	(74.6)	(12.5)	(0.3)
2.49	2.46	46.8	52.0	1.1	0
		(48.9)	(49.6)	(1.4)	(0.0)

[a] Amounts in parentheses are computed from the equilibrium constants given in the text, using the mean of the CH$_3$O/P ratios from the reactants and the products.

These constants are similar to those obtained[19] for the equilibrium between the sulfur-free ester of phosphorus acid and phosphorus trichloride. At a 1:1 ratio of halogen to the organic group, we observed mole ratios of PG$_3$:PG$_2$Cl:PGCl$_2$:PCl$_3$ of 0.7:7:8.5:0.3 for the case where G = SC$_4$H$_9$ as compared to 1:7:7:1 for G = OC$_6$H$_5$. In the completely random case, these ratios equal 1:3:3:1.

Discussion

The most interesting finding presented in this paper is that alkyl mercapto groups do not exchange with alkoxyl groups under conditions where ester interchange is noted for either the sulfur-free esters or the esters where all oxygens have been substituted by sulfur. Thus far, we have been unable to show whether this is due to large positive values of the equilibrium constants (as expressed in the form of eq. 1–3) or is attributable to the lack of a mechanism for interchange, *i.e.*, kinetic control. A similar situation is found in the case of the dialkyl phosphites in which no interchange of the hydrogen for the alkoxyl group is observed under conditions where alkoxyl groups have long reached equilibrium with respect to ester interchange and where interchange of the hydrogens directly bonded to the phosphorus probably also takes place readily.[17]

As has also been demonstrated by others,[20] ester interchange or the related interchange of alkyl groups between esters and alcohols is a good method for preparation of the mixed esters of the acids based on a single phosphorus atom. It is also a suitable preparative method for esters of the completely sulfur-substituted thio acids of phosphorus. For the purpose of estimating yields for a given equilibration step, this paper shows that, for ester interchange, an adequate ap-

(19) E. Fluck, J. R. Van Wazer, and L. C. D. Groenweghe, *J. Am. Chem. Soc.*, **81**, 6363 (1959). Figure 2 in this paper is in error in that the point at 50 mole % of PCl$_3$ where lines B and C cross should be at 43% of the total phosphorus instead of at 34% as shown. Also see E. Fluck and J. R. Van Wazer, *Z. anorg. allgem. Chem.*, **307**, 113 (1961).

(20) *e.g.*, F. W. Hoffmann, R. G. Roth, and T. C. Simmons, *J. Am. Chem. Soc.*, **80**, 5937 (1958); G. M. Kosolapoff, *ibid.*, **73**, 4989 (1951). Also see F. W. Hoffmann, R. J. Ess, and R. P. Usinger, *ibid.*, **78**, 5817 (1956); B. A. Arbuzov and V. S. Vinogradova, *Dokl. Akad. Nauk SSSR*, **83**, 79 (1952); W. C. Rueggeberg and J. Chernack, *J. Am. Chem. Soc.*, **70**, 1802 (1948).

proximation is obtained by assuming random redistribution of alkyl groups, where steric hindrance is not a factor. Preparations of mixed alkyl phosphites (including the "dialkyl phosphonates") reorganize at room temperature. For example, pure dimethyl ethyl phosphite isolated as a gas chromatography fraction was found to reorganize appreciably within several days, as evidenced by the appearance and growth of three additional peaks in the gas chromatogram. This means that data obtained on so-called "pure" mixed esters of this type, as made by conventional methods, may be questionable, especially if the data were obtained on aged samples.

The results given herein show that even ester interchange deviates from randomness when sufficiently precise measurements are employed. Moreover, there seems to be no simple relationship between the devia-

tions from randomness for scrambling equilibria involving exchange of RO– and PO– substitutents of the esters of polyacids and the deviations for RO– and R′O– exchange in the esters of ortho acids.

Thermodynamic treatment of the data of this paper shows that, in all cases, the free energy of formation of the mixed esters from the compounds containing only one kind of alkoxyl group deviates from the random case by less than 0.25 kcal., which probably represents the enthalpy of the ester-interchange reaction.[6]

Nonaqueous Coordination Phenomena—Complexes of Hexamethylphosphoramide. III. Other Cationic Complexes

By JOHN T. DONOGHUE[1] and RUSSELL S. DRAGO

The following complexes of hexamethylphosphoramide, $OP[N(CH_3)_2]_3$ (HMPA), have been prepared: $[Fe(HMPA)_6](ClO_4)_3$, $[Cr(HMPA)_6](ClO_4)_3$, $[Fe(HMPA)_4](ClO_4)_2$, $[Cu(HMPA)_4](ClO_4)_2$, $[Mn(HMPA)_4](ClO_4)_2$, $[Mg(HMPA)_4](ClO_4)_2$, $[Ca(HMPA)_4](ClO_4)_2$, $[Ba(HMPA)_4](ClO_4)_2$, $[Al(HMPA)_4](ClO_4)_3$, $Pb(HMPA)_6](ClO_4)_2$, $[Ag(HMPA)_2]ClO_4$, and $[Ag(HMPA)](ClO_4)$. In this article, we report for the first time conclusive evidence to establish a tetrahedral structure for a cationic iron(II) complex. The spectral and magnetic data for $[Fe(HMPA)_4]^{+2}$ support a tetrahedral configuration for the cation and the X-ray powder pattern indicates strict isomorphism with known tetrahedral structures such as those of the M-$(HMPA)_4^{+2}$ complexes of Zn^{+2}, Co^{+2}, and Ni^{+2}. Spectral data on the Fe^{+3} and Cr^{+3} compounds indicate an octahedral configuration for the $[M(HMPA)_6^{+3}]$ complexes and suggest that toward Cr^{+3} HMPA is nearly as strong a donor as dimethyl sulfoxide. The unexpected four-coordinate HMPA complexes of Ca^{+2}, Mg^{+2}, Ba^{+2}, and Mn^{+2} also appear to be tetrahedral on the basis of X-ray powder pattern evidence.

Introduction

In earlier papers, it was shown that hexamethylphosphoramide (HMPA) formed tetrahedral complexes with Co(II) and Ni(II).[2,3] A planar complex was isolated with copper(II) nitrate[3] and a D_{2d}-like structure was proposed for the complex obtained with $Ni(NO_3)_2$. The unusual tetrahedral coordination of HMPA with Ni(II) prompted us to investigate the coordinating properties of this ligand toward other metal ions. In this paper, we report some unexpected four-coordinate cations of Ca(II), Mg(II), Ba(II), and Al(III). Spectral data for a four-coordinate Mn(II) complex of HMPA are in accord with properties reported for other tetrahedral manganese complexes.[4-11]

Iron(II) complexes present an interesting situation. The difference in crystal field stabilization energies for tetrahedral and octahedral fields is only 3 kcal. mole^{-1} in favor of the octahedral complex.[12] Yet, until very recently tetrahedral Fe(II) was unknown. In 1961, Gill[12] reported the preparation and isolation of solid compounds of FeX_4^{-2} (X = halogen). These compounds are cream-colored solids exhibiting magnetic moments of ~5.3 B.M. The solution spectra are interesting in that there are no apparent (d–d) transitions between ~500 and 2000 mμ. Below 450 mμ, very intense charge-transfer bands are observed. The X-ray powder diagrams of these halo complexes indicate strict isomorphism with the corresponding derivatives of Mn(II), Co(II), Ni(II), and Zn(II),[13] a fact which would

(1) Universal Match Foundation Fellow; abstracted in part from Ph.D. Thesis of John T. Donoghue, University of Illinois, Urbana, Illinois, 1963.

(2) J. T. Donoghue and R. S. Drago, *Inorg. Chem.*, **1**, 866 (1962).

(3) J. T. Donoghue and R. S. Drago, *ibid.*, **2**, 572 (1963).

(4) C. K. Jørgensen, *Acta Chem. Scand.*, **11**, 53 (1957).

(5) F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Am. Chem. Soc.*, **84**, 167 (1962).

(6) F. A. Cotton and E. Bannister, *J. Chem. Soc.*, 1873 (1960).

(7) C. Furlani and A. Furlani, *J. Inorg. Nucl. Chem.*, **19**, 51 (1961).

(8) H. Schlafer, *Z. physik. Chem.* (Frankfurt), **4**, 116 (1955).

(9) L. Naldini and A. Sacco, *Gazz. chim. ital.*, **89**, 2258 (1959).

(10) L. Naldini, *ibid.*, **90**, 1337 (1960).

(11) D. M. L. Goodgame and F. A. Cotton, *J. Chem. Soc.*, 3735 (1961).

(12) N. S. Gill, *ibid.*, 3512 (1961).

(13) N. S. Gill and R. S. Nyholm, *ibid.*, 3997 (1959).