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Redistribution Equilibria in Fluorophosphorus Compounds.¹ IV. Scrambling of Fluorine vs. Chlorine vs. Bromine between Phosphoryl, Phosphonyl, and Phosphinyl Moieties

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Received February 27, 1973

Quantitative data were obtained on the exchange of fluorine vs. chlorine vs. bromine between the phosphoryl, methylphosphonyl, and dimethylphosphinyl moieties, by means of ¹H, ¹⁹F, and ³¹P nmr. The equilibrium distributions are described in terms of sets of independent constants. The distinctive features of fluorine in its redistribution reactions, when compared with the other halogens, are as follows: (i) F vs. Cl exchanges are considerably slower than Cl vs. Br exchanges on given centers; (ii) accumulation of fluorine on any central atom is always favored, whereas the other halogens redistribute essentially at random; (iii) there is a definite preferential affinity of fluorine for the methylphosphonyl moiety over both phosphoryl and dimethylphosphinyl moieties. Additional experiments are reported which involve ethyl-, benzyl-, and phenylphosphonyl moieties.

Redistribution reactions play an important part in controlling phosphorus chemistry.² However, studies on the redistribution equilibria involving the exchange of fluorine-phosphorus bonds have been undertaken only very recently.^{1,3,4} Moreover, there appears to have been done little work on the exchange of substituents between two or more different phosphorus-based central moieties^{5,6} and none on the exchange between differently alkylated tetracoordinated phosphorus atoms, apart from the very particular exchange of the atoms which are "double bonded" to phosphorus.^{7,8}

The interest in such studies, with respect to a better knowledge of bond energies, has been stressed in a recent review.⁹

The present series of papers is aimed at collecting information on the occurrence, extent, and rate of scrambling of fluorine atoms vs. other common substituents in fluorophosphorus compounds. Molecular distributions at equilibrium are measured in the homogeneous phase in order to establish, on a quantitative basis, the relative stability of the mixed species as well as the relative affinity of fluorine vs. various other substituents for typical phosphorus-based centers. This work is further intended at affording an empirical basis for the *a priori* prediction of unknown equilibrium constants and also appears to be a potent method for apprehending bond energy nonadditivities along a substitution series.¹⁰

The present paper specifically is devoted to the quantitative study of the scrambling equilibria of fluorine vs. chlorine vs. bromine atoms between central moieties which are representative of some of the broadest classes of tetracoordinated phosphorus derivatives, namely, phosphoryl, phosphonyl, and phosphinyl halides, under experimental conditions where

the alkyl groups do not undergo exchange. The following systems were investigated quantitatively: {(F, Cl)-(P(O), CH₃P(O))},¹¹ {(F, Cl)-(CH₃P(O), (CH₃)₂P(O))}, and {(F, Cl)-P(O)} for the competition of fluorine vs. chlorine on the above series of centers; {(Cl, Br)-(P(O), CH₃P(O))} and {(Cl, Br)-(CH₃P(O), (CH₃)₂P(O))} for the related chlorine vs. bromine competition. Some further experiments are reported which compare the scrambling equilibria on methyl-, ethyl-, benzyl-, and phenylphosphonyl moieties in order to check the general scope of our conclusions.

Experimental Section

Phosphorus oxychloride and phenylphosphonyl dichloride were commercial products. Phosphorus oxyfluoride,¹² methylphosphonyl dichloride,¹³ difluoride,¹³ and dibromide,¹³ dimethylphosphinyl chloride¹⁴ and fluoride,¹⁵ ethylphosphonyl dichloride¹³ and difluoride,¹³ benzylphosphonyl dichloride¹⁶ and difluoride,¹³ and phenylphosphonyl difluoride¹³ were prepared according to the literature. All reactants and solvents were dried and redistilled under nitrogen before use and their purity was checked by nmr. After use the vessels and nmr tubes having contained fluorophosphorus compounds were decontaminated in an alcoholic solution of sodium hydroxide (1:1:1 NaOH-EtOH-H₂O).¹³

The sample mixtures were prepared by weighing the desired amounts of the chosen ingredients directly in standard 5-mm o.d. nmr tubes. A volume of dry benzene was added, except for system {(Cl, Br)-(P(O), CH₃P(O))} which had to be investigated by ³¹P nmr, before the tubes were sealed. The sample tubes were filled so as to reduce the vapor phase to a minimum volume. Thick-walled tubes were used when phosphorus oxyfluoride was present or expected to form. The samples were heated uniformly to 120° and periodically analyzed by ¹H and ¹⁹F nmr on a Jeol C-60 HL spectrometer immediately after cooling the samples to room temperature. The equilibrium data were obtained long after the spectra did not show any further change with time. The ³¹P spectra for the system {(Cl, Br)-(P(O), CH₃P(O))} were measured on a Perkin-Elmer Model R-10 apparatus.

Peak assignment in the nmr spectra was achieved on the basis of known chemical shifts,^{1,4,17} characteristic spin multiplicity, and material balance calculations (Table I). The formalism, techniques

(11) This notation conveniently represents the exchange of fluorine vs. chlorine between the phosphoryl and methylphosphonyl moieties.³ In the system {(F, Cl)-P(O)} there is only one moiety.³

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Table I. ^1H and ^{19}F Nmr Data

Compd	^1H					^{19}F	
	$\delta(\text{CH}_3)^a$	$\delta(\text{CH}_2)^a$	$J_{\text{CH}_3-\text{P}}$, Hz	$J_{\text{CH}_2-\text{P}}$, Hz	$J_{\text{CH}_2-\text{P}-\text{F}}$, Hz	δ^b	$J_{\text{P}-\text{F}}$, Hz
$\text{C}_2\text{H}_5\text{P}(\text{O})\text{F}_2^c$	1.30	2.22	24.0		5.0	67.5	1120
$\text{C}_2\text{H}_5\text{P}(\text{O})\text{FCl}^c$	1.32	2.40	27.2		4.7	42.5	1130
$\text{C}_2\text{H}_5\text{P}(\text{O})\text{Cl}_2^c$	1.35	2.62	29.4	13.8			
$\text{PhCH}_2\text{P}(\text{O})\text{F}_2$		3.55		18.8	3.9	66.7	1120
$\text{PhCH}_2\text{P}(\text{O})\text{FCl}$		3.70		16.5	4.1	43.0	1162
$\text{PhCH}_2\text{P}(\text{O})\text{Cl}_2$		3.92		14.1			
$\text{PhP}(\text{O})\text{F}_2$						66.0	1078
$\text{PhP}(\text{O})\text{FCl}$						38.0	1134
$(\text{CH}_3)_2\text{P}(\text{O})\text{F}^d$	1.85		15.5			66.4	990
$(\text{CH}_3)_2\text{P}(\text{O})\text{Cl}$	2.20		14.0				

^a Ppm from TMS are taken positively toward decreasing fields. ^b Ppm from CCl_3F are taken positively toward increasing fields.
^c $J_{\text{CH}_3\text{CH}_2} = 7.2$ Hz. ^d $J_{\text{CH}_3\text{PF}} = 8.5$ Hz.

for quantitatively evaluating the molecular distributions, and equilibrium constants with standard errors and data reduction procedures are detailed in general reviews^{9,18} and in previous papers^{1,3} in this series.

Results

I. Exchange of Fluorine vs. Chlorine Atoms between the Phosphoryl, Methylphosphonyl, and Dimethylphosphinyl Moieties. The equilibrium concentrations of the nine possible molecular species which are expected from the exchange of the two halogens between the central moieties of the above series will be completely determined by the following set of five independent constants

$$K_1(\text{PO}) = [\text{P}(\text{O})\text{F}_3][\text{P}(\text{O})\text{FCl}_2] / [\text{P}(\text{O})\text{F}_2\text{Cl}]^2 \quad (1)$$

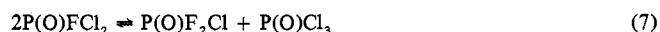
$$K_2(\text{PO}) = [\text{P}(\text{O})\text{F}_2\text{Cl}][\text{P}(\text{O})\text{Cl}_3] / [\text{P}(\text{O})\text{FCl}_2]^2 \quad (2)$$

$$K_1(\text{CH}_3\text{PO}) = [\text{CH}_3\text{P}(\text{O})\text{F}_2][\text{CH}_3\text{P}(\text{O})\text{Cl}_2] / [\text{CH}_3\text{P}(\text{O})\text{FCl}]^2 \quad (3)$$

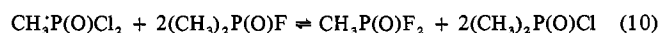
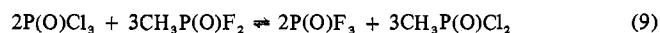
$$K_1(\text{PO}, \text{CH}_3\text{PO}) = [\text{P}(\text{O})\text{F}_3]^2 [\text{CH}_3\text{P}(\text{O})\text{Cl}_2]^3 / [\text{P}(\text{O})\text{Cl}_3]^2 [\text{CH}_3\text{P}(\text{O})\text{F}_2]^3 \quad (4)$$

$$K_1(\text{CH}_3\text{PO}, (\text{CH}_3)_2\text{PO}) = [\text{CH}_3\text{P}(\text{O})\text{F}_2][(\text{CH}_3)_2\text{P}(\text{O})\text{Cl}]^2 / [\text{CH}_3\text{P}(\text{O})\text{Cl}_2][(\text{CH}_3)_2\text{P}(\text{O})\text{F}]^2 \quad (5)$$

where brackets denote concentrations. Constants of eq 1-3 represent the distributions of the halogens on the phosphoryl and phosphonyl moieties taken separately. They correspond to the disproportionation of the three possible mixed species, according to



The two independent "intersystem" constants of eq 4 and 5, which are necessary to correlate the three distinct centers, are derived from the equilibria



Scrambling of fluorine and chlorine atoms was observed to occur in all of the 15 sample mixtures prepared for this study. At 120° exchange becomes noticeable in the proton spectra after ca. 6 hr. The time required to reach equilibrium ranges from ca. 8 weeks, for the exchange of fluorine vs. chlorine

between the methylphosphonyl and dimethylphosphinyl moieties, to 5 months where phosphoryl moieties are present. No exchange involving methyl groups was observed under these experimental conditions. In all the systems under study equilibrium was reached from both sides; *i.e.*, sample mixtures were prepared from both pairs of parent species, for example, in the case of the system $\{(\text{F}, \text{Cl})-\text{P}(\text{O}), \text{CH}_3\text{P}(\text{O})\}$, by mixing $\text{P}(\text{O})\text{F}_3$ with $\text{CH}_3\text{P}(\text{O})\text{Cl}_2$ as well as by mixing $\text{P}(\text{O})\text{Cl}_3$ with $\text{CH}_3\text{P}(\text{O})\text{F}_2$. Each sample mixture was defined by two overall composition parameters, $R = [\text{F}] / [\text{total P}]$ and

$$R' = [\text{CH}_3\text{P}(\text{O})] / [\text{total P}] \quad (11)$$

Both ^1H and ^{19}F nmr were needed for quantitatively assaying the complex sample mixtures of the system $\{(\text{F}, \text{Cl})-\text{P}(\text{O}), \text{CH}_3\text{P}(\text{O})\}$. Since the concentration of one of the species, $\text{P}(\text{O})\text{Cl}_3$, can only be obtained by difference, it was further desirable to undertake a separate study of the single-center-based system $\{(\text{F}, \text{Cl})-\text{P}(\text{O})\}$.

The molar distributions at equilibrium are given in Table II. Equilibrium constants were computed for each sample mixture. Theoretical distributions, as computed from the weighted averaged constants, are given in parentheses; they are in good agreement with the experimentally determined ones. Further agreement is found when the overall compositions, from the weight of the ingredients, are compared with those obtained from the nmr measurements. It must also be noted that the equilibrium constants do not show any significant dependence upon the sample compositions except for one sample in the system $\{(\text{Cl}, \text{Br})-\text{P}(\text{O}), \text{CH}_3\text{P}(\text{O})\}$.

Although the constants K_1 (from eq 4 and 5) are best suited for the description of equilibrated systems and for the calculation of theoretical distributions, these constants alone cannot truly represent the relative affinities of the substituents for a given pair of central moieties when the distributions on each of the two centers in competition are not random or are of comparable magnitude. A constant, the significance of which is more directly perceivable, is given as

$$K_{\text{aff}} = [\text{F}-\text{P}(\text{O})][\text{CH}_3\text{P}(\text{O})] / [\text{F}-\text{P}(\text{O})\text{CH}_3][\text{P}(\text{O})] \quad (12)$$

for the example of system $\{(\text{F}, \text{Cl})-\text{P}(\text{O}), \text{CH}_3\text{P}(\text{O})\}$, where the quantities in brackets represent the total concentration of each type of bonds at equilibrium.

II. Exchange of Chlorine vs. Bromine between the Phosphoryl, Phosphonyl, and Phosphinyl Moieties. This study was performed under the same experimental conditions as above, so as to allow a direct comparison of the behavior of fluorine, chlorine, and bromine with respect to the scrambling phenomenon. Constants of the same format (eq 1-5,

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Table II. Experimental and Calculated (in Parentheses) Equilibrium Data for the System $\{(F, Cl)-(P(O), CH_3P(O), (CH_3)_2P(O))\}$ at 120°

A. System $\{(F, Cl)-P(O)\}$											
$R = [F]/[P]$	Molar distributions					K_1	K_2				
	OPF ₃	OPF ₂ Cl	OPFCl ₂	OPCl ₃							
1.68 ^a	25.6 ^b	31.9	27.0	15.5	0.67	0.68					
1.68 ^b	(26.3) ^c	(31.1)	(27.0)	(15.6)							
2.00	23.4	32.7	23.2	10.7	0.72	0.11					
1.89	(33.6)	(32.5)	(22.9)	(10.8)							
2.05	35.3	31.1	22.5	11.1	0.82	0.68					
1.91	(34.4)	(32.6)	(22.5)	(10.4)							

B. System $\{(F, Cl)-P(O)-(P(O), CH_3P(O))\}$												
$R = [F]/[P]$	$R' = [CH_3P(O)]/[P]$	Molar distributions							K_1	K_2	$K_{CH_3P(O)}$	K_I
		OPF ₃	OPF ₂ Cl	OPFCl ₂	OPCl ₃	CH ₃ -P(O)F ₂	CH ₃ -P(O)FCl	CH ₃ -P(O)Cl ₂				
0.75 ^{a,f}	0.37 ^a	3.9 ^b	9.3	19.5	29.7	6.6	10.2	20.8	0.88	1.32	0.54	
0.73 ^b	0.38 ^b	(2.6) ^d	(7.2)	(18.4)	(33.8)	(10.8)	(10.9)	(16.8)	0.73			
1.09 ^g	0.67	6.1	9.8	11.1	8.8	22.4	18.8	23.0	0.71	1.46	0.54	
1.13	0.64	(4.1)	(7.0)	(11.5)	(13.4)	(28.5)	(18.2)	(17.3)	0.70			
1.30 ^g	0.69	6.8	6.2	6.2	5.0	36.1	21.6	18.1	1.09	1.40	0.23	
1.33	0.76	(4.2)	(5.7)	(7.4)	(6.7)	(40.6)	(20.3)	(15.1)	0.81			
1.42 ^f	0.71	7.4	7.3	7.3	4.9	36.9	19.8	16.4	1.01	1.54	0.20	
1.38	0.73	(5.4)	(6.7)	(8.1)	(6.9)	(40.7)	(19.0)	(13.2)	0.67			
1.46 ^g	0.70	6.3	4.1	2.4	1.2	52.1	21.2	12.7	0.90	1.48	0.40	
1.55	0.86	(4.1)	(4.0)	(3.6)	(2.3)	(55.7)	(19.8)	(10.5)	0.85			
1.51 ^f	0.75	8.8	6.8	5.8	3.0	45.3	18.5	11.8	1.10	1.56	0.15	
1.55	0.76	(6.8)	(6.7)	(6.3)	(4.2)	(48.6)	(17.8)	(9.7)	0.60			

C. System $\{(F, Cl)-(CH_3P(O), (CH_3)_2P(O))\}$												
$R = [F]/[P]$	$R' = [CH_3P(O)]/[P]$	Molar distributions					$K_{CH_3P(O)}$	K_I				
		CH ₃ P(O)F ₂	CH ₃ P(O)FCl	CH ₃ P(O)Cl ₂	(CH ₃) ₂ -P(O)F	(CH ₃) ₂ -P(O)Cl						
0.50 ^{a,h}	0.25 ^a	10.7	3.8	2.1	22.4	61.0	1.69	37				
0.48 ^b	0.24 ^b	(11.7) ^e	(4.3)	(2.0)	(21.3)	(60.7)						
1.14	0.57	51.5	8.0	2.1	8.1	30.3	1.70	34				
1.19	0.60	(50.2)	(8.6)	(2.1)	(9.1)	(30.0)						
1.25	0.62	51.2	13.7	5.2	10.3	19.6	1.42	36				
1.26	0.63	(50.5)	(14.4)	(4.0)	(9.5)	(21.6)						
1.47	0.73	57.2	9.7	2.7	14.3	16.1	1.63	27				
1.40	0.70	(58.5)	(9.2)	(2.3)	(13.9)	(16.1)						

^a From the ingredients. ^b From the nmr data. ^c Calculated from $\bar{K}_1 = 0.73$ and $\bar{K}_2 = 0.67$. ^d Calculated from $\bar{K}_1 = 0.95$, $\bar{K}_2 = 0.71$, $\bar{K}_{CH_3P(O)} = 1.49$, and $\bar{K}_I = 0.24$. ^e Calculated from $\bar{K}_{CH_3P(O)} = 1.62$ and $\bar{K}_I = 34$. ^f By mixing OPF₃ with CH₃P(O)Cl₂. ^g By mixing OPF₃ with CH₃P(O)Cl₂. ^h By mixing CH₃P(O)Cl₂ and (CH₃)₂P(O)Cl with (CH₃)₂P(O)F. Other samples of the system are prepared by mixing CH₃P(O)F₂ with (CH₃)₂P(O)Cl.

with F and Cl, respectively, replaced by Cl and Br), were used to describe the equilibrium distributions.

It was found that the exchange reactions of chlorine vs. bromine between the three centers under study are much faster than those of fluorine vs. chlorine between the same centers. Thus the exchange becomes already noticeable after less than 1 hr at 120° in the system $\{(Cl, Br)-(P(O), CH_3P(O))\}$ and is even faster in the system $\{(Cl, Br)-(CH_3P(O), (CH_3)_2P(O))\}$, which makes it necessary to measure the nmr spectra immediately after the tubes have been rapidly cooled to room temperature. Equilibrium was attained in ca. 1 week at 120° in these systems.

The equilibrium distributions are given in Table III. They confirm that the distribution of chlorine vs. bromine on both phosphoryl² and phosphonyl⁴ moieties are essentially random. They further show that there is a preferential affinity of chlorine for both methyl-substituted phosphorus moieties over the phosphoryl moiety. The intersystem constants for the exchange of fluorine vs. bromine on a given pair of centers may be evaluated (Table V) from the above measured constants according to

$$K_I(F, Br) = (K_I(F, Cl))(K_I(Cl, Br)) \quad (13)$$

III. Exchange of Fluorine vs. Chlorine on the Ethyl-, Benzyl-, and Phenylphosphonyl Moieties. We investigated and compared the series of systems $\{(F, Cl)-RP(O)\}$, where $R = CH_3, C_2H_5, PhCH_2,$ and Ph , in order to determine the influence of the nature of the group R on the equilibrium distributions. The competition of the two halogens between the methyl- and phenylphosphonyl moieties was examined further. The time necessary to reach equilibrium in these studies was roughly the same as that for the exchange on the methylphosphonyl moiety. Equilibrium data are given in Table IV, from which the following set of constants was evaluated, based on eq 14. For $R = CH_3, C_2H_5, PhCH_2,$ and Ph , respectively, $\bar{K}_1 = 1.45 \pm 0.20^3$ and 1.50 ± 0.07^{19} , 1.67 ± 0.30 , 1.41 ± 0.15 , and 1.16 ± 0.11 and 1.33 ± 0.50^{19} ; $\bar{K}_1(CH_3-PO, PhPO) = 2.50 \pm 0.90$.

(19) From the system $\{(F, Cl)-(CH_3P(O), PhP(O))\}$.

Table III. Experimental and Calculated (in Parentheses) Equilibrium Data for the System $\{(Cl, Br)-(P(O), CH_3P(O), (CH_3)_2P(O))\}$ at 120°

A. System $\{(Cl, Br)-(P(O), CH_3P(O))\}$											
Molar distributions											
$R = [F]/[P]$	$R' = [CH_3P(O)]/[P]$	OPCl ₃	OPCl ₂ -Br	OPCl-Br ₂	OPBr ₃	CH ₃ P-(O)Cl ₂	CH ₃ P-(O)ClBr	CH ₃ P-(O)Br ₂	K_1 K_2	$K_{CH_3P(O)}$	$10^3 \times K_I$
0.95 ^{a,e}	0.47 ^a	1.4 ^b	8.3	20.0	16.3	16.0	23.5	14.5	0.40	0.41	5
0.96 ^b	0.54 ^b	(1.6) ^c	(9.0)	(20.3)	(15.1)	(13.9)	(25.1)	(15.0)	0.34		
1.22 ^e	0.61	2.9	11.5	18.7	9.0	23.8	25.0	9.1	0.41	0.34	6
1.23	0.58	(3.5)	(12.3)	(17.8)	(8.5)	(22.2)	(25.9)	(9.9)	0.30		
1.40 ^e	0.70	4.0	9.0	8.8	3.0	36.9	30.5	7.8	0.42	0.31	18
1.43	0.75	(3.8)	(9.1)	(9.1)	(3.0)	(37.2)	(29.9)	(7.9)	0.34		
1.81 ^f	0.40	16.7	24.0	15.0	3.4	20.4	17.3	3.2	0.43	0.28	96
1.71	0.41	(14.3)	(24.2)	(16.8)	(3.8)	(24.7)	(13.8)	(2.5)	0.36		

B. System $\{(Cl, Br)-(CH_3P(O), (CH_3)_2P(O))\}$

Molar distributions									
$R = [Cl]/[P]$	$R' = [CH_3P(O)]/[P]$	CH ₃ P-(O)Cl ₂	CH ₃ P-(O)ClBr	CH ₃ P-(O)Br ₂	(CH ₃) ₂ -P(O)Cl	(CH ₃) ₂ -P(O)Br	$K_{CH_3P(O)}$	K_I	
0.34 ^{a,g}	0.66 ^a	3.3 ^b	19.7	43.7	7.1	26.2	0.38	1.03	
0.33 ^b	0.67 ^b	(3.3) ^d	(19.4)	(44.3)	(7.0)	(26.0)			
0.46 ^g	0.54	7.9	24.2	30.4	12.7	24.8	0.41	0.99	
0.53	0.62	(7.9)	(24.5)	(29.7)	(12.9)	(25.1)			

^a From the ingredients. ^b From the nmr data. ^c Calculated from $\bar{K}_1 = 0.41$, $\bar{K}_2 = 0.33$, $\bar{K}_{CH_3P(O)} = 0.33$, and $\bar{K}_I = 16 \times 10^{-3}$. ^d Calculated from $\bar{K}_{CH_3P(O)} = 0.39$ and $\bar{K}_I = 1.01$. ^e By mixing CH₃P(O)Cl₂ with OPBr₃. ^f By mixing CH₃P(O)Br₂ with OPCI₃. ^g By mixing CH₃P(O)Br₂ with (CH₃)₂P(O)Cl.

Table IV. Experimental and Calculated (in Parentheses) Equilibrium Data for the Systems $\{(F, Cl)-RP(O)\}$ at 120°

A. System $\{(F, Cl)-C_2H_5P(O)\}$										
Molar distributions										
$R = [F]/[P]$	C ₂ H ₅ P(O)F ₂	C ₂ H ₅ P(O)FCl	C ₂ H ₅ P(O)Cl ₂	$K_{C_2H_5P(O)}$						
1.00 ^a	36.0 ^b (36.1) ^c	28.0 (27.8)	36.0 ^f (36.1)	1.65						
1.03	36.6 (37.5)	30.1 (27.9)	33.3 (34.6)	1.34						
1.36	56.3 (55.4)	23.6 (25.3)	20.1 (19.3)	2.02						
B. System $\{(F, Cl)-PhCH_2P(O)\}$										
Molar distributions										
$R = [F]/[P]$	PhCH ₂ P(O)F ₂	PhCH ₂ P(O)FCl	PhCH ₂ P(O)Cl ₂	$K_{PhCH_2P(O)}$						
1.20 ^a	45.9 ^b (45.6) ^d	28.7 (28.8)	25.4 ^f (25.6)	1.41						
1.45	59.7 (59.9)	25.2 (25.1)	15.1 (15.0)	1.42						
C. System $\{(F, Cl)-PhP(O)\}$										
Molar distributions										
$R = [F]/[P]$	PhP(O)F ₂	PhP(O)FCl	PhP(O)Cl ₂	$K_{PhP(O)}$						
0.95 ^a	32.1 ^b (31.7) ^e	30.5 (31.6)	37.4 ^f (36.7)	1.29						
0.99	32.8 (33.6)	33.2 (31.7)	34.0 (34.7)	1.01						
1.00	34.0 (34.1)	31.6 (31.7)	34.4 (34.2)	1.17						
D. System $\{(F, Cl)-(CH_3P(O), PhP(O))\}$ at 120°										
Molar distributions										
$R = [F]/[P]$	$R' = [CH_3P(O)]/[P]$	CH ₃ -P(O)F ₂	CH ₃ -P(O)FCl	CH ₃ -P(O)Cl ₂	PhP-(O)F ₂	PhP-(O)FCl	PhP-(O)Cl ₂	$K_{CH_3P(O)}$	$K_{PhP(O)}$	K_I
0.92 ^{a,h}	0.54 ^a	19.8 ^b	15.0	16.5	10.9	13.1	24.7	1.45	1.57	2.72
0.90 ^b	0.51 ^b	(19.5) ^g	(14.8)	(16.8)	(11.1)	(14.1)	(23.8)			
1.28	0.64	34.3	16.0	11.5	15.9	12.9	9.4	1.54	0.90	1.76
1.29	0.62	(35.6)	(15.8)	(10.6)	(15.3)	(11.4)	(11.3)			
1.49	0.74	50.1	16.3	8.1	12.4	7.0	6.1	1.53	1.54	3.04
1.48	0.74	(49.0)	(16.6)	(8.4)	(13.0)	(7.4)	(5.6)			

^a From the ingredients. ^b From the nmr data. ^c Calculated from $\bar{K}_{C_2H_5P(O)} = 1.67$. ^d Calculated from $\bar{K}_{PhCH_2P(O)} = 1.41$. ^e Calculated from $\bar{K}_{PhP(O)} = 1.16$. ^f Determined with using the ratio of the reagents. Consequently the values of R derived from the weighting of the ingredients and from the nmr data are the same. ^g Calculated from $\bar{K}_{CH_3P(O)} = 1.50$, $\bar{K}_{PhP(O)} = 1.33$, and $\bar{K}_I = 2.50$. ^h By mixing CH₃P(O)Cl₂ with PhP(O)F₂. Other samples of the system are prepared by mixing CH₃P(O)F₂ with PhP(O)Cl₂.

Discussion

The equilibrium constants evaluated in parts I and II of this study are summarized in Table V. It is noteworthy to stress the good agreement which is found between the values

of a given constant obtained from several independent studies. The agreement between calculated and experimental distributions or overall compositions further demonstrates the self-consistency of the description of the redistribution phenomenon.

Table V. Equilibrium Constants Relative to F vs. Cl vs. Br Exchange between Phosphoryl, Phosphonyl, and Phosphinyl Moieties, at 120°

Systems	$K_1(\text{PO})$	$K_2(\text{PO})$	$K_1(\text{CH}_3\text{PO})$	$K_1(\text{PO}, \text{CH}_3\text{PO})$	$K_1(\text{CH}_3\text{PO}, (\text{CH}_3)_2\text{PO})$	$K_1(\text{PO}, (\text{CH}_3)_2\text{PO})$
{(F, Cl)-(P(O), CH ₃ P(O))}	0.95 ± 0.14	0.71 ± 0.08	1.49 ± 0.08	0.24 ± 0.03		
{(Cl, Br)-(P(O), CH ₃ P(O))}	0.41 ± 0.02	0.33 ± 0.04	0.33 ± 0.08	(16 ± 5) × 10 ⁻³		
{(F, Br)-(P(O), CH ₃ P(O))}				(3.8 ± 1.8) × 10 ⁻³ ^a		
{(F, Cl)-(CH ₃ P(O), (CH ₃) ₂ P(O))}			1.62 ± 0.11		34 ± 4	
{(Cl, Br)-(CH ₃ P(O), (CH ₃) ₂ P(O))}			0.39 ± 0.02		1.01 ± 0.03	
{(F, Br)-(CH ₃ P(O), (CH ₃) ₂ P(O))}					34 ± 5 ^a	
{(F, Cl)-(P(O), (CH ₃) ₂ P(O))}						8.16 ± 1.98
{(Cl, Br)-(P(O), (CH ₃) ₂ P(O))}						1.33 ± 0.36
{(F, Br)-(P(O), (CH ₃) ₂ P(O))}						0.33 ± 0.08
{(F, Cl)-P(O)}	0.73 ± 0.06	0.67 ± 0.02				
{(Cl, Br)-P(O)} ²⁵	0.41 ± 0.01 ^b	0.34 ± 0.01 ^b				
{(F, Cl)-CH ₃ P(O)} ³			1.45 ± 0.20			
{(Cl, Br)-CH ₃ P(O)} ⁴			0.36 ± 0.04 ^c			

^a Derived from eq 13. ^b At 130°. ^c At 25°.

The present study further supports the idea that redistribution reactions involving the breakage and making of phosphorus to fluorine bonds are as general a phenomenon as those involving the bonds of phosphorus to the other halogens.

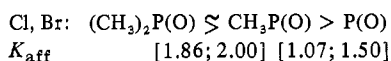
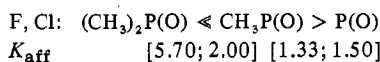
The distinctive features of fluorine, when compared to the other halogens and pseudohalogens, appear to be the following.

(i) The exchange of fluorine vs. chlorine is 1–2 orders of magnitude slower than the exchange of chlorine vs. bromine on the same centers and in comparable conditions. This probably accounts for its having been long overlooked since the scrambling thus interferes less frequently with the isolation of pure mixed species than in the case of the other halogens. The rationale that halogen exchange is accelerated by methyl substitution on phosphorus^{3,20} also applies to the fluorine vs. chlorine exchanges and is thus further borne out.

(ii) While the exchange of chlorine with the other halogens and pseudohalogens on both phosphoryl²¹ and methylphosphonyl⁴ moieties is almost random, the constants for the exchange of fluorine vs. chlorine on these centers is found to be significantly larger than would be expected for random statistics. Moreover it exemplifies the less common case where the mixed species are less favored than would be expected from random distribution of the bonds, *i.e.*, additive bond energies. Since parallel observations also have been made for the exchange of fluorine vs. chlorine atoms on other phosphorus-based central moieties⁴ as well as on boron²² and silicon-based^{23,24} moieties, it appears that favored accumulation of fluorine on a given atom is a general rule.

(iii) There is no significant preferential partition of chlorine and bromine between the phosphonyl and the phosphinyl moieties, and there is only a slight preference of chlorine for these two centers over the phosphoryl center. On the con-

trary there is a strong preferential affinity of fluorine over chlorine and bromine (from eq 13) for the methylphosphonyl over both dimethylphosphinyl and phosphoryl moieties. These results may be summarized in the following way



where the first figure in each set of brackets is the averaged value of K_{aff} calculated from the experimental distributions according to eq 6, while the second figure is the value expected for these constants in the case of a random distribution of the substituents.

Thus there appears to be no uniform trend in the distribution of fluorine, chlorine, and bromine between the phosphoryl, phosphonyl, and phosphinyl moieties, and the results can obviously not be accounted for in a simple way on the basis, for example, of Pearson's HSAB concept^{25,26} or on any monotonous variation on π -bonding difference between F-P and Cl-P bonds along a substitution series.^{23,27}

(iv) Little variation was found in $K_1(\text{RPO})$ when R changes from methyl to ethyl, benzyl, or phenyl. Nor is there any obvious preferential partition of fluorine and chlorine when methyl and phenylphosphonyl moieties are in competition. We therefore expect the redistribution data obtained on the methyl derivatives to be representative of the exchange of the halogens between the phosphoryl, phosphonyl, and phosphinyl moieties in general, insofar that no particular steric effects are involved.

Registry No. C₂H₅P(O)F₂, 753-98-0; C₂H₅P(O)FCl, 865-61-2; C₂H₅P(O)Cl₂, 1066-50-8; PhCH₂P(O)F₂, 41698-25-3; PhCH₂P(O)FCl, 41698-26-4; PhCH₂P(O)Cl₂, 1499-19-0; PhP(O)F₂, 657-39-6; PhP(O)FCl, 4762-45-2; (CH₃)₂P(O)F, 753-70-8; (CH₃)₂P(O)Cl, 1111-92-8; F, 7782-41-4; Cl, 7782-50-5; Br, 7726-95-6; OPF₃, 13478-20-1; OPCI₃, 10025-87-3; CH₃P(O)F₂, 676-99-3; CH₃P(O)Cl₂, 676-97-1; OPBr₃, 7789-59-5; CH₃P(O)Br₂, 19430-64-9; (CH₃)₂P(O)Br, 41698-31-1; PhP(O)Cl₂, 824-72-6.

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