Substituent Effects at Elements Other than Carbon. I. **Phosphorus Acids**

MARVIN CHARTON

Department of Chemistry, Pratt Institute, School of Engineering and Science, Brooklyn, New York 11205

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Ionization constants of substituted phosphonic and phosphinic acids, rate constants for the benzylation of substituted dithiophosphinates, and ionization constants of substituted phosphazenes are successfully correlated by the extended Hammett equation using the σ_{I} and σ_{R} substituent constants defined for substituents bonded to carbon. The average value of ϵ (a parameter which measures the composition of the electrical effect) for the substituted phosphonic and phosphinic acids is 0.32; for the phosphazenes ϵ is 0.25. Thus these sets show an electrical effect which corresponds in composition to the σ_m constants. The magnitude of the electrical effect in substituted phosphonic and phosphinic acids is somewhat less than that observed for substituted carboxylic acids.

We have previously had occasion to study the application of the Hammett equation¹ (eq 1) to the ionization constants of substituted carboxylic acids² and substituted amidines.³ It seemed of interest to consider, for purposes of comparison, the extension of the Hammett equation to substituted phosphonic acids, phosphinic acids, and phosphazenes. Kabachnik⁴ has proposed a modified Hammett equation (eq 2) for use with the substituted phosphorus compounds. The

$$Q_{\mathbf{X}} = \rho \, \sigma_{\mathbf{X}} + h \tag{1}$$

$$Q_{\mathbf{X}} = \rho_{\phi} \sigma_{\phi \mathbf{X}} + h \tag{2}$$

necessary σ_{ϕ} values were defined from the pK_a values of disubstituted phosphinic acids, XYPO(OH), in water at 25°, ρ_{ϕ} for this reaction being assigned a value of 1.000 and $\sigma_{\rm H}$ a value of 0. Thus, the reference compound is $H_2PO(OH)$ for which Kabachnik gives pK = 1.00. Equation 2 has been used for the correlation of pK_a values of substituted phosphonic and phosphinic acids in water and in ethanol-water mixtures.

It is of interest to determine whether the electrical effects of a substituent bonded to phosphorus are of the same type as those exhibited by a substituent bonded to carbon. Furthermore, we would like to know whether the magnitude of the electrical effects of a substituent bonded to phosphorus is comparable with that of the electrical effects of a substituent bonded to carbon. The Kabachnik equation does not answer these questions. To provide answers we can correlate data for substituted phosphorus sets with the equation proposed by Taft⁵ (eq 3). A significant correlation as

$$Q_{\rm X} = \alpha \sigma_{\rm I} + \beta \sigma_{\rm R} + h \tag{3}$$

determined by statistical tests, will answer the first question. In the event of a significant correlation the magnitude of α and β will answer the second. We have

(1) H. H. Jaffé, Chem. Rev., 58, 191 (1953); R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley & Sons, Inc., New York, N. Y., 1956, p 565; V. Palm, Russ. Chem. Rev. (Engl. Transl.), 31, 471 (1961); P. R. Wells, Chem. Rev., 63, 171 (1963); C. D. Ritchie and W. F. Sager, Jr., Prog. Phys. Org. Chem., 2, 323 (1963).

(2) M. Charton, Abstracts of the 140th National Meeting of the American Chemical Society, Chicago, Ill., 1961, p 91Q.

(3) M. Charton. J. Org. Chem., 30, 969 (1965).
(4) M. I. Kabachnik, Zeit. Chem., 1, 2893 (1961).

therefore correlated data from the literature for the ionization of substituted phosphonic (I) and phosphinic (II) acids, for substituted phosphazenes (III and IV).



We have also examined the rate constants for the benzylation of salts of substituted dithiophosphinic acids. Data used in the correlations are given in Table I. The σ_I constants used were taken from our compilation⁶ unless otherwise noted (Table II). The $\sigma_{\rm R}$ constants required were obtained from⁵ eq 4 using the σ_p constants of McDaniel and Brown⁷ unless otherwise noted (Table II).

$$\sigma_{\rm R} = \sigma_p - \sigma_1 \tag{4}$$

Statistical factors have been applied to the ionization constants where necessary. Thus, for the substituted phosphonic acids when X = OH (K₁ for *o*-phosphonic acid) a statistical factor of $\frac{2}{3}$ was used, as there are three ionizable protons in this compound and two in the other members of the group. For the substituted hydrogen phosphonates $(K_2 \text{ of } I)$ when X = OH a statistical factor of $\frac{1}{2}$ is required. For the substituted phosphinic acids when X, Y = Ph, OH a statistical factor of $\frac{1}{2}$ is required.

Results

The results of the correlations with eq 3 are given in Table III.

 σ_{ϕ} Constants.—We have correlated the σ_{ϕ} values of Kabachnik⁴ with eq 3 (set 1). The results are significant at the 99.9% confidence level. A "t" test shows that the β value is significantly different from 0 at the 99% confidence level. Thus the evidence indicates a small but important resonance effect in the reactions

⁽⁵⁾ R. W. Taft, Jr., and I. C. Lewis, J. Amer. Chem. Soc., 80, 2436 (1958).

⁽⁶⁾ M. Charton, J. Org. Chem., 29, 1222 (1964).

⁽⁷⁾ D. H. McDaniel and H. C. Brown, ibid., 23, 420 (1958).

		$\mathbf{T}_{\mathbf{T}}$	ABLE	I
DATA	Used	IN	THE	CORRELATIONS

1.	σ_{ϕ} constants	a								
	X	OH	MeO	EtO	PrO	<i>i</i> -PrO	BuO	Me	Et	Pr
	σ.	-0.343	-0.124	-0.314 -	0 315	-0 291	-0 411	_0.9	65 -1 1	-1 -1 177
	v	2 Dn	B.,	4 B. (CHOI		- 0.8		
	Λ	<i>i</i> -r	Du				COL	CH_2	Br CH	21 CH ₂ OH
	σ_{ϕ}	-1.300	-1.219	-1.546 -	0.034	0.272	0.30	-0.0	-0.	-0.546
	X	CF_3	\mathbf{Ph}							
	σ_{ϕ}	0.50	-0.481							
2.3	k = K, value	s of XPO(O	H), in water a	t 25° ¢						
-, 0	v v	DL DL			CU D.	00	otto	01		
	л 	Ph			Un ₂ Dr	0012	CHU	3 CF	1_2 CI Bu	ICH ₂ t-Bu
	pK_{s1}	1.824°	1.91	1.30	1.14	1.63	1.14	1	.40 2	.84 2.79
	pK_{a_2}	7.070%	7.15	6.72	6.52	4.81	5.61	6	.30 8	.65 8.88
	x	<i>i</i> -Bu	s-Bu	Bu	<i>i</i> -Pr	Pr	Et	N	fe C	F. MeO
	nK	2 70	2 74	2 50	2 66	2 40	2 43		20 1	16 1 546
	PILA1	2.10	0 40	2.00	2.00	4,49	2.40	4	.00 1	.10 1.04
	pA _{a2}	8.43	8.48	8.19	8.44	8.18	8.05	7	.74 3	.93 6.314
	X	EtO	F	PhCH ₂	он	AcO	BuS			
	pK_{a1}	1.60^{d}	0.52	1.85	2.497'	1.17^{h}	2.21	i		
	nK	6 624	4.80*	7.4	7.510	4 884	5 93			
A	W walnog	of VDO/OH) in water at	20 ⁰ i	1.01	1100	0.00			
4.	prai values	M AFO(OII	J2 III WALEF AL		011	OTTO				
	X	Me	HUCH ₂	CICH ₂	OH	CHCI2				
	pK_{s}	2.38	1.91	1.40	2.15^{k}	1.14				
5.	$\mathbf{p}K_{\bullet}$, values	of XPO(OH)2 in 75% aque	eous ethanol at	; 22° '					
	X	PhO	н	Ph	OH	c-C ₄ H				
		2 19	9 15	2 06	1 244	4 80	-11			
	pra	61.6	0.10	0.90 ~~ ⁰	4.04*	4.00				
6.	pK_s values of	of XZPO(OH	l) in water at :	25° m						
	X, Z	Me, Me	Et, Et	Pr, Pr	<i>i</i> -Pr, <i>i</i> -	Pr B	3u, Bu	<i>t</i> -Bu, <i>t</i> -B	u Ph, F	Ph
	pK.	3.08	3.29	3.46	3.56		3.41	4.24	2.1'	•
	Y Z	OH OH	Et OEt	OMe OMe	OEt OF	Et OP	r OPr	OB ₁₁ OF	R11	
	м, <i>Ц</i>	0.1, 011	0.07	1 204	1 204		=04	1 704	^{ju}	
	pr.	4.044	4.41*	1.29-	-0	T	. 595	1.720		
7.	pK_a values of	of XZPO (OI	H) in 7% ethat	nol-water at 2	5-4					
	X, Z	MeO, MeO	EtO, EtC) PrO, P i	rO Pł	1 0, 0H	Me, M	ſe	Bu, Bu	<i>i</i> -Bu, <i>i</i> -Bu
	nK.	1.25	1.37	1.52		1.769	3.13		3.50	3.70
	X Z	Ph Ph	Pr. Ph	<i>i</i> -Pr P	h C.	H. Ph	C.H. C	H.		• • • •
	л., Ц V	0.20	0.717	0 00		0 06+	0 241	5-+ 3		
_	pra	2.32	<i>4.11</i>	4.84	~0	2.20	2.54			
8.	pK_a values of	of XZPO(OF	i) in 50% etha	nol-water at 2	5-7					
	X, Z	Pr, Ph	<i>i</i> -Pr, Ph	C_2H_3 , (DEt Ca	H_3, C_2H_3	C_2H_2 ,	Ph		
	nK.	4.15	4.28	3.18		3.59	3.53			
0	nK values	F XZPO(OH	() in 80% etha	nol-water at 2	5° «					
5.	V 7	Man Man		D_{-}	-0 M	• M•	D., D.		2 D / D.	DL DL
	л, 2	meo, meo	EIO, EU	$J = \mathbf{r}0, \mathbf{r}1$	io M	e, wie	Du, D	1	<i>1</i> -Би, <i>1</i> -Би	rn, rn
	$\mathrm{p}K_{\mathbf{a}}$	3.01	3.15	3.29		5.15	5.63		5.63	4.14
	X, Z	PhO, OH	PhO, Ph	O C2H2, H	EtO C ₂	H ₂ , Ph	C_2H_2, C_2	H,	Pr, Ph	<i>i</i> -Pr, Ph
	nK	,	~	3 81		4.29	4.34	•	4.72	4.89
	1/11.0	3.66	2.71	0.01						
10	$p_{\rm La}$	3.66 of XMePO((2.71 H) in water a	t 20° i						
10.	pK_a values o	3.66 of XMePO(C	$\begin{array}{c} 2.71 \\ \text{OH} \text{ in water a} \\ S(i \mathbf{Pr}) \end{array}$	$t 20^{\circ} i$	OF	400		Ν.	оч	Б
10.	pK_a values o X	3.66 of XMePO(C SPr	2.71)H) in water a S(<i>i</i> -Pr)	t 20° <i>i</i> O- <i>i</i> -Pr	OEt	4-C ₆ H	[₄Cl	Me	OH	F
10.	pK_{a} values o X pK_{a}	3.66 of XMePO(C SPr 2.03	2.71)H) in water a S(<i>i</i> -Pr) 2.13	t 20° <i>i</i> O- <i>i</i> -Pr 2.38	OEt 2.25	4-C ₆ H 2.3	[₄C] 9	Me 3.08	OH 2.68•	F 1.94
10. 11.	pK_a values o X pK_a pK_a values o	3.66 of XMePO(C SPr 2.03 of X-c-C ₆ H ₁₁]	2.71 DH) in water a S(<i>i</i> -Pr) 2.13 PO(OH) in 759	t 20° <i>i</i> O- <i>i</i> -Pr 2.38 % aqueous eth	OEt 2.25 anol at 22°	4-C ₆ H 2.39	[₄C] 9	Me 3.08	OH 2.68•	F 1.94
10. 11.	pK_{a} pK_{a} values of pK_{a} pK_{a} values of X	3.66 of XMePO(C SPr 2.03 of X-c-C ₆ H ₁₁] PhO	2.71 DH) in water a S(<i>i</i> -Pr) 2.13 PO(OH) in 759 H	t 20° <i>i</i> O- <i>i</i> -Pr 2.38 % aqueous eth c-C ₆ H ₁₁ O	OEt 2.25 anol at 22° Ph	4-C ₆ H 2.39 1	[₄C] 9 H•	Me 3.08 c-C ₆ H ₁₁	OH 2.68•	F 1.94
10. 11.	pK_a values of X pK_a pK_a values of X nK_a values of X	3.66 of XMePO(C SPr 2.03 of X-c-C ₆ H ₁₁] PhO 3.60	2.71)H) in water a S(i-Pr) 2.13 PO(OH) in 759 H 3.91	t 20° i O-i-Pr 2.38 % aqueous eth c-C ₆ H ₁₁ O 4.73	OEt 2.25 anol at 22° Ph 5.02	4-C ₆ H 2.39 1 OH	[4C] 9 H• 10	Me 3.08 c-C ₆ H ₁₁ 5.92	OH 2.68•	F 1.94
10. 11.	pK_a values of X pK_a pK_a values of X pK_a values of X pK_a pK_a values of X	3.66 of XMePO(C SPr 2.03 of X-c-C ₆ H ₁₁] PhO 3.60 of X 6 C H ₂ J	2.71)H) in water a S(i-Pr) 2.13 PO(OH) in 750 H 3.91 PO(OH) in 950	t 20° <i>i</i> O- <i>i</i> -Pr 2.38 % aqueous eth c-C ₆ H ₁₁ O 4.73	OEt 2.25 anol at 22° Ph 5.02 anol at 22°	4-C ₆ H 2.39 1 0H 5.1	14Cl 9 H• 10	Me 3.08 c-C ₆ H ₁₁ 5.92	OH 2.68•	F 1.94
10. 11. 12.	pK_{a} values of X pK_{a} values of X pK_{a} values of X pK_{a} values of X	3.66 of XMePO(C SPr 2.03 of X-c-C ₆ H ₁₁] PhO 3.60 of X-c-C ₆ H ₁₁]	2.71 DH) in water a S(i-Pr) 2.13 PO(OH) in 759 H 3.91 PO(OH) in 959	t 20° i O-i-Pr 2.38 % aqueous eth c - $C_6H_{11}O$ 4.73 % aqueous eth	OEt 2.25 anol at 22° Ph 5.02 anol at 22°	4-C ₆ H 2.39 1 0 1 5.1 1	L4Cl 9 H• 10	Me 3.08 c-C ₆ H ₁₁ 5.92	OH 2.68*	F 1.94
10. 11. 12.	pK_{a} pK_{a} values of pK_{a} pK_{a} values of X pK_{a} values of X	3.66 of XMePO(C SPr 2.03 of X-c-C ₆ H ₁₁] PhO 3.60 of X-c-C ₆ H ₁₁ PhO	2.71)H) in water a S(<i>i</i> -Pr) 2.13 PO(OH) in 759 H 3.91 PO(OH) in 959 H	t 20° i O-i-Pr 2.38 % aqueous eth c-C ₆ H ₁₁ O 4.73 % aqueous eth c-C ₆ H ₁₀ O	OEt 2.25 anol at 22° Ph 5.02 anol at 22° Ph	4-C ₆ H 2.33 1 0 1 5 1	L4Cl 9 H• 10 H•	Me 3.08 c-C ₆ H ₁₁ 5.92 c-C ₆ H ₁₁	OH 2.68•	F 1.94
10. 11. 12.	pK_{a} pK_{a} values of x pK_{a} values of X pK_{a} values of X pK_{a} values of X pK_{a}	3.66 of XMePO(C SPr 2.03 of X-c-C ₆ H ₁₁] PhO 3.60 of X-c-C ₆ H ₁₁] PhO 4.19	2.71 DH) in water a S(<i>i</i> -Pr) 2.13 PO(OH) in 750 H 3.91 PO(OH) in 950 H 4.55	t 20° i O-i-Pr 2.38 % aqueous eth $c-C_6H_{11}O$ 4.73 % aqueous eth $c-C_6H_{11}O$ 5.42	OEt 2.25 anol at 22° Ph 5.02 anol at 22° Ph 5.60	4-C ₆ H 2.39 1 5.1 1 0H 5.1	L4Cl 9 H• 10 H• 95	Me 3.08 c-C ₆ H ₁₁ 5.92 c-C ₆ H ₁₁ 6.64	OH 2.68*	F 1.94
10. 11. 12. 13.	pK_a values of pK_a values of pK_a values of x pK_a values of X pK_a values of X pK_a values of x	3.66 of XMePO(C SPr 2.03 of X-c-C ₆ H ₁₁] PhO 3.60 of X-c-C ₆ H ₁₁] PhO 4.19 of X-c-C ₆ H ₁₀	2.71 DH) in water a S(i-Pr) 2.13 PO(OH) in 756 H 3.91 PO(OH) in 956 H 4.55 DPOP(OH) in	t 20° i O-i-Pr 2.38 % aqueous eth $c-C_6H_{11}O$ 4.73 % aqueous eth $c-C_6H_{11}O$ 5.42 75% aqueous eth	$\begin{array}{c} \text{OEt} \\ 2.25 \\ \text{anol at } 22^{\circ} \\ \text{Ph} \\ 5.02 \\ \text{anol at } 22^{\circ} \\ \text{Ph} \\ 5.60 \\ \text{ethanol at } \end{array}$	4-C ₆ H 2.39 1 5.7 1 0H 5.9 22° 1	L(Cl 9 H• 10 H• 95	Me 3.08 c-C ₆ H ₁₁ 5.92 c-C ₆ H ₁₁ 6.64	OH 2.68*	F 1.94
10. 11. 12. 13.	pK_a values of X pK_a values of X	3.66 of XMePO(C SPr 2.03 of X-c-C ₆ H ₁₁] PhO 3.60 of X-c-C ₆ H ₁₁] PhO 4.19 of X-c-C ₆ H ₁₀ (PhO	2.71)H) in water a S(i-Pr) 2.13 PO(OH) in 750 H 3.91 PO(OH) in 950 H 4.55 DPOP(OH) in H	t 20° <i>i</i> O- <i>i</i> -Pr 2.38 % aqueous eth <i>c</i> -C ₆ H ₁₁ O 4.73 % aqueous eth <i>c</i> -C ₆ H ₁₀ O 5.42 75% aqueous - <i>c</i> -C ₆ H ₁₀ O	OEt 2.25 anol at 22° Ph 5.02 anol at 22° Ph 5.60 ethanol at 2 Ph	4-C ₆ H 2.3 1 5.7 1 0H 5.1 22° 1	L(Cl 9 H• 10 H• 95 c-C4H11	Me 3.08 c-C ₆ H ₁₁ 5.92 c-C ₆ H ₁₁ 6.64	OH 2.68"	F 1.94
10. 11. 12. 13.	pK_a values of X pK_a values of X	3.66 of XMePO(C SPr 2.03 of X-c-C $_{6}H_{11}$ PhO 3.60 of X-c-C $_{6}H_{11}$ PhO 4.19 of X-c-C $_{6}H_{11}$ PhO 4.64	2.71 DH) in water a S(i-Pr) 2.13 PO(OH) in 756 H 3.91 PO(OH) in 956 H 4.55 DPOP(OH) in H 2.83	t 20° <i>i</i> O- <i>i</i> -Pr 2.38 % aqueous eth c -C $_{6}H_{11}O$ 4.73 % aqueous eth c -C $_{6}H_{11}O$ 5.42 75% aqueous eth c -C $_{6}H_{11}O$ 3.81	OEt 2.25 anol at 22° Ph 5.02 anol at 22° Ph 5.60 ethanol at 2 Ph 3 8	4-C ₆ H 2.33 ¹ OH 5.1 22° ¹	L ₄ Cl 9 H• 10 H• 95 c-C ₆ H ₁₁ 4 73	Me 3.08 c-C ₆ H ₁₁ 5.92 c-C ₆ H ₁₁ 6.64	OH 2.684	F 1.94
10. 11. 12. 13.	pK_a values of X pK_a values of X	3.66 of XMePO(C SPr 2.03 of X-c-C ₆ H ₁₁ J PhO 3.60 of X-c-C ₆ H ₁₁ J PhO 4.19 of X-c-C ₆ H ₁₁ C PhO 1.64	2.71 DH) in water a S(i-Pr) 2.13 PO(OH) in 759 H 3.91 PO(OH) in 959 H 4.55 DPOP(OH) in H 2.83 DPO(OH) in 0	t 20° <i>i</i> O- <i>i</i> -Pr 2.38 % aqueous eth <i>c</i> -C ₆ H ₁₁ O 4.73 % aqueous eth <i>c</i> -C ₆ H ₁₁ O 5.42 75% aqueous <i>c</i> -C ₆ H ₁₁ O 3.81	OEt 2.25 anol at 22° Ph 5.02 anol at 22° Ph 5.60 ethanol at 2 Ph 3.88	4-C ₆ H 2.39 1 0 5.1 5.1 22° 1 5.1 5.1 5.1 5.1 6 3 22° 1 6 3	L4Cl 9 H• 10 H• 95 c-C6H11 4.73	Me 3.08 c-C ₆ H ₁₁ 5.92 c-C ₆ H ₁₁ 6.64	OH 2.68*	F 1.94
10. 11. 12. 13. 14.	pK_a values of pK_a values of pK_a values of x pK_a values of x pK_a values of x pK_a values of x pK_a values of x	3.66 of XMePO(C SPr 2.03 of X-c-C ₆ H ₁₁] PhO 3.60 of X-c-C ₆ H ₁₁] PhO 4.19 of X-c-C ₆ H ₁₁ 0 PhO 1.64 of X-c-C ₆ H ₁₁ 0	2.71 (i-Pr) 2.13 PO(OH) in 759 H 3.91 PO(OH) in 959 H 4.55 OPOP(OH) in $H2.83OPO(OH)$ in 9.9	t 20° <i>i</i> O- <i>i</i> -Pr 2.38 % aqueous eth <i>c</i> -C ₆ H ₁₁ O 4.73 % aqueous eth <i>c</i> -C ₆ H ₁₁ O 5.42 75% aqueous <i>c</i> -C ₆ H ₁₁ O 3.81	OEt 2.25 anol at 22° Ph 5.02 anol at 22° Ph 5.60 ethanol at 2 Ph 3.8 chanol at 22°	4-C ₆ H 2.3 1 5.1 0 1 22 ^o 1 3 3 ^o 1	L(Cl 9 H• 10 H• 95 c-C6H11 4.73	Me 3.08 c-C ₆ H ₁₁ 5.92 c-C ₆ H ₁₁ 6.64	OH 2.684	F 1.94
10. 11. 12. 13. 14.	pK_a values of pK_a values of pK_a values of pK_a values of X pK_a values of X pK_a values of X pK_a values of X pK_a values of X	3.66 of XMePO(C SPr 2.03 of X-c-C ₆ H ₁₁] PhO 3.60 of X-c-C ₆ H ₁₁] PhO 4.19 of X-c-C ₆ H ₁₀ PhO 1.64 of X-c-C ₆ H ₁₀ (PhO	2.71 DH) in water a S(i-Pr) 2.13 PO(OH) in 759 H 3.91 PO(OH) in 959 H 4.55 DPOP(OH) in 959 H 2.83 DPOP(OH) in 959 c-C_6H ₁₁ O	t 20° <i>i</i> O- <i>i</i> -Pr 2.38 % aqueous eth <i>c</i> -C ₆ H ₁₁ O 4.73 % aqueous eth <i>c</i> -C ₆ H ₁₁ O 5.42 75% aqueous eth <i>c</i> -C ₆ H ₁₁ O 3.81 5% aqueous eth H	OEt 2.25 anol at 22° Ph 5.02 anol at 22° Ph 5.60 ethanol at 2 Ph 3.8 shanol at 22 Ph	4-C ₆ H 2.39 1 5.1 2 22 ^{° 1} 3 3 ^{° 1}	L(Cl 9 H• 10 H• 95 c-C6H11 4.73 c-C6H11	Me 3.08 c-C ₆ H ₁₁ 5.92 c-C ₆ H ₁₁ 6.64	OH 2.68*	F 1.94
10. 11. 12. 13. 14.	pK_a values of pK_a values of pK_a values of pK_a values of x pK_a values of X	3.66 of XMePO(C SPr 2.03 of X-c-C ₆ H ₁₁ PhO 3.60 of X-c-C ₆ H ₁₁ PhO 4.19 of X-c-C ₆ H ₁₁ PhO 1.64 of X-c-C ₆ H ₁₁ PhO 1.64 of X-c-C ₆ H ₁₁ PhO 3.08	2.71)H) in water a S(i-Pr) 2.13 PO(OH) in 756 H 3.91 PO(OH) in 956 H 4.55 DPOP(OH) in 9 H 2.83 DPO(OH) in 9. $c-C_6H_{11}O$ 4.43	t 20° <i>i</i> O- <i>i</i> -Pr 2.38 % aqueous eth $c-C_6H_{11}O$ 4.73 % aqueous eth $c-C_6H_{11}O$ 5.42 75% aqueous et $c-C_6H_{11}O$ 3.81 5% aqueous et H 3.40	OEt 2.25 anol at 22° Ph 5.02 anol at 22° Ph 5.60 ethanol at 22 Ph 3.8 shanol at 22 Ph 4.4	4-C ₆ H 2.39 1 5.1 2 22 ^{° 1} 3 22 ^{° 1} 3 22 ^{° 1} 2 22 ^{° 1} 3 22 ^{° 1}	L(Cl 9 H• 10 H• 95 c-C ₆ H ₁₁ 4.73 c-C ₆ H ₁₁ 5.42	Me 3.08 c-C ₆ H ₁₁ 5.92 c-C ₆ H ₁₁ 6.64	OH 2.68*	F 1.94
 10. 11. 12. 13. 14. 15. 	pK_a pK_a values of pK_a values of pK_a values of pK_a values of pK_a values of pK_a values of pK_a values of pK_a val	3.66 of XMePO(C SPr 2.03 of X-c-C ₆ H ₁₁ PhO 3.60 of X-c-C ₆ H ₁₁ PhO 4.19 of X-c-C ₆ H ₁₁ PhO 1.64 of X-c-C ₆ H ₁₀ PhO 1.64 of X-c-C ₆ H ₁₀ PhO 3.08 of XPhOPO(2.71)H) in water a S(i-Pr) 2.13 PO(OH) in 75 H 3.91 PO(OH) in 95 H 4.55 DPOP(OH) in 9 L 2.83 DPO(OH) in 9 $c-C_{6}H_{11}O$ 4.43 OH) in 75% a	t 20° <i>i</i> O- <i>i</i> -Pr 2.38 % aqueous eth c -C $_{6}H_{11}O$ 4.73 % aqueous eth c -C $_{6}H_{11}O$ 5.42 75% aqueous eth 3.81 5% aqueous eth 3.40 queous ethano	OEt 2.25 anol at 22° Ph 5.02 anol at 22° Ph 5.60 ethanol at 22 Ph 3.8 shanol at 22 Ph 4.4	4-C ₆ H 2.33 1 0 1 5.1 22 ^{° 1} 3 22 ^{° 1} 3 3 1 2 2 1 2	L4Cl 9 H• 10 H• 95 c-C6H11 4.73 c-C6H11 5.42	Me 3.08 c-C ₆ H ₁₁ 5.92 c-C ₆ H ₁₁ 6.64	OH 2.684	F 1.94
 10. 11. 12. 13. 14. 15. 	pK_a values of pK_a values of pK_a values of pK_a values of pK_a values of pK_a values of pK_a values of pK_a values of pK_a values of pK_a values of	3.66 of XMePO(C SPr 2.03 of X-c-C $_{6}H_{11}$ PhO 3.60 of X-c-C $_{6}H_{11}$ PhO 4.19 of X-c-C $_{6}H_{11}$ PhO 1.64 of X-c-C $_{6}H_{11}$ PhO 3.08 of XPhOPO(PhO	2.71 DH) in water a S(i-Pr) 2.13 PO(OH) in 754 H 3.91 PO(OH) in 954 H 4.55 DPOP(OH) in 954 H 2.83 DPOP(OH) in 956 A 4.43 OH) in 75% a c-C_6HuO	t 20° <i>i</i> O- <i>i</i> -Pr 2.38 % aqueous eth c -C $_{6}H_{11}O$ 4.73 % aqueous eth c -C $_{6}H_{11}O$ 5.42 75% aqueous eth c -C $_{6}H_{11}O$ 3.81 5% aqueous eth 3.40 queous ethanol OH•	OEt 2.25 anol at 22° Ph 5.02 anol at 22° Ph 5.60 ethanol at 22 Ph 3.8 shanol at 22 Ph 4.4 l at 22° ^{<i>i</i>}	4-C ₆ H 2.39 1 0 1 5.1 5.1 22 ^{° 1} 3 22 ^{° 1} 3 3 2 ^{° 1} 2	L4Cl 9 H• 10 H• 95 c-C6H11 4.73 c-C6H11 5.42	Me 3.08 c-C ₆ H ₁₁ 5.92 c-C ₆ H ₁₁ 6.64	OH 2.68*	F 1.94
 10. 11. 12. 13. 14. 15. 	pK_a pK_a values of X pK_a values of X	3.66 of XMePO(C SPr 2.03 of X-c-C ₆ H ₁₁] PhO 3.60 of X-c-C ₆ H ₁₁] PhO 4.19 of X-c-C ₆ H ₁₁ O PhO 1.64 of X-c-C ₆ H ₁₁ O PhO 3.08 of X-c-C ₆ H ₁₁ O PhO 3.08	2.71 DH) in water a S(i-Pr) 2.13 PO(OH) in 759 H 3.91 PO(OH) in 959 H 4.55 DPOP(OH) in 959 H 2.83 DPOP(OH) in 9. c-C_6H ₁₁ O 4.43 OH) in 75% a c-C_6H ₁₁ O	t 20° i O-i-Pr 2.38 % aqueous eth c-C_6H ₁₁ O 4.73 % aqueous eth c-C_6H ₁₁ O 5.42 75% aqueous eth c-C_6H ₁₁ O 3.81 5% aqueous eth 3.40 queous ethanol OH• 2.42	OEt 2.25 anol at 22° Ph 5.02 anol at 22° Ph 5.60 ethanol at 22 Ph 3.8 shanol at 22 Ph 4.4 l at 22° ' Ph	4-C ₆ H 2.3 1 5.1 0H 22 ⁰ 1 3 2 ⁰ 1 4 2	L4Cl 9 H• 10 H• 95 c-C6H11 4.73 c-C6H11 5.42 c-C6H11	Me 3.08 c-C ₆ H ₁₁ 5.92 c-C ₆ H ₁₁ 6.64	OH 2.684	F 1.94
 10. 11. 12. 13. 14. 15. 	pK_a values of pK_a values of pK_a values of pK_a values of X pK_a values of X	3.66 of XMePO(C SPr 2.03 of X-c-C ₆ H ₁₁] PhO 3.60 of X-c-C ₆ H ₁₁] PhO 4.19 of X-c-C ₆ H ₁₀ PhO 1.64 of X-c-C ₆ H ₁₀ PhO 1.64 of X-c-C ₆ H ₁₀ PhO 3.08 of XPhOPO(PhO 2.28	2.71 DH) in water a S(i-Pr) 2.13 PO(OH) in 759 H 3.91 PO(OH) in 959 H 4.55 DPOP(OH) in 959 H 2.83 DPO(OH) in 9. $c-C_6H_{11}O$ 4.43 OH) in 75% a $c-C_6H_{11}O$ 2.64	t 20° i O-i-Pr 2.38 % aqueous eth c -C $_6$ H $_{11}$ O 4.73 % aqueous eth c -C $_6$ H $_{11}$ O 5.42 75% aqueous eth c -C $_6$ H $_{11}$ O 3.81 5% aqueous et H 3.40 queous ethanol OH• 3.43	OEt 2.25 anol at 22° Ph 5.02 anol at 22° Ph 5.60 ethanol at 22 Ph 3.8 hanol at 22 Ph 4.4 l at 22° ⁷ Ph 2.88	4-C ₆ H 2.39 1 5.1 0 1 22° 1 3 22° 1 3 22° 1 3 22° 1 3 2 2 3 3 2 4 5 5	L(Cl 9 H• 10 H• 95 c-C ₆ H ₁₁ 4.73 c-C ₆ H ₁₁ 5.42 c-C ₆ H ₁₁ 3.60	Me 3.08 c-C ₆ H ₁₁ 5.92 c-C ₆ H ₁₁ 6.64	OH 2.68*	F 1.94
 10. 11. 12. 13. 14. 15. 16. 	pK_a values of pK_a values of pK_a values of pK_a values of pK_a values of pK_a values of X pK_a values of X pK_a values of X p	3.66 of XMePO(C SPr 2.03 of X-c-C ₆ H ₁₁] PhO 3.60 of X-c-C ₆ H ₁₁] PhO 4.19 of X-c-C ₆ H ₁₀ PhO 1.64 of X-c-C ₆ H ₁₀ PhO 1.64 of X-c-C ₆ H ₁₀ PhO 2.28 of XPhOPO(2.71 DH) in water a S(i-Pr) 2.13 PO(OH) in 759 H 3.91 PO(OH) in 959 H 4.55 DPOP(OH) in 959 C-C_6H ₁₁ O 4.43 OH) in 75% a c-C_6H ₁₁ O 2.64 OH) in 95% a	t 20° i O-i-Pr 2.38 % aqueous eth $c-C_6H_{11}O$ 4.73 % aqueous eth $c-C_6H_{11}O$ 5.42 75% aqueous eth $c-C_6H_{11}O$ 3.81 5% aqueous eth 3.40 queous ethanol OH• 3.43 queous ethanol	OEt 2.25 anol at 22° Ph 5.02 anol at 22° Ph 5.60 ethanol at 22 Ph 3.8 shanol at 22 Ph 4.4 l at 22° ² l at 22° ²	4-C ₆ H 2.39 1 5.1 0 22° 1 3 22° 1 3 3° 1 2 2	L(Cl 9 H• 10 H• 95 c-C ₆ H ₁₁ 4.73 c-C ₆ H ₁₁ 5.42 c-C ₆ H ₁₁ 3.60	Me 3.08 c-C ₆ H ₁₁ 5.92 c-C ₆ H ₁₁ 6.64	OH 2.68*	F 1.94
 10. 11. 12. 13. 14. 15. 16. 	pK_a values of pK_a values of pK_a values of pK_a values of pK_a values of X pK_a values of X	3.66 of XMePO(C SPr 2.03 of X-c-C ₆ H ₁₁ PhO 3.60 of X-c-C ₆ H ₁₁ PhO 4.19 of X-c-C ₆ H ₁₁ PhO 1.64 of X-c-C ₆ H ₁₁ PhO 1.64 of X-c-C ₆ H ₁₀ PhO 2.28 of XPhOPO(PhO 2.28 of XPhOPO(PhO	2.71)H) in water a S(i-Pr) 2.13 PO(OH) in 75 ^o H 3.91 PO(OH) in 95 ^o H 4.55 DPOP(OH) in 9 $c^{-C_{6}H_{11}O}$ 4.43 OH) in 75% a $c^{-C_{6}H_{11}O}$ 2.64 OH) in 95% a $c^{-C_{6}H_{11}O}$	t 20° i O-i-Pr 2.38 % aqueous eth $c-C_6H_{11}O$ 4.73 % aqueous eth $c-C_6H_{11}O$ 5.42 75% aqueous eth 3.81 5% aqueous eth 3.40 queous ethanol OH• 3.43 queous ethanol OH•	OEt 2.25 anol at 22° Ph 5.02 anol at 22° Ph 3.8 chanol at 22° Ph 4.4 l at 22° ' Ph 2.8 l at 22° ' Ph	4-C ₆ H 2.33 1 0 1 22 ⁰ 1 3 22 ⁰ 1 3 3 2 2 5 3 4 2 5 5 3 4 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5	L ₄ Cl 9 H• 10 H• 95 c-C ₆ H ₁₁ 4.73 c-C ₆ H ₁₁ 5.42 c-C ₆ H ₁₁ 3.60 c-C ₆ H ₁₁	Me 3.08 c-C ₆ H ₁₁ 5.92 c-C ₆ H ₁₁ 6.64	OH 2.684	F 1.94
 10. 11. 12. 13. 14. 15. 16. 	pK_a pK_a values of pK_a values of pK_a values of pK_a values of pK_a values of	3.66 of XMePO(C SPr 2.03 of X-c-C ₆ H ₁₁ PhO 3.60 of X-c-C ₆ H ₁₁ PhO 4.19 of X-c-C ₆ H ₁₁ PhO 1.64 of X-c-C ₆ H ₁₁ PhO 1.64 of X-c-C ₆ H ₁₁ PhO 2.28 of XPhOPO(PhO 1.91	2.71 DH) in water a S(i-Pr) 2.13 PO(OH) in 75 ⁴ H 3.91 PO(OH) in 95 ⁶ H 4.55 DPOP(OH) in 95 ⁶ H 2.83 DPO(OH) in 95 ⁶ 4.43 OH) in 75 ⁶ % a c-C ₆ H ₁₁ O 2.64 OH) in 95 ⁶ % a c-C ₆ H ₁₁ O 3.08	t 20° i O-i-Pr 2.38 % aqueous eth c -C $_{6}H_{11}O$ 4.73 % aqueous eth c -C $_{6}H_{11}O$ 5.42 75% aqueous eth c-C $_{6}H_{11}O$ 3.81 5% aqueous eth 3.40 queous ethanol OH• 3.43 queous ethanol OH• 4.13	OEt 2.25 anol at 22° Ph 5.02 anol at 22° Ph 5.60 ethanol at 22 Ph 3.8 shanol at 22° Ph 4.4 l at 22°' Ph 2.8 l at 22°' Ph 3.3	4-C ₆ H 2.33 1 0H 5.1 22 ^o 1 3 22 ^o 1 3 2 2 5 5 5 5 5	I_4Cl 9 H• 10 H• 95 $c-C_6H_{11}$ 4.73 $c-C_6H_{11}$ 5.42 $c-C_6H_{11}$ 5.42 $c-C_6H_{11}$ 5.42 $c-C_6H_{11}$ 4.73	Me 3.08 c-C ₆ H ₁₁ 5.92 c-C ₆ H ₁₁ 6.64	OH 2.684	F 1.94
 10. 11. 12. 13. 14. 15. 16. 17. 	pK_a values of pK_a values of pK_a values of pK_a values of pK_a values of pK_a values of pK_a values of pK_a values of pK_a values of pK_a values of pK_a values of pK_a values of pK_a	3.66 of XMePO(C SPr 2.03 of X-c-C ₆ H ₁₁] PhO 3.60 of X-c-C ₆ H ₁₁] PhO 4.19 of X-c-C ₆ H ₁₁ PhO 4.19 of X-c-C ₆ H ₁₁ PhO 1.64 of X-c-C ₆ H ₁₁ PhO 1.64 of X-c-C ₆ H ₁₁ PhO 2.28 of XPhOPO(PhO 1.91 of XPhOPO(0)	2.71)H) in water a S(i-Pr) 2.13 PO(OH) in 75% H 3.91 PO(OH) in 95% H 4.55 DPOP(OH) in 95% H 2.83 DPO(OH) in 95% a c-C_6H ₁₁ O 2.64 OH) in 95% a c-C_6H ₁₁ O	t 20° i O-i-Pr 2.38 % aqueous eth $c-C_6H_{11}O$ 4.73 % aqueous eth $c-C_6H_{11}O$ 5.42 75% aqueous eth c-C_6H_{11}O 3.81 5% aqueous eth 3.40 queous ethanol OH• 4.13 ueous ethanol	OEt 2.25 anol at 22° Ph 5.02 anol at 22° Ph 5.60 ethanol at 22° Ph 3.8 hanol at 22° Ph 4.4 1 at 22° i Ph 2.8 1 at 22° i Ph 3.3 at 22° i	4-C ₆ H 2.39 1 5.1 22 ⁰ 1 22 ⁰ 1 3 2 1 2 5 5 5 5	L(Cl 9 H• 10 H• 95 c-C6H11 4.73 c-C6H11 5.42 c-C6H11 3.60 c-C6H11 4.19	Me 3.08 c-C ₆ H ₁₁ 5.92 c-C ₆ H ₁₁ 6.64	OH 2.68*	F 1.94
 10. 11. 12. 13. 14. 15. 16. 17. 	pK_a values of pK_a values of pK_a values of pK_a values of X pK_a values of X	3.66 of XMePO(C SPr 2.03 of X-c-C ₆ H ₁₁] PhO 3.60 of X-c-C ₆ H ₁₁] PhO 4.19 of X-c-C ₆ H ₁₁ PhO 4.19 of X-c-C ₆ H ₁₁ PhO 1.64 of X-c-C ₆ H ₁₁ PhO 1.64 of X-c-C ₆ H ₁₁ PhO 2.28 of XPhOPO(PhO 1.91 of XPhOPO(0 PhO 0 0 PhO	2.71)H) in water a S(i-Pr) 2.13 PO(OH) in 759 H 3.91 PO(OH) in 959 H 4.55 DPOP(OH) in 959 H 2.83 DPO(OH) in 9. c-C_6H ₁₁ O 2.64 OH) in 95% a c-C_6H ₁₁ O 3.08 H) in 75% aqu	t 20° i O-i-Pr 2.38 % aqueous eth c-C ₆ H ₁₁ O 4.73 % aqueous eth c-C ₆ H ₁₁ O 5.42 75% aqueous eth c-C ₆ H ₁₁ O 3.81 5% aqueous eth 3.40 queous ethanol OH• 4.13 ueous ethanol a	OEt 2.25 anol at 22° Ph 5.02 anol at 22° Ph 5.60 ethanol at 22° Ph 3.8 chanol at 22° Ph 4.4 1 at 22° i Ph 3.3 at 22° i OH	4-C ₆ H 2.3 1 5.1 22 ⁰ 1 3 22 ⁰ 1 4 3 2 2 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5	L(Cl 9 H• 10 H• 95 c-C ₆ H ₁₁ 4.73 c-C ₆ H ₁₁ 5.42 c-C ₆ H ₁₁ 3.60 c-C ₆ H ₁₁ 4.19	Me 3.08 c-C ₆ H ₁₁ 5.92 c-C ₆ H ₁₁ 6.64	OH 2.684	F 1.94
 10. 11. 12. 13. 14. 15. 16. 17. 	pK_a values of pK_a values of pK_a values of pK_a values of pK_a values of pK_a values of X pK_a values of X	3.66 of XMePO(C SPr 2.03 of X-c-C ₆ H ₁₁] PhO 3.60 of X-c-C ₆ H ₁₁] PhO 4.19 of X-c-C ₆ H ₁₁ PhO 4.19 of X-c-C ₆ H ₁₀ PhO 1.64 of X-c-C ₆ H ₁₀ PhO 2.28 of XPhOPO(PhO 1.91 of XPhPO(O PhO	2.71)H) in water a S(i-Pr) 2.13 PO(OH) in 756 H 3.91 PO(OH) in 956 H 4.55 DPOP(OH) in 956 H 2.83 DPO(OH) in 956 c-C ₆ H ₁₁ O 2.64 OH) in 95% a c-C ₆ H ₁₁ O 3.08 H) in 75% aqu	t 20° i O-i-Pr 2.38 % aqueous eth $c-C_6H_{11}O$ 4.73 % aqueous eth $c-C_6H_{11}O$ 5.42 75% aqueous eth $c-C_6H_{11}O$ 3.81 5% aqueous eth anol OH• 3.43 queous ethanol OH• 4.13 neous ethanol a $c-C_6H_{11}O$	OEt 2.25 anol at 22° Ph 5.02 anol at 22° Ph 5.60 ethanol at 22° Ph 3.8 hanol at 22° Ph 4.4 1 at 22°' Ph 2.8 1 at 22°' Ph 3.3 at 22°' OH•	4-C ₆ H 2.3 1 0 1 22° 1 3 22° 1 3 2 2 2 5 5 5 5 2 2	L ₄ Cl 9 H• 10 H• 95 c-C ₆ H ₁₁ 4.73 c-C ₆ H ₁₁ 5.42 c-C ₆ H ₁₁ 3.60 c-C ₆ H ₁₁ 4.19 h	Me 3.08 c-C ₆ H ₁₁ 5.92 c-C ₆ H ₁₁ 6.64	OH 2.68*	F 1.94
 10. 11. 12. 13. 14. 15. 16. 17. 	pK_a values of pK_a values of pK_a values of pK_a values of pK_a values of pK_a values of pK_a values of X pK_a values of X	3.66 of XMePO(C SPr 2.03 of X-c-C ₆ H ₁₁ PhO 3.60 of X-c-C ₆ H ₁₁ PhO 4.19 of X-c-C ₆ H ₁₁ PhO 4.19 of X-c-C ₆ H ₁₀ PhO 1.64 of X-c-C ₆ H ₁₀ PhO 2.28 of XPhOPO(PhO 1.91 of XPhOPO(PhO 2.85	2.71)H) in water a S(i-Pr) 2.13 PO(OH) in 75° H 3.91 PO(OH) in 95° H 4.55 DPOP(OH) in 95° <i>c</i> -C ₆ H ₁₁ O 2.64 OH) in 75% aqu <i>c</i> -C ₆ H ₁₁ O 3.08 H) in 75% aqu H 3.11	t 20° i O-i-Pr 2.38 % aqueous eth $c-C_6H_{11}O$ 4.73 % aqueous eth $c-C_6H_{11}O$ 5.42 75% aqueous eth $c-C_6H_{11}O$ 3.81 5% aqueous eth anol OH• 3.43 queous ethanol OH• 4.13 ueous ethanol $c-C_6H_{11}O$ 3.83	$\begin{array}{c} {\rm OEt} \\ 2.25 \\ {\rm anol\ at\ 22}^{\circ} \\ {\rm Ph} \\ 5.02 \\ {\rm anol\ at\ 22}^{\circ} \\ {\rm Ph} \\ 5.60 \\ {\rm ethanol\ at\ 22} \\ {\rm Ph} \\ 3.8 \\ {\rm shanol\ at\ 22}^{\circ} \\ {\rm H} \\ 2.8 \\ {\rm l\ at\ 22}^{\circ} \\ {\rm Ph} \\ 3.3 \\ {\rm at\ 22}^{\circ} \\ {\rm OH} \\ 4.26 \end{array}$	4-C ₆ H 2.33 1 0 1 22 ⁰ 1 22 ⁰ 1 3 22 ⁰ 1 2 3 4 2 2 5 3 4 2 2 7 4 2 2 7 4 2 4 2	$ \begin{array}{c} \text{L}\text{Cl} \\ 9 \\ \text{H}^{\bullet} \\ 10 \\ \text{H}^{\bullet} \\ 95 \\ \text{c}\text{-}\text{C}_{\bullet}\text{H}_{11} \\ 4.73 \\ \text{c}\text{-}\text{C}_{\bullet}\text{H}_{11} \\ 5.42 \\ \text{c}\text{-}\text{C}_{\bullet}\text{H}_{11} \\ 3.60 \\ \text{c}\text{-}\text{C}_{\bullet}\text{H}_{11} \\ 4.19 \\ \text{h} \\ 10 \end{array} $	Me 3.08 c-C ₆ H ₁₁ 5.92 c-C ₆ H ₁₁ 6.64	OH 2.684	F 1.94
 10. 11. 12. 13. 14. 15. 16. 17. 18. 	pK_a values of pK_a values of pK_a values of pK_a values of pK_a values of pK_a values of pK_a values of pK_a valu	3.66 of XMePO(C SPr 2.03 of X-c-C ₆ H ₁₁] PhO 3.60 of X-c-C ₆ H ₁₁] PhO 4.19 of X-c-C ₆ H ₁₁ PhO 1.64 of X-c-C ₆ H ₁₁ (PhO 1.64 of X-c-C ₆ H ₁₁ (PhO 2.28 of XPhOPO(C PhO 1.91 of XPhOPO(O PhO 2.85 of XPhPO(O)	2.71)H) in water a S(i-Pr) 2.13 PO(OH) in 754 H 3.91 PO(OH) in 954 H 4.55)POP(OH) in 95 $C-C_{6}H_{11}O$ 2.64 OH) in 95% aquestic and a second se	t 20° i O-i-Pr 2.38 % aqueous eth c -C $_{6}H_{11}O$ 4.73 % aqueous eth c -C $_{6}H_{11}O$ 5.42 75% aqueous eth 5% aqueous eth 5% aqueous eth 3.40 queous ethanol OH• 4.13 neous ethanol a c -C $_{6}H_{11}O$ 3.83 neous ethanol a	OEt 2.25 anol at 22° Ph 5.02 anol at 22° Ph 5.60 ethanol at 22 Ph 3.8 chanol at 22° Ph 2.8 l at 22°' Ph 3.3 at 22°' OH* 4.26 at 22°'	4-C ₆ H 2.33 1 0 1 22 ⁰ 1 3 22 ⁰ 1 3 2 2 1 2 2 2 1 2 2 2 2 2 2 2 2 2 2 2	$ \begin{array}{c} \text{L}\text{Cl} \\ 9 \\ \text{H} \\ 10 \\ \text{H} \\ 95 \\ \text{c}\text{-}\text{C}_6\text{H}_{11} \\ 4.73 \\ \text{c}\text{-}\text{C}_6\text{H}_{11} \\ 5.42 \\ \text{c}\text{-}\text{C}_6\text{H}_{11} \\ 3.60 \\ \text{c}\text{-}\text{C}_6\text{H}_{11} \\ 4.19 \\ \text{h} \\ 10 \end{array} $	Me 3.08 c-C ₆ H ₁₁ 5.92 c-C ₆ H ₁₁ 6.64	OH 2.68*	F 1.94
 10. 11. 12. 13. 14. 15. 16. 17. 18. 	pK_a values of pK_a values of pK_a values of pK_a values of pK_a v	3.66 of XMePO(C SPr 2.03 of X-c-C ₆ H ₁₁] PhO 3.60 of X-c-C ₆ H ₁₁] PhO 4.19 of X-c-C ₆ H ₁₁ PhO 4.19 of X-c-C ₆ H ₁₁ PhO 1.64 of X-c-C ₆ H ₁₁ PhO 2.28 of XPhOPO(C PhO 2.28 of XPhOPO(C PhO 2.85 of XPhPO(O PhO 2.85 of XPhOPO(C PhO 2.85	2.71)H) in water a S(i-Pr) 2.13 PO(OH) in 754 H 3.91 PO(OH) in 956 H 4.55 DPOP(OH) in 956 C-C_8H_{11}O 4.43 OH) in 756 a c-C_6H_{11}O 2.64 OH) in 9576 aqu H 3.11 H) in 9576 aqu H	t 20° i O-i-Pr 2.38 % aqueous eth $c-C_6H_{11}O$ 4.73 % aqueous eth $c-C_6H_{11}O$ 5.42 75% aqueous eth $c-C_6H_{11}O$ 3.81 5% aqueous eth 3.40 queous ethanol 0H• 4.13 ueous ethanol s $c-C_6H_{11}O$ 3.83 ueous ethanol s $c-C_6H_{11}O$ 3.83 ueous ethanol s $c-C_6H_{11}O$ 3.83	OEt 2.25 anol at 22° Ph 5.02 anol at 22° Ph 5.60 ethanol at 22° Ph 3.8 hanol at 22° Ph 3.8 hanol at 22° Ph 2.8 l at 22° ^l Ph 3.8 hanol at 22° Ph 3.8 hanol at 22° Ph 4.4 at 22° ^l Ph 3.8 hanol at 22° Ph 4.26 at 22° ^l Ph 3.8 Ph 2.8 l at 22° ^l Ph 3.8 Ph 2.8 l at 22° ^l Ph 3.8 Ph 2.8 Ph 3.8 Ph 2.8 Ph 3.8 Ph 2.8 Ph 3.8 Ph 2.8 Ph 3.8 Ph 2.8 Ph 3.8 Ph 2.8 Ph 3.8 Ph 2.8 Ph 3.8 Ph 4.26 Ph 4.26 Ph	4-C ₆ H 2.39 1 0 1 22 ⁰ 1 2 2 ⁰ 1 2 2 5 5 5 2 2 9 1 6 5 5 5 2 9 1 6 6 5 5 2 9 1 6 7 1 6 7 1 6 7 1 6 7 1 6 7 1 7 1 7 1	L4Cl 9 H• 10 H• 95 c-C6H11 4.73 c-C6H11 5.42 c-C6H11 3.60 c-C6H11 4.19 h 10 c-C6H11	Me 3.08 c-C ₆ H ₁₁ 5.92 c-C ₆ H ₁₁ 6.64	OH 2.68*	F 1.94
 10. 11. 12. 13. 14. 15. 16. 17. 18. 	pK_a values of pK_a values of pK_a values of pK_a values of pK_a values of pK_a v	3.66 of XMePO(C SPr 2.03 of X-c-C ₆ H ₁₁] PhO 3.60 of X-c-C ₆ H ₁₁] PhO 4.19 of X-c-C ₆ H ₁₁ PhO 4.19 of X-c-C ₆ H ₁₁ PhO 1.64 of X-c-C ₆ H ₁₁ PhO 1.64 of X-c-C ₆ H ₁₁ PhO 2.28 of XPhOPO(C PhO 1.91 of XPhOPO(O PhO 2.85 of XPhOPO(O PhO 3.32	2.71)H) in water a S(i-Pr) 2.13 PO(OH) in 759 H 3.91 PO(OH) in 959 H 4.55 DPOP(OH) in 959 C-C_8HnO 2.63 OH) in 75% a c-C_6HnO 3.08 H) in 75% aqu H 3.11 H) in 95% aqu H 3.69	t 20° i O-i-Pr 2.38 % aqueous eth $c-C_6H_{11}O$ 4.73 % aqueous eth $c-C_6H_{11}O$ 5.42 75% aqueous eth $c-C_6H_{11}O$ 3.81 5% aqueous eth 3.40 queous ethanol OH• 4.13 ueous ethanol s $c-C_6H_{11}O$ 3.83 1eous ethanol s $c-C_6H_{11}O$ 4.42	$\begin{array}{c} {\rm OEt} \\ 2.25 \\ {\rm anol\ at\ } 22^\circ \\ {\rm Ph} \\ 5.02 \\ {\rm anol\ at\ } 22^\circ \\ {\rm Ph} \\ 5.60 \\ {\rm ethanol\ at\ } 22^\circ \\ {\rm Ph} \\ 3.8 \\ {\rm hanol\ at\ } 22^\circ \\ {\rm Hat\ } 22^\circ \\ {\rm I\ at\ } 22^\circ \\ {\rm Hat\ } 22^\circ \\ {\rm OH} \\ {\rm 4.26} \\ {\rm at\ } 22^\circ \\ {\rm Ph\ } \\ 4.7 \end{array}$	4-C ₆ H 2.3 1 0H 5.1 22 ⁹ 1 4 22 ⁹ 1 4 2 4 2 4 4 2 4 4 4 4 4 4 4 4 4 4 4 4 4	I_4Cl 9 H^* 10 H^* 95 $c^-C_6H_{11}$ 5.42 $c^-C_6H_{11}$ 5.42 $c^-C_6H_{11}$ 3.60 $c^-C_6H_{11}$ 4.19 h 10 $c^-C_6H_{11}$ 5.60	Me 3.08 c-C ₆ H ₁₁ 5.92 c-C ₆ H ₁₁ 6.64	OH 2.684	F 1.94
 10. 11. 12. 13. 14. 15. 16. 17. 18. 19 	pK_a values of pK_a values of pK_a values of pK_a values of pK_a values of pK_a values of X pK_a values of X	3.66 of XMePO(C SPr 2.03 of X-c-C ₆ H ₁₁] PhO 3.60 of X-c-C ₆ H ₁₁] PhO 4.19 of X-c-C ₆ H ₁₁ PhO 4.19 of X-c-C ₆ H ₁₀ PhO 1.64 of X-c-C ₆ H ₁₀ PhO 3.08 of XPhOPO(0 PhO 2.85 of XPhOPO(0 PhO 2.85 of XPhPO(0) PhO 3.32 of XPhOO(0)	2.71)H) in water a S(i-Pr) 2.13 PO(OH) in 756 H 3.91 PO(OH) in 956 H 4.55 DPOP(OH) in 956 H 2.83 DPOP(OH) in 9 c-C ₆ H ₁₁ O 4.43 OH) in 75% a c-C ₆ H ₁₁ O 2.64 OH) in 95% aqu H 3.11 H) in 95% aqu H 3.69 I) in 75% acu	t 20° i O-i-Pr 2.38 % aqueous eth $c-C_6H_{11}O$ 4.73 % aqueous eth $c-C_6H_{11}O$ 5.42 75% aqueous eth $c-C_6H_{11}O$ 3.81 5% aqueous eth anol OH• 4.13 ueous ethanol s $c-C_6H_{11}O$ 3.83 ueous ethanol s $c-C_6H_{11}O$	OEt 2.25 anol at 22° Ph 5.02 anol at 22° Ph 5.60 ethanol at 22° Ph 3.8 hanol at 22° Ph 4.4 1 at 22°' Ph 3.3 at 22°' OH• 4.26 at 22°' Ph 4.26 A 22°' Ph 4.26 A 22°' Ph 4.26 A 22°' Ph 4.26 A 22°' Ph 4.74 A 22°' Ph 4.76 A 22°' Ph	4-C ₆ H 2.3 1 5.1 22° 1 3 22° 1 3 22° 1 3 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	$ \begin{array}{c} \text{L}\text{Cl} \\ 9 \\ \text{H}^{\bullet} \\ 10 \\ \text{H}^{\bullet} \\ 95 \\ \text{c}\text{-}\text{C}_{6}\text{H}_{11} \\ 4.73 \\ \text{c}\text{-}\text{C}_{6}\text{H}_{11} \\ 5.42 \\ \text{c}\text{-}\text{C}_{6}\text{H}_{11} \\ 3.60 \\ \text{c}\text{-}\text{C}_{6}\text{H}_{11} \\ 4.19 \\ \text{h} \\ 10 \\ \text{c}\text{-}\text{C}_{6}\text{H}_{11} \\ 5.60 \end{array} $	Me 3.08 c-C ₆ H ₁₁ 5.92 c-C ₆ H ₁₁ 6.64	OH 2.68*	F 1.94
 10. 11. 12. 13. 14. 15. 16. 17. 18. 19. 	pK_a values of pK_a values of pK_a values of pK_a values of pK_a values of pK_a values of pK_a values of X pK_a values of X	3.66 of XMePO(C SPr 2.03 of X-c-C ₆ H ₁₁] PhO 3.60 of X-c-C ₆ H ₁₁] PhO 4.19 of X-c-C ₆ H ₁₁ PhO 4.19 of X-c-C ₆ H ₁₀ PhO 1.64 of X-c-C ₆ H ₁₀ PhO 2.85 of XPhOPO(O PhO 2.85 of XPhOPO(O PhO 3.32 of XPhOPO(O PhO 3.32 of XPHOO(OF VI	2.71 DH) in water a S(i-Pr) 2.13 PO(OH) in 75° H 3.91 PO(OH) in 95° H 4.55 DPOP(OH) in 95° $c-C_6H_{11}O$ 2.64 OH) in 75°% aqu H 3.11 H) in 95% aqu H 3.69 H) in 75% aqu	t 20° i O-i-Pr 2.38 % aqueous eth $c-C_6H_{11}O$ 4.73 % aqueous eth $c-C_6H_{11}O$ 5.42 75% aqueous eth $c-C_6H_{11}O$ 3.81 5% aqueous eth anol OH• 3.43 queous ethanol $c-C_6H_{11}O$ 3.83 leous ethanol a $c-C_6H_{11}O$ 3.83 leous ethanol a $c-C_6H_{11}O$ 3.83	OEt 2.25 anol at 22° Ph 5.02 anol at 22° Ph 5.60 ethanol at 22° Ph 3.8 shanol at 22° Ph 4.4 1 at 22°' Ph 2.8 1 at 22°' OH• 4.26 at 22°' Ph 3.3	4-C ₆ H 2.33 1 0 1 0 22 ⁰ 1 1 22 ⁰ 1 1 22 ⁰ 1 1 2 2 4 2 2 4 1 4 1 4 1 4 1 4 1 4 1 4 1 4 1 4 1 1 1 1 1 1 1 1 1 1 1 1 1	L4Cl 9 H• 10 H• 95 c-C6H11 4.73 c-C6H11 5.42 c-C6H11 3.60 c-C6H11 4.19 h 10 c-C6H11 5.42 c-C6H11 5.42 c-C6H11 3.60 c-C6H11 4.19 c-C6H11 5.60 c-C6H11 5.60 c-C6H11 5.60	Me 3.08 c-C ₆ H ₁₁ 5.92 c-C ₆ H ₁₁ 6.64	OH 2.684	F 1.94
 10. 11. 12. 13. 14. 15. 16. 17. 18. 19. 	pK_a values of pK_a values of pK_a values of pK_a values of pK_a	3.66 of XMePO(C SPr 2.03 of X-c-C ₆ H ₁₁] PhO 3.60 of X-c-C ₆ H ₁₁] PhO 4.19 of X-c-C ₆ H ₁₁ PhO 1.64 of X-c-C ₆ H ₁₁ PhO 1.64 of X-c-C ₆ H ₁₁ PhO 1.64 of X-c-C ₆ H ₁₁ PhO 2.28 of XPhOPO(0 PhO 2.85 of XPhOPO(0 PhO 2.85 of XPhPO(0 PhO 3.32 of XHPO(0 PhO 3.32 of XHPO(0 PhO 3.52 of X-c-C ₆ PhO 5.55 of XHPO(0 PhO 5.55 of XHPO(0) PhO 5.55 of XHPO(0) XHPO(0) XHPO(0) XHPO(0) XHPO(0) XHPO(0) XHP	2.71 DH) in water a S(i-Pr) 2.13 PO(OH) in 75 ⁶ H 3.91 PO(OH) in 95 ⁶ H 4.55 DPOP(OH) in 95 ⁷ H 2.83 DPO(OH) in 95 ⁷ a c-C ₆ H ₁₁ O 2.64 OH) in 75 ⁷ % aqu H 3.11 H) in 95 ⁷ % aqu H 3.69 H) in 75 ⁷ % aqu c-C ₆ H ₁₁ O 2.64	t 20° i O-i-Pr 2.38 % aqueous eth $c-C_6H_{11}O$ 4.73 % aqueous eth $c-C_6H_{11}O$ 5.42 75% aqueous eth 3.81 5% aqueous eth 3.40 queous ethanol OH• 3.43 queous ethanol $c-C_6H_{11}O$ 3.83 leous ethanol $c-C_6H_{11}O$ c-C	$\begin{array}{c} {\rm OEt} \\ 2.25 \\ {\rm anol\ at\ 22^{\circ}} \\ {\rm Ph} \\ 5.02 \\ {\rm anol\ at\ 22^{\circ}} \\ {\rm Ph} \\ 5.60 \\ {\rm ethanol\ at\ 22^{\circ}} \\ {\rm Ph} \\ 3.8 \\ {\rm shanol\ at\ 22^{\circ}} \\ {\rm H} \\ 4.4 \\ {\rm l\ at\ 22^{\circ}}^{\prime} \\ {\rm Ph} \\ 2.8 \\ {\rm l\ at\ 22^{\circ}}^{\prime} \\ {\rm Ph} \\ 3.3 \\ {\rm at\ 22^{\circ}}^{\prime} \\ {\rm OH^{\bullet}} \\ 4.26 \\ {\rm at\ 22^{\circ}}^{\prime} \\ {\rm Ph} \\ 4.7 \\ {\rm t\ 22^{\circ}}^{\prime} \\ {\rm Ph} \\ \end{array}$	4-C ₆ H 2.33 1 0H 5.1 22° 1 1 22° 1 22° 1 2 2 2 2 2 2 2 2 2 2 2 2 2	I_4Cl 9 H^{\bullet} 10 H^{\bullet} 95 $c-C_6H_{11}$ 4.73 $c-C_6H_{11}$ 5.42 $c-C_6H_{11}$ 3.60 $c-C_6H_{11}$ 4.19 h 10 $c-C_6H_{11}$ 5.42 $c-C_6H_{11}$ 3.60 $c-C_6H_{11}$ 4.19 h 10 $c-C_6H_{11}$ 5.42 $c-C_6H_{11}$ 3.60 $c-C_6H_{11}$ 4.19 h 10 $c-C_6H_{11}$ 4.20 $c-C_6H_{11}$ 4.20 $c-C_6H_{11}$ 3.60 $c-C_6H_{11}$ 4.19 $c-C_6H_{11}$ 4.19 $c-C_6H_{11}$ 4.19 $c-C_6H_{11}$ 4.19 $c-C_6H_{11}$ 4.19 $c-C_6H_{11}$ 4.19 $c-C_6H_{11}$ 4.19 $c-C_6H_{11}$ 4.19 $c-C_6H_{11}$ 5.60 $c-C_6H_{11}$ 5.60	Me 3.08 c-C ₆ H ₁₁ 5.92 c-C ₆ H ₁₁ 6.64	OH 2.68*	F 1.94

				Та	BLE I (Contin	nued)			
20.	pK_a values of	of XHPO(OH	l) in 95% aqueo	us ethanol	at 22° 1				
	x	н	$c-C_6H_{11}O$	OH.	\mathbf{Ph}	<i>c</i> -C6	H11		
	pK_{a}	2.94	3.40	4.31	3.69	4.5	5		
21.	Rate consta	nts for the be	nzylation of Na	+XZPS2- in	n ethanol at 25'	° a			
	X, Z	PhO, PhO	MeO, MeO	EtO, I	EtO <i>i</i> -PrO), <i>i</i> -PrO	BuO, BuO	Ph, Ph	Me, PrO
	$-\log k$	3.91	3.84	3.8	4 3	.60	3.72	3.28	3.51
	X, Z	Me, BuO	Et, Et	Pr,	Pr Bu	, Bu	<i>i</i> -Pr, <i>i</i> -Pr		
	$-\log k$	3.56	3.34	3.3	4 3	. 33	3.26		
22.	pK_a values of	of N ₈ P ₈ X ₆ in I	PhNO2 at 25° t						
	x	EtO	$PhCH_{2}O$	\mathbf{EtS}	$PhCH_{2}S$	\mathbf{PhS}	\mathbf{Et}	\mathbf{Ph}	Me ₂ N
	pK_{a}	0.20	-2.10	-2.75	-4.15	-4.80	6.40	1.50	7.60
23.	pK_a values of	of N ₄ P ₄ X ₈ in	PhNO2 at 25° *						
	x	EtO	\mathbf{Et}	\mathbf{Ph}	Me_2N	EtNH	MeNH		
	pK_n	0.60	7.60	2.20	8.30	8.10	8.20		

^e Reference 4. ^b W. J. Polestak and H. K. Zimmerman, J. Phys. Chem., 60, 787 (1956). ^c L. D. Freedman and G. O. Doak, Chem. Rev., 57, 479 (1957). ^d W. D. Kumler and J. J. Eiler, J. Amer. Chem. Soc., 65, 2355 (1943). ^e L. N. Devonshire and H. A. Rowley, Inorg. Chem., 1, 680 (1962). ^f P. Salomaa, L. L. Schaleger, and F. A. Long, J. Amer. Chem. Soc., 86, 1 (1964). Includes a statistical factor of $\frac{3}{2}$. ^e K. S. Pitzer, *ibid.*, 59, 2365 (1967). Includes a statistical factor of $\frac{3}{2}$. ^b F. Litman and L. C. Tuttle, Arch. Biochem., 13, 373 (1947). ⁱ D. C. Dittmer, O. B. Ramsay, and K. E. Spalding, J. Org. Chem., 28, 1273 (1963). ^j A. A. Neimysheva, V. I. Savchuk, and I. L. Knunyants, Zh. Obshch. Khim., 36, 500 (1966). ^{*} Includes statistical factor of $\frac{2}{3}$. ^j D. F. Peppard, G. W. Mason, and C. M. Andrejasich, J. Inorg. Nucl. Chem., 27, 697 (1965). ^m P. C. Crofts and G. M. Kosolapoff, J. Amer. Chem. Soc., 75, 3379, 4903 (1953). ⁿ P. Lestauries and P. Rumpf, Compt. Rend., 228, 1018 (1949). ^o Reference f. Includes statistical factor of $\frac{1}{3}$. ^p A. I. Razumov and S. D. Khen, Zh. Obshch. Khim., 26, 2233 (1956). Includes statistical factor of $\frac{1}{3}$. ^e Reference 4. ^r M. I. Kabachnik, I. A. Mastryukova, and T. A. Melenteva, Zh. Obshch Khim., 32, 267 (1962); 33, 382 (1963). ^e Includes statistical factor of $\frac{1}{3}$. ^e D. Feakins, W. A. Last, and R. A. Shaw, Chem. Ind. (London), 510 (1962); D. Feakins, W. A. Last, N. Neemuchwala, and R. A. Show, *ibid.*, 164 (1963).

				$\mathbf{T}_{\mathbf{A}}$	ABLE II				
	8	SUBSTITU	ent Constan	TS FROM	Sources Other TH.	AN REF 6 AND	7		
х	$\sigma_{\mathbf{I}}$	Ref	σ_p	Ref	x	σ_{I}	Ref	σ_p	\mathbf{Ref}
CH ₂ Cl			0.12	a	$4-C_6H_4Cl$	0.13	b	0.081	b
CH ₂ Br			0.12	a	\mathbf{SPr}			0.06	b
CH_2I			0.09	a	O-i-Pr			-0.31	b
CH ₂ OH			-0.01	a	$c - C_6 H_{11}$			-0.14	с
CHCl ₂	0.31	d	0.185	e	c-C ₆ H ₁₁ O			-0.31	b
CCl_{3}	0.43	d	0.407	е	AcO	0.42	f		
BuS			0.04	ь	\mathbf{PhO}			-0.14	ь
PhCH ₂ O	0.34	q	-0.23	ь	$PhCH_2S$			0.07	b
\mathbf{PhS}			0.075	h	MeNH	0.10	i		
Me_2N	0.10	j			t-BuCH ₂			-0.17	$_{k}$
0.17			~ ~				·		~

^a O. Exner and J. Jonas, Coll. Czech. Chem. Commun., **27**, 2296 (1962). ^b Calculated as described in M. Charton, J. Org. Chem., **28**, 3121 (1963). ^c Calculated from $\sigma_p = \sigma_I + \sigma_R$ assuming σ_R equal to that for *i*-Pr. ^d Calculated from $\sigma_I = \sigma^*/6.23$. ^eJ. Hine and W. C. Bailey, Jr., J. Amer. Chem. Soc., **81**, 2025 (1959). ^f C. D. Ritchie and W. Sager, Jr., ref 1. ^g σ_m was calculated as in b. σ_I was then obtained from $\sigma_I = (3\sigma_m - \sigma_p)/2$. ^h H. H. Szmant and G. Suld, J. Amer. Chem. Soc., **78**, 3400 (1956). ⁱ Assumed equal to σ_I for NH₂ and Me₂N. ^j P. R. Wells, ref 1. ^k Calculated from $\sigma_{p, XCH_2} = m\sigma_{I,X} + c$. ^l Calculated from pK_a of XCH₂CO₂H. See ref 6.

of some substituted pentcovalent phosphorus compounds.

Phosphonic Acids.--Significant correlation is obtained for the first ionization constants of substituted phosphonic acids (set 2a). Omission of the value for $X = CCl_3$ improved the results (set 2b). The authors who reported this value have remarked that they consider it dubious. Exclusion of the value for $X = PhCH_2$ resulted in further improvement. A value of 2.3 has been reported for the pK_a of this compound; this value seems in better accord with our results. Results for this set are probably not so good as they possibly could be because of the difficulty of measuring reliable pK_a values in this range of acid strength. The results obtained for the second ionization constants of substituted phosphonic acids are excellent, particularly in view of the number of different sources for the data. Omission of the value for $X = CCl_3$ gave no meaningful difference in the results; we therefore conclude that the value of pK_a for this compound is reasonably good.

In set 2, β is significant at the 90% confidence level, in set 3 at the 99.9% confidence level. Again our results indicate a significant resonance effect. We have not included the value for $X = H(pK_1, pK_2 \text{ of phosphorus}$ acid) in either set 2 or set 3. The values cited in the literature (1.8 and 6.2, respectively) differ greatly from the calculated values (2.30 and 7.69, respectively).

Good correlation was obtained for the pK_a values of phosphonic acids in water at 20° (set 4). The correlation obtained for the phosphonic acids in 75% aqueous ethanol was not significant. Exclusion of the value for X = H gave a very good correlation (sets 5a and 5b).

Phosphinic Acids.—For our purposes we consider acids of the type XZPO(OH) as phosphinic acids. When Z is not constant the phosphinic acid sets have been correlated with eq 5 which assumes that the effect

				RESULTS	OF CORRELATION	s with Eq	3 and Eq 4					
Set	2	-8	ų	R^{a}	E^{b}	24	8d	$s_{\alpha}d$	88 ^d	s_h^d	ne	C.L.
1	-4.01	-0.760	-0.915	0.946	72.92	0.386	0.606	0.335	0.243	0.0670	20	6.69
- 6	3 17	0.520	2.30	0.846	26.39	0.259	0.667	0.438	0.452	0.113	24	66.66
3 42	3.56	0.796	2.26	0.878	33.73	0.341	0.679	0.436	0.431	0.104	23	6.66
C	3.62	797	2.31	0.887	35.14	0.361	0.695	0.434	0.426	0.105	22	6.99
2 o	7 79	2.17	7.69	0.974	196.3	0.259	0.331	0.390	0.402	0.100	24	6.60
•	3.52	1.74	1.97	0.994	83.45	0.413	0.0795	0.299	0.179	0.0550	ŝ	97.5
μų	20.0	4 01	3.81	0.800	1.779	0.883	0.623	3.82	2.39	0.417	ŝ	< 90.06 >
5 2	6.83	2.76	4.34	0.99999	17730	0.850	0.00651	0.0400	0.0266	0.00586	4	0.66
64	5.64	1.98	2.54	0.946	42.40	0.947	0.959	1.04	0.724	0.262	13	6 .66
	3.45	0.395	2.98	0.942	35.21	0.922	0.816	0.891	0.570	0.154	12	6.60
- 0	5 74	1.58	4.27	0.997	170.8	0.874	0.458	0.428	0.284	0.0469	5	0.69
	00 8	0 439	4.98	0.956	58.95	0.922	0.952	0.789	0.538	0.151	14	66.66
01	2.64	0.934	2.65	0.906	11.41	0.558	0.193	0.554	0.388	0.140	8	97.5
110	40.00	4 30	4.79	0.781	2.343	0.899	0.683	4.14	2.45	0.453	9	<90.0
411	8 46	2.81	5.48	0.996	134.7	0.864	0.102	0.618	0.388	0.0903	S	0.66
19.0	00 0	5 07	5.41	0.820	3.070	0.899	0.667	4.05	2.40	0.443	9	< 90.0
104	0 61	3 61	60.09	0.998	201.0	0.864	0.0892	0.542	0.340	0.0792	ũ	99.5
120	0.60	5 33	3.58	0.792	1.687	0.928	0.732	5.38	3.57	0.496	ŋ	< 90.06 >
125	8 40	3 30	4.22	0.995	52.47	0.909	0.144	1.07	0.754	0.133	4	90.06
001 041	10.8	5.03	4.18	0.814	1.971	0.928	0.764	5.61	3.72	0.518	5	< 90.06 >
146	0.69	3.92	4.85	0.994	40.82	0.909	0.183	1.36	0.957	0.168	4	< 90.0
170	5.80	2.46	3.18	0.948	8.845	0.864	0.248	1.51	0.944	0.220	5	< 90.0
91 91	10.4	4 52	3.64	0.968	15.03	0.864	0.328	2.00	1.25	0.292	ð	90.06
179	8 38	4.11	3.92	0.789	2.469	0.899	0.630	3.82	2.26	0.418	9	< 90.0
171	8.03	2.72	4.57	0.9993	686.6	0.864	0.0424	0.258	0.161	0.0376	5	99.5
184	9.55	4.87	4.48	0.794	1.702	0.928	0.768	5.64	3.74	0.520	5	0.06
181	8.39	2.83	5.16	0.997	81.12	0.909	0.127	0.945	0.666	0.117	4	0.06
10a	7.89	3.61	3.14	0.778	1.533	0.942	0.436	4.50	2.18	0.290	ũ	0.06
104	7.28	2.68	3.49	0.976	9.868	0.924	0.177	1.84	0.927	0.158	4	90.0
20a	9.37	4.79	3.56	0.727	1,121	0.942	0.639	6.60	3.20	0.426	ņ	90.0
90F	8 59	3.48	4.06	0.927	3.049	0.924	0.347	3.60	1.82	0.310	4	90.0
212	0.212	-0.444	-3.21	0.946	38.05	0.937	0.238	0.257	0.197	0.0690	12	6.99
58	32.6	8.58	3.55	0.988	106.3	0.159	4.67	2.43	1.10	0.638	œ	6.99
3	30.8	7.10	5.12	0.984	46.58	0.316	3.48	3.69	0.986	0.643	9	0.99
^a Multink	e correlation coefficient.	^b F test for sig	gnificance of regr	ession. • I	artial correlation	coefficient fo	or o _l with or.	^d Standard	errors of the es	stimate, α , β , and	l h. • Nui	nber of points
in the set.	/ Confidence level for	regression.)									

TABLE III

$$Q_{\rm X} = \alpha \Sigma \sigma_{\rm I} + \beta \Sigma \sigma_{\rm R} + h \tag{5}$$

of multiple substituents is additive and ignores interaction terms. The results obtained for the XZPO(OH)in water (set 6), 7% aqueous ethanol (set 7), and 80%aqueous ethanol (set 9) are excellent; very good results were obtained for the pK_a values in 50% aqueous ethanol (set 8). Significant values of β were obtained for sets 6 and 8 but not for sets 7 and 9. The values of rshow, however, that σ_{I} and σ_{R} are highly correlated for these sets and therefore the separation of the electrical effect into its components is difficult. All of the sets of XZPO(OH) in which Z is a constant substituent that included X = H as a substituent did not give significant correlations (sets 11a, 12a, 13a, 14a, 17a, 18a, 19a, and 20a). Exclusion of the value for X = H improved the results in all cases, significant correlations being obtained for sets 11b, 12b, 13b, 17b, and 18b. The remaining sets, 14b, 19b, and 20b, did not give significant correlations, owing at least in part to the small size of the set. When the constant substituent is Me, good correlation was obtained (set 10). When the constant substituent was PhO, the data in 75%aqueous ethanol (set 15) did not give a significant correlation; the data in 95% aqueous ethanol did (set **16**)

Dithiophosphinates.—As excellent correlation is obtained for these data (set 21). It must be noted, however, that neither β nor, in particular, α have a high degree of significance. The results show that this reaction is essentially independent of substituent effects.

Phosphazenes.—Excellent (set 22) and very good (set 23) correlations were obtained for these sets. Values of β are significant in both sets.

Discussion

Of the 23 sets studied 19 gave significant correlations with eq 3 or 4. We conclude, therefore, that the effects of substituents bonded to pentacovalent phosphorus may be represented as a function of the $\sigma_{\rm I}$ and $\sigma_{\rm R}$ constants developed for substituents bonded to carbon. It is unnecessary to define new substituent constants.

Composition of the Electrical Effect.—To describe the composition of the electrical effects, we can make use of the parameter ϵ , defined as

$$\epsilon = \delta / \lambda \tag{6}$$

where any substituent constant may be written

$$\sigma = \lambda \sigma_{\rm I} + \delta \sigma_{\rm R} \tag{7}$$

Then from eq 1

$$Q_{\mathbf{X}} = \rho \lambda \sigma_{\mathbf{I}} + \rho \delta \sigma_{\mathbf{R}} + Q_{\mathbf{H}} \tag{8}$$

which is equivalent to eq 3 with $\alpha = \rho \lambda$, $\beta = \rho \delta$ and

		Tabi	LE IV		
		VALUE	ES OF ϵ		
Set	e	Set	e	Set	e
1	0.191	9	0.113ª	17b	0.339
2c	0.220	10	0.354	18b	0.337
3	0.281	11b	0.332	19b	b
4	0.494	12b	0.376	20b	ь
5b	0.404	13b	0.400	21	с
6	0.351	14b	ь	22	0.264
7	0.124ª	15	b	23	0.230
8	0.278	16	0.435		

 ${}^{\mathfrak{o}}\beta$ not significant. ${}^{\mathfrak{o}}$ Correlation not significant. ${}^{\mathfrak{o}}\alpha$ not significant.

therefore

$$= \beta/\alpha$$
 (9)

Values of ϵ for the sets studied are given in Table IV. The average value of ϵ for the phosphoric (V, Z = OH) and phosphinic (V) acids is 0.32 (for sets 2c-13b and 16b-18b). We have shown that ionization constants of acids of the type VI⁸ and of carboxylic acids VII² are best correlated by the σ_m constants for which $\epsilon = 0.33$. Thus the composition of the electrical effect in V is comparable with that in VI and VII. For the substituted phosphazenes VIII, an average ϵ value of 0.25 is obtained. We have shown³ that ionization constants of amidines, IX, are best correlated by the σ_m constants. Thus substituent effects upon pK_a values of phospazenes are comparable with those upon the pK_a values of amidines. It would seem that, to a good approximation, data for substituted pentacovalent phosphorus compounds can be correlated with the σ_m constants.



Magnitude of the Electrical Effect.—We may compare α for the ionization of substituted phosphonic acids in water at 25° with ρ for the ionization of substituted carboxylic acids under the same conditions; the values are 3.62 and about 8, respectively. Thus the phosphonic acids are decidedly less sensitive to substituent effects than are the carboxylic acids. This may well be due to molecular geometry. Owing to the larger covalent radius of phosphorus compared with carbon the ionizable proton is significantly further removed from the substituent in the phosphorus oxy acids than it is in the carboxylic acids.

(8) M. Charton, J. Org. Chem., 30, 557 (1965).