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

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Received August 28, 1968

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 phsophazenes 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 equation[1] (eq 1) to the ionization constants of substituted carboxylic acids[2] 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. Kabachnik[4] has proposed a modified Hammett equation (eq 2) for use with the substituted phosphorus compounds. The

$$Q_X = \rho\sigma_X + h \quad (1)$$

$$Q_X = \rho_\phi\sigma_{\phi X} + h \quad (2)$$

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 σ_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.

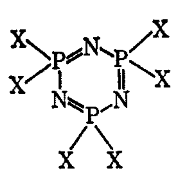
It is of interest to determine whether the electrical effects of a substituent bonded to phosphorus are of the same type as those exhibited by a substituent bonded to carbon. Furthermore, we would like to know whether the magnitude of the electrical effects of a substituent bonded to phosphorus is comparable 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 Taft[5] (eq 3). A significant correlation as

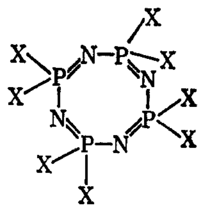
$$Q_X = \alpha\sigma_I + \beta\sigma_R + h \quad (3)$$

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

$XPO(OH)_2$
I

$XZPO(OH)$
II


III


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 compilation[6] unless otherwise noted (Table II). The σ_R constants required were obtained from[5] eq 4 using the σ_p constants of McDaniel and Brown[7] unless otherwise noted (Table II).

$$\sigma_R = \sigma_p - \sigma_I \quad (4)$$

Statistical factors have been applied to the ionization constants where necessary. Thus, for the substituted phosphonic acids when X = OH (K_1 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 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 Kabachnik[4] 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

(1) H. H. Jaffé, *Chem. Rev.*, **53**, 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).

(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).

TABLE I

DATA USED IN THE CORRELATIONS

1. σ_ϕ constants[a]

X	OH	MeO	EtO	PrO	*i*-PrO	BuO	Me	Et	Pr
σ_ϕ	−0.343	−0.124	−0.314	−0.315	−0.291	−0.411	−0.965	−1.101	−1.177
X	*i*-Pr	Bu	*t*-Bu	CH_2Cl	$CHCl_2$	CCl_3	CH_2Br	CH_2I	CH_2OH
σ_ϕ	−1.300	−1.219	−1.546	−0.034	0.272	0.30	−0.01	−0.11	−0.546
X	CF_3	Ph							
σ_ϕ	0.50	−0.481							

2, 3. pK_a values of $XPO(OH)_2$ in water at 25° [c]

X	Ph	CH_2OH	CH_2I	CH_2Br	CCl_2	$CHCl_3$	CH_2Cl	$BuCH_2$	*t*-Bu
pK_{a1}	1.824[b]	1.91	1.30	1.14	1.63	1.14	1.40	2.84	2.79
pK_{a2}	7.070[b]	7.15	6.72	6.52	4.81	5.61	6.30	8.65	8.88
X	*i*-Bu	*s*-Bu	Bu	*i*-Pr	Pr	Et	Me	CF_3	MeO
pK_{a1}	2.70	2.74	2.59	2.66	2.49	2.43	2.38	1.16	1.54[b]
pK_{a2}	8.43	8.48	8.19	8.44	8.18	8.05	7.74	3.93	6.31[d]
X	EtO	F	$PhCH_2$	OH	AcO	BuS			
pK_{a1}	1.60[d]	0.52[e]	1.85	2.497[f]	1.17[h]	2.21[i]			
pK_{a2}	6.62[d]	4.80[e]	7.4	7.51[g]	4.88[h]	5.93[i]			

4. pK_{a1} values of $XPO(OH)_2$ in water at 20° [j]

X	Me	$HOCH_2$	$ClCH_2$	OH	$CHCl_2$
pK_a	2.38	1.91	1.40	2.15[k]	1.14

5. pK_{a1} values of $XPO(OH)_2$ in 75% aqueous ethanol at 22° [l]

X	PhO	H	Ph	OH	*c*-C_6H_{11}
pK_a	3.13	3.15	3.96	4.34[k]	4.80

6. pK_a values of XZPO(OH) in water at 25° [m]

X, Z	Me, Me	Et, Et	Pr, Pr	*i*-Pr, *i*-Pr	Bu, Bu	*t*-Bu, *t*-Bu	Ph, Ph
pK_a	3.08	3.29	3.46	3.56	3.41	4.24	2.1[n]
X, Z	OH, OH	Et, OEt	OMe, OMe	OEt, OEt	OPr, OPr	OBu, OBu	
pK_a	2.622[o]	2.27[p]	1.29[d]	1.39[d]	1.59[d]	1.72[d]	

7. pK_a values of XZPO (OH) in 7% ethanol–water at 25° [a]

X, Z	MeO, MeO	EtO, EtO	PrO, PrO	PhO, OH	Me, Me	Bu, Bu	*i*-Bu, *i*-Bu
pK_a	1.25	1.37	1.52	1.76[q]	3.13	3.50	3.70
X, Z	Ph, Ph	Pr, Ph	*i*-Pr, Ph	C_2H_3, Ph	C_2H_3, C_2H_3		
pK_a	2.32	2.71[r]	2.82[r]	2.26[r]	2.54[r]		

8. pK_a values of XZPO(OH) in 50% ethanol–water at 25°[r]

X, Z	Pr, Ph	*i*-Pr, Ph	C_2H_3, OEt	C_2H_3, C_2H_3	C_2H_3, Ph
pK_a	4.15	4.28	3.18	3.59	3.53

9. pK_a values of XZPO(OH) in 80% ethanol–water at 25° [a]

X, Z	MeO, MeO	EtO, EtO	PrO, PrO	Me, Me	Bu, Bu	*i*-Bu, *i*-Bu	Ph, Ph
pK_a	3.01	3.15	3.29	5.15	5.63	5.63	4.14
X, Z	PhO, OH	PhO, PhO	C_2H_3, EtO	C_2H_3, Ph	C_2H_3, C_2H_3	Pr, Ph	*i*-Pr, Ph
pK_a	3.66	2.71	3.81	4.29	4.34	4.72	4.89

10. pK_a values of XMePO(OH) in water at 20° [j]

X	SPr	S(*i*-Pr)	O-*i*-Pr	OEt	4-C_6H_4Cl	Me	OH	F
pK_a	2.03	2.13	2.38	2.25	2.39	3.08	2.68[s]	1.94

11. pK_a values of X-*c*-C_6H_{11}PO(OH) in 75% aqueous ethanol at 22° [l]

X	PhO	H	*c*-$C_6H_{11}O$	Ph	OH[s]	*c*-C_6H_{11}
pK_a	3.60	3.91	4.73	5.02	5.10	5.92

12. pK_a values of X-*c*-C_6H_{11}PO(OH) in 95% aqueous ethanol at 22° [l]

X	PhO	H	*c*-$C_6H_{11}O$	Ph	OH[s]	*c*-C_6H_{11}
pK_a	4.19	4.55	5.42	5.60	5.95	6.64

13. pK_a values of X-*c*-C_6H_{11}OPOP(OH) in 75% aqueous ethanol at 22° [l]

X	PhO	H	*c*-$C_6H_{11}O$	Ph	*c*-C_6H_{11}
pK_a	1.64	2.83	3.81	3.83	4.73

14. pK_a values of X-*c*-C_6H_{11}OPO(OH) in 95% aqueous ethanol at 22° [l]

X	PhO	*c*-$C_6H_{11}O$	H	Ph	*c*-C_6H_{11}
pK_a	3.08	4.43	3.40	4.42	5.42

15. pK_a values of XPhOPO(OH) in 75% aqueous ethanol at 22° [l]

X	PhO	*c*-$C_6H_{11}O$	OH[s]	Ph	*c*-C_6H_{11}
pK_a	2.28	2.64	3.43	2.85	3.60

16. pK_a values of XPhOPO(OH) in 95% aqueous ethanol at 22° [l]

X	PhO	*c*-$C_6H_{11}O$	OH[s]	Ph	*c*-C_6H_{11}
pK_a	1.91	3.08	4.13	3.32	4.19

17. pK_a values of XPhPO(OH) in 75% aqueous ethanol at 22° [l]

X	PhO	H	*c*-$C_6H_{11}O$	OH[s]	Ph	*c*-C_6H_{11}
pK_a	2.85	3.11	3.83	4.26	4.10	5.02

18. pK_a values of XPhPO(OH) in 95% aqueous ethanol at 22° [l]

X	PhO	H	*c*-$C_6H_{11}O$	Ph	*c*-C_6H_{11}
pK_a	3.32	3.69	4.42	4.70	5.60

19. pK_a values of XHPO(OH) in 75% aqueous ethanol at 22° [l]

X	H	*c*-$C_6H_{11}O$	OH[s]	Ph	*c*-C_6H_{11}
pK_a	2.70	2.83	3.45	3.11	3.91

TABLE I (*Continued*)

20. pK_a values of XHPO(OH) in 95% aqueous ethanol at 22° [l]

X	H	c-$C_6H_{11}O$	OH[s]	Ph	c-C_6H_{11}
pK_a	2.94	3.40	4.31	3.69	4.55

21. Rate constants for the benzylation of $Na^+XZPS_2^-$ in ethanol at 25° [a]

X, Z	PhO, PhO	MeO, MeO	EtO, EtO	i-PrO, i-PrO	BuO, BuO	Ph, Ph	Me, PrO
−Log k	3.91	3.84	3.84	3.60	3.72	3.28	3.51
X, Z	Me, BuO	Et, Et	Pr, Pr	Bu, Bu	i-Pr, i-Pr		
−Log k	3.56	3.34	3.34	3.33	3.26		

22. pK_a values of $N_3P_3X_6$ in $PhNO_2$ at 25° [t]

X	EtO	$PhCH_2O$	EtS	$PhCH_2S$	PhS	Et	Ph	Me_2N
pK_a	0.20	−2.10	−2.75	−4.15	−4.80	6.40	1.50	7.60

23. pK_a values of $N_4P_4X_8$ in $PhNO_2$ at 25° [t]

X	EtO	Et	Ph	Me_2N	EtNH	MeNH
pK_a	0.60	7.60	2.20	8.30	8.10	8.20

[a] 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 $\frac{2}{3}$. [g] K. S. Pitzer, *ibid.*, **59,** 2365 (1967). Includes a statistical factor of $\frac{1}{2}$. [h] 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). [k] Includes statistical factor of $\frac{2}{3}$. [l] 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 $\frac{1}{2}$. [q] Reference 4. [r] M. I. Kabachnik, I. A. Mastryukova, and T. A. Melenteva, *Zh. Obshch Khim.*, **32,** 267 (1962); **33,** 382 (1963). [s] Includes statistical factor of $\frac{1}{2}$. [t] 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).

TABLE II

SUBSTITUENT CONSTANTS FROM SOURCES OTHER THAN REF 6 AND 7

X	σ_I	Ref	σ_p	Ref	X	σ_I	Ref	σ_p	Ref
CH_2Cl			0.12	*a*	4-C_6H_4Cl	0.13	*b*	0.081	*b*
CH_2Br			0.12	*a*	SPr			0.06	*b*
CH_2I			0.09	*a*	O-i-Pr			−0.31	*b*
CH_2OH			−0.01	*a*	c-C_6H_{11}			−0.14	*c*
$CHCl_2$	0.31	*d*	0.185	*e*	c-$C_6H_{11}O$			−0.31	*b*
CCl_3	0.43	*d*	0.407	*e*	AcO	0.42	*f*		
BuS			0.04	*b*	PhO			−0.14	*b*
$PhCH_2O$	0.34	*g*	−0.23	*b*	$PhCH_2S$			0.07	*b*
PhS			0.075	*h*	MeNH	0.10	*i*		
Me_2N	0.10	*j*			t-$BuCH_2$			−0.17	*k*

[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 $\sigma_I = \sigma^*/6.23$. [e] J. 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 NH_2 and Me_2N. [j] P. R. Wells, ref 1. [k] Calculated from $\sigma_{p,XCH_2} = m\sigma_{I,X} + c$. [l] Calculated from pK_a of XCH_2CO_2H. 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 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

TABLE III

RESULTS OF CORRELATIONS WITH EQ 3 AND EQ 4

Set	$-\alpha$	$-\beta$	h	R[a]	F[b]	r[c]	s[d]	s_α[d]	s_β[d]	s_h[d]	n[e]	C.L.[f]
1	−4.01	−0.760	−0.915	0.946	72.92	0.386	0.606	0.335	0.243	0.0670	20	99.9
2a	3.17	0.520	2.30	0.846	26.39	0.259	0.667	0.438	0.452	0.113	24	99.9
2b	3.56	0.796	2.26	0.878	33.73	0.341	0.679	0.436	0.431	0.104	23	99.9
2c	3.62	0.797	2.31	0.887	35.14	0.361	0.695	0.434	0.426	0.105	22	99.9
3	7.72	2.17	7.69	0.974	196.3	0.259	0.331	0.390	0.402	0.100	24	99.9
4	3.52	1.74	1.97	0.994	83.45	0.413	0.0795	0.299	0.179	0.0550	5	97.5
5a	7.20	4.01	3.81	0.800	1.779	0.883	0.623	3.82	2.39	0.417	5	<90.0
5b	6.83	2.76	4.34	0.99999	17730	0.850	0.00651	0.0400	0.0266	0.00586	4	99.0
6	5.64	1.98	2.54	0.946	42.40	0.947	0.959	1.04	0.724	0.262	13	99.9
7	3.45	0.395	2.98	0.942	35.21	0.922	0.816	0.891	0.570	0.154	12	99.9
8	5.74	1.58	4.27	0.997	170.8	0.874	0.458	0.428	0.284	0.0469	5	99.0
9	3.90	0.439	4.98	0.956	58.95	0.922	0.952	0.789	0.538	0.151	14	99.9
10	2.64	0.934	2.65	0.906	11.41	0.558	0.193	0.554	0.388	0.140	8	97.5
11a	8.84	4.30	4.79	0.781	2.343	0.899	0.683	4.14	2.45	0.453	6	<90.0
11b	8.46	2.81	5.48	0.996	134.7	0.864	0.102	0.618	0.388	0.0903	5	99.0
12a	9.99	5.07	5.41	0.820	3.070	0.899	0.667	4.05	2.40	0.443	6	<90.0
12b	9.61	3.61	6.09	0.998	201.0	0.864	0.0892	0.542	0.340	0.0792	5	99.5
13a	9.60	5.33	3.58	0.792	1.687	0.928	0.732	5.38	3.57	0.496	5	<90.0
13b	8.49	3.39	4.22	0.995	52.47	0.909	0.144	1.07	0.754	0.133	4	90.0
14a	10.8	5.93	4.18	0.814	1.971	0.928	0.764	5.61	3.72	0.518	5	<90.0
14b	9.62	3.92	4.85	0.994	40.82	0.909	0.183	1.36	0.957	0.168	4	<90.0
15	5.89	2.46	3.18	0.948	8.845	0.864	0.248	1.51	0.944	0.220	5	<90.0
16	10.4	4.52	3.64	0.968	15.03	0.864	0.328	2.00	1.25	0.292	5	90.0
17a	8.38	4.11	3.92	0.789	2.469	0.899	0.630	3.82	2.26	0.418	6	<90.0
17b	8.03	2.72	4.57	0.9993	686.6	0.864	0.0424	0.258	0.161	0.0376	5	99.5
18a	9.55	4.87	4.48	0.794	1.702	0.928	0.768	5.64	3.74	0.520	5	90.0
18b	8.39	2.83	5.16	0.997	81.12	0.909	0.127	0.945	0.666	0.117	4	90.0
19a	7.89	3.61	3.14	0.778	1.533	0.942	0.436	4.50	2.18	0.290	5	90.0
19b	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	5	90.0
20b	8.52	3.48	4.06	0.927	3.049	0.924	0.347	3.60	1.82	0.310	4	90.0
21	0.212	−0.444	−3.21	0.946	38.05	0.937	0.238	0.257	0.197	0.0690	12	99.9
22	32.6	8.58	3.55	0.988	106.3	0.159	4.67	2.43	1.10	0.638	8	99.9
23	30.8	7.10	5.12	0.984	46.58	0.316	3.48	3.69	0.986	0.643	6	99.0

[a] Multiple correlation coefficient. [b] F test for significance of regression. [c] Partial correlation coefficient for σ_I with σ_R. [d] Standard errors of the estimate, α, β, and h. [e] Number of points in the set. [f] Confidence level for regression.

$$Q_X = \alpha\Sigma\sigma_I + \beta\Sigma\sigma_R + h \quad (5)$$

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 r show, 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 σ_I and σ_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

$$\epsilon = \delta/\lambda \quad (6)$$

where any substituent constant may be written

$$\sigma = \lambda\sigma_I + \delta\sigma_R \quad (7)$$

Then from eq 1

$$Q_X = \rho\lambda\sigma_I + \rho\delta\sigma_R + Q_H \quad (8)$$

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

TABLE IV

VALUES OF ϵ

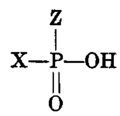
Set	ϵ	Set	ϵ	Set	ϵ
1	0.191	9	0.113[a]	17b	0.339
2c	0.220	10	0.354	18b	0.337
3	0.281	11b	0.332	19b	[b]
4	0.494	12b	0.376	20b	[b]
5b	0.404	13b	0.400	21	[c]
6	0.351	14b	[b]	22	0.264
7	0.124[a]	15	[b]	23	0.230
8	0.278	16	0.435		

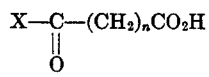
[a] β not significant. [b] Correlation not significant. [c] α not significant.

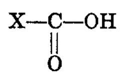
therefore

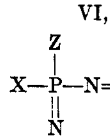
$$\epsilon = \beta/\alpha \quad (9)$$

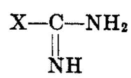
Values of ϵ for the sets studied are given in Table IV. The average value of ϵ for the phosphoric (V, Z = OH) and phosphinic (V) acids is 0.32 (for sets 2c–13b and 16b–18b). We have shown that ionization constants of acids of the type VI[8] and of carboxylic acids VII[2] are best correlated by the σ_m constants for which ϵ = 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 shown[3] 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.


V


VI, n = 1, 2, 3


VII


VIII


IX

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).