PHOSPHONIC ACIDS AND ESTERS

VI*. A TAFT EQUATION CORRELATION FOR ALKYLPHOSPHONIC ACID

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The applicability of the Hammett equation to the acid dissociation constants of arylphosphonic[2] and arylphosphinic[3] acids and, in modified form[4], to a variety of phosphoric acid derivatives and their mono- and di-thio analogs[5] has been demonstrated. By extension of the relationship to phosphonic and phosphinic acids containing carboxy substituents, substituent values (σ) for the PO_3H^-, PO_3^{2-}, and PO_2H^- groups were obtained[2,3]. However, in both arylphosphonic and phosphinic acids, the possibility of $d\pi$–$p\pi$ bonding between the phosphoryl group and the benzene ring exists and the σ values obtained may not be direct measures of the inductive strength of the phosphorus-containing group. Although this effect is probably quite small and possibly negligible**, it was of interest to apply the Taft equation[7] to the acid dissociation constants of alkylphosphonic acids. The demonstration of a linear $\rho\sigma^*$ relationship for these acids would allow extension of the treatment to alkylidene bisphosphonic acids as a possible method for the determination of σ^* values for the $-PO_3H^-$ and related groups. In the alkylphosphonic acids, the possibility of $d\pi$–$p\pi$ bonding is absent and a derived σ^* should be directly related to the inductive strength of the phosphono group. Freedman and Doak[8] and Schwarzenbach and Zurc[9] have concluded that qualitatively the PO_3H^- group is electron-attracting in an aliphatic environment.

Plots of log K/K_0 (K_0 = ionization constant for methylphosphonic acid) for the first ionization constant of twenty (I–XX) and for the second ionization constant of seventeen (I–III, V, VI, XI–XXII) alkylphosphonic acids versus the corresponding values of σ^*[7] were linear. The acidities of six acids (XI, XIII, XVI, XX–XXII) were determined in the present study; the remaining values of ionization constants measured at 25° in water were taken from the literature[10–12]***. The data were analyzed by the least squares method to give

$$\log K_1 = -2.47 + 1.121\,\sigma^* \qquad (1)$$

$$\log K_2 = -7.77 + 1.177\,\sigma^* \qquad (2)$$

The fit of the data to the equation was satisfactory[13] as indicated by correlation coefficients (r) and standard deviations (s): equation (1), $r = 0.977$, $s = 0.131$;

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[*] For Part V see ref. 1.

[**] Studies of the ultraviolet absorption spectra of arylphosphonic acids have indicated this effect to be minimal, *cf.* ref. 6.

[***] The dissociation constants recorded are nonthermodynamic values since liquid junction potential and activity corrections were not made. *Cf.* ref. 8, pp. 491–492.

equation (2), $r = 0.986$, $s = 0.163$. Observed acidities, σ^* values and acidities calculated by equations (1) and (2) are recorded in Table 1.

In the Taft treatment of the primary ionization constant, only the strongly acidic trichloromethyl (XXII) and dichloromethyl (XXI) acids deviated from the linear relationship. Such a deviation is not unexpected because of the inaccuracy in σ^* for highly halogenated groups[7], and the polar saturation effect observed in aliphatic series[7] [as experimentally determined, (XXI) is a stronger acid than (XXII)].

Deviations from linearity in the second ionization constant relationship were observed for the branched alkylphosphonic acids (IV, VII–X); in each case, the acids were found to be less acidic than predicted by equation (2). This acid weakening effect is probably due to a steric inhibition of solvation of the di-anion; similar steric effects on acidity have been observed in the carboxylic acids[7,14] and steric interference with solvation is a common factor in producing non-linear Taft relationships[7,15]. It is of interest to note that the branched acids do not deviate in the pK_1 plot; this lack of deviation would imply a markedly more complex and extensive solvation of the di-anion than of the mono-anion. Since it is reasonable to expect the di-anion to be more highly solvated, steric effects would be expected to exert more noticeable influence on pK_2 than on pK_1.

The reaction constant values (ρ^*) for the two ionization steps (+1.121, +1.177)

TABLE 1

ACIDITIES OF ALKYLPHOSPHONIC ACIDS, $RP(O)(OH)_2$

Compound	*R*	σ^*	*Calculated*[a]		*Observed*		
			pK_1	pK_2	pK_1	pK_2	*Ref.*
(I)	CH_3	0.00	2.47	7.77	2.38	7.74	10
(II)	C_2H_5	—0.10	2.58	7.89	2.43	7.85	10, 11
(III)	*n*-C_3H_7	—0.115	2.60	7.91	2.49	8.06	10, 12
(IV)	iso-C_4H_9	—0.125	2.61	7.92	2.70	8.43[b]	10
(V)	*n*-C_4H_9	—0.130	2.61	7.92	2.59	8.19	10
(VI)	*n*-C_6H_{13}	—0.16	2.65	7.98	2.60	7.90	10
(VII)	neo-C_5H_{10}	—0.165	2.65	7.96	2.84	8.65[b]	10
(VIII)	iso-C_3H_7	—0.190	2.68	7.99	2.66	8.44[b]	10
(IX)	*sec*-C_4H_9	—0.210	2.71	8.02	2.74	8.48[b]	10
(X)	*tert*-C_4H_9	—0.320	2.83	8.15	2.79	8.88[b]	10
(XI)	$C_6H_5CH_2CH_2$	+0.08	2.38	7.68	2.55	7.83	*c*
(XII)	$C_6H_5CH_2$	+0.225	2.22	7.51	2.30	7.55	11
(XIII)	$(C_6H_5)_2CH$	+0.405	2.02	7.29	2.19	7.09	*c*
(XIV)	$C_6H_5CH{=}CH$	+0.41	2.01	7.29	2.00	7.10	11
(XV)	$HOCH_2$	+0.555	1.85	7.12	1.91	7.15	10
(XVI)	$C_6H_5OCH_2$	+0.85	1.52	6.77	1.38	6.75	*c*
(XVII)	ICH_2	+0.85	1.52	6.77	1.30	6.72	10
(XVIII)	$BrCH_2$	+1.03	1.32	6.56	1.14	6.52	10
(XIX)	$ClCH_2$	+1.05	1.30	6.54	1.40	6.30	10
(XX)	$C_6H_5C{\equiv}C$	+1.35	0.96	6.18	1.14	6.30	*c*
(XXI)	Cl_2CH	+1.94	0.30	5.49	1.14[d]	5.58	*c*
(XXII)	Cl_3C	+2.65	—0.50	4.65	1.63[d]	4.71	*c*

[a] From equations (1) and (2).

[b] Deviates from linearity in equation (2); observed values not used in derivation of equation (2).

[c] Acidity values determined in this study by standard methods[10,11]; authentic samples of these acids were prepared by established procedures.

[d] Deviates from linearity in equation (1); observed values not used in derivation of equation (1).

indicate that the electrical effect of the substituents are transmitted to the ionizing phosphonic acid group to a lesser extent than they are to the carboxy group of aliphatic carboxylic acids[7] ($\rho^* = +1.721$). A similar relationship of reaction constants from Hammett plots of phenylphosphonic and benzoic acids has been observed and, by comparison with the aryl boronic and arsonic acids, it has been concluded that ρ values for the ionization of acids depends strongly on the polarizability of the central atom of the acidic group[2]. The relationship between the ρ^* values for the aliphatic phosphonic and carboxylic acids supports this concept, but the paucity of data regarding the acidities of alkylboronic and -arsonic acids does not allow a more complete test. Strikingly, the ρ^* values for both the first and second ionizations are quite similar indicating that the inductive effect of the substituent is transmitted to both the acid and the mono-anion to approximately the same extent. This result may be fortuitous since it would be anticipated that the differing polarizabilities of the uncharged acid and the charged anion would lead to different susceptibilities to inductive effects. This anticipation is borne out of the ρ values for the first (0.755) and second (0.949) dissociations of phenylphosphonic acids in water; in 50% ethanol the relationship is reversed, ρ for the first ionization (0.986) being larger than that for the second (0.885)[2]. While a study of the ionization of phosphonic acids may offer a means for determining the susceptibilities of chemically similar neutral and charged species to inductive effects, it is apparent that entropy and enthalpy effects are important and a precise thermodynamic study is required.

TABLE 2

ACIDITIES OF ALKYLIDENEBISPHOSPHONIC ACIDS, $R[P(O)(OH)_2]_2$

Compound	*R*	*Observed*[a]		*Calculated*[b]	
		pK_2	pK_3	σ^{*c}	σ^{*d}
(XXIII)	$-CH_2-$	2.57	6.87	—0.09	+0.76
(XXIV)	$-CH_2CH(CH_3)-$	2.60	7.00	—0.12	+0.65
(XXV)	$-(CH_2)_3-$	2.65	7.34	—0.16	+0.35
(XXVI)	$-(CH_2)_4-$	2.75	7.54	—0.25	+0.19

[a] From ref. 9.
[b] For the group $-RP(O)(OH)O^-$.
[c] From equation (1) and pK_2.
[d] From equation (2) and pK_3.

The demonstration of linearity in the above relations made feasible an extension of the treatment to methylene bisphosphonic acid (XXIII) in an effort to obtain a σ^* value for the phosphono group. The acidities of a number of alkylidenebisphosphonic acids have been determined[9] and the values are recorded in Table 2. Since only an approximate value (< 2) was reported for the first ionization constant of (XXIII), the treatment must be restricted to the second and third ionizations of the acid.

$$H_2O_3P{-}CH_2{-}PO_3H^- \longrightarrow {}^-HO_3P{-}CH_2{-}PO_3H^-$$

$${}^-HO_3P{-}CH_2{-}PO_3H^- \longrightarrow {}^-HO_3P{-}CH_2{-}PO_3^{2-}$$

These two consecutive ionizations may be considered as the first and second ionizations of an alkylphosphonic acid, $RP(O)(OH)_2$, with $R = -CH_2P(O)(OH)O^-$ and application of equations (1) and (2) to the observed pK_2 and pK_3 values for (XXIII) should yield a σ^* value for the $-CH_2P(O)(OH)O^-$ group*. The σ^* values obtained by this approach are shown in Table 2 and from the divergence of the two values it is apparent that the Taft relationship fails for (XXIII). This failure could arise from either a steric inhibition of solvation of the anion formed on ionization** analogous to the behavior of the branched alkylphosphonic acids or by the operation of an electrostatic field effect arising from the charged substituent. Some support for this explanation is provided by similar treatment of the bis-acids (XXIV)–(XXVI). The divergence between the two calculated values of σ^* for each substituent decreases with the number of intervening methylene groups, but remains approximately constant for the branched bisphosphonic acid (XXIV) relative to (XXIII); in (XXIII) and (XXIV), the steric bulk of the substituent group is similar. Both field and steric effects associated with the substituent group would be expected to decrease markedly, as observed, with the distance between the group and the ionizing center[16].

As a further test of the possibility of $d\pi$–$p\pi$ bonding between a benzene ring and the phosphono group, equations (1) and (2) were applied to phenylphosphonic acid. The calculated values ($pK_1 = 1.80$, $pK_2 = 7.06$) are, within the limits of accuracy of equations (1) and (2), in excellent agreement with the experimentally observed values ($pK_1 = 1.83$[2], 1.60[17]; $pK_2 = 7.07$[2], 6.85[17]). The direct dependence of the acidity of this acid on $\sigma^*_{C_6H_5}$ and the lack of any real divergence between calculated and observed acidities reconfirms the essentially negligible character of such bonding[6,18].

Further approaches to the determination of inductive substituent constants for phosphono and related groups by Taft treatments of phosphorus substituted acetic acids are in progress.

SUMMARY

The Taft equation has been found to apply satisfactorily to the first and second dissociations of alkylphosphonic acids. Observed deviations may be attributed to steric inhibition of solvation and imply markedly different solvations for the mono- and di-anions; the reaction constants for the two di-ssociations are nearly identical. Attempted assignments of σ^* values to the $-PO_3H^-$ group by application of the relationship to bisphosphonic acids failed.

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[*] The σ^* for the group $-P(O)(OH)O^-$ could be approximated by the standard treatment for reduction of substituent inductive effect by an intervening methylene group, *cf.* ref. 7, p. 592.

[**] The substituent group is itself fairly bulky and because of its charged nature would be expected to be highly solvated and therefore bulkier than simple covalent radii consideration would indicate.

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