COMPLEX FORMATION BETWEEN METAL IONS AND AROMATIC PHOSPHONIC ACIDS—I

THE THERMODYNAMIC IONIZATION CONSTANTS OF AROMATIC PHOSPHONIC ACIDS

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Abstract—Thermodynamic ionization constants have been determined at $25 \pm 0.1^{\circ}$ C for a variety of aromatic phosphonic acids. In the case of *meta* and *para* substituted acids Hammett σ and ρ values have also been obtained. In the *ortho* substituted acids investigated, evidence has been found for the formation of intramolecular hydrogen bonds in which the phosphonic acid group behaves as either the proton donor or the proton acceptor, depending on the substituent. Both potentiometric and spectrophotometric methods were used in these determinations.

INTRODUCTION

THE COMPOUND 2-hydroxyphenylphosphonic acid was found to behave differently from phosphonic acids not containing an *ortho* hydroxy group in its reactions with some metal cations. Thus while this acid formed highly coloured, water soluble complexes with the Fe^{3+} and UO_2^{2+} ions, other phosphonic acids yielded colourless insoluble compounds. Similar effects have previously been reported for the arsonic acid and carboxylic acid analogues[1, 2].

A prior requisite for the evaluation of the stability constants of these water soluble complexes is a knowledge of the ionization constants of the acid from which the ligand is derived. Although ionization constants have been reported for a series of aromatic phosphonic acids[3] no results are yet available for 2-hydroxyphenylphosphonic acid. In addition, activity coefficients were not considered in earlier determinations and hence the values reported are non-thermodynamic. It was thus thought desirable to study, not only the ionization and complexation equilibria involving 2-hydroxyphenylphosphonic acid, but also those of other phosphonic acids, for the purposes of understanding both the effects of an ortho substituent and the interaction of ionized forms of the phosphonic acid group with the aromatic system.

Thermodynamic pK values and Hammett parameters for a series of aromatic phosphonic acids are presented in this paper.

EXPERIMENTAL

Apparatus

Ionization constants were obtained mainly from potentiometric titration data. However in the case of slightly soluble acids or those with exceedingly high or low pK values spectrophotometric methods were used. The apparatus used in these determinations has been described earlier[4].

Ionization constants were calculated using an I.B.M. 1800 computer.

Materials

The commercially available reagents, phenylphosphonic acid, 4-methoxyphenylphosphonic acid, 4-methylphenylphosphonic acid and 3,4-dimethylphenylphosphonic acid were all recrystallized from water before use. The compound 4-nitrophenylphosphonic acid was prepared from the corresponding diazonium fluoroborate by the Doak Freedman reaction[5]. Reduction of an aqueous solution of this acid (20 g) with sodium borohydride (5 g) in the presence of palladium on charcoal catalyst (0.5 g) gave 4-aminophenylphosphonic acid in 88 per cent yield. This reagent, when diazotized with nitrous acid and heated to 50°C afforded 4-hydroxyphenylphosphonic acid (50 per cent yield), which was isolated by evaporation to dryness and subsequent recrystallization of the residue from 6N HCl. The reagent 3-nitrophenylphosphonic acid was prepared in 72 per cent yield by the addition, with stirring of phenylphosphonic acid (30 g) to a nitrating mixture consisting of a 1:1 ratio of concentrated nitric and sulfuric acids (80 ml). The mixture was concentrated to a small volume under reduced pressure and the product which solidified was recrystallized repeatedly from water. The 3-amino and 3-hydroxy derivatives were obtained in a manner similar to their para isomers.

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The reagent 2-hydroxyphenylphosphonic acid was obtained in quantitative yield by the hydrogenation of 2benzyloxyphenylphosphonic acid, using 10 per cent palladium on charcoal catalyst and 1 atm pressure of hydrogen. This compound in turn was obtained from 2-benzyloxyaniline[6], which had earlier been prepared by the benzylation of 2-nitrophenol[7] and subsequent reduction of the nitro group using alcoholic ammonium sulfide[8]. The reagent 2-methoxyphenylphosphonic acid was prepared from 2methoxyaniline via the diazonium fluoroborate intermediate.

AnalaR grade potassium hydroxide was freed from carbonate by passage through a column of Deacidite FF (OH⁻ form) and then standardized with potassium hydrogen phthalate.

Theory

The expressions for the thermodynamic ionization constants of polyprotic acids represented by H_nL are as follows

$$K_{1}^{T} = \frac{f_{1}^{2}[H^{+}][H_{n-1}L^{-}]}{[H_{n}L]}$$
(1)

$$K_{2}^{T} = \frac{f_{2}[\mathrm{H}^{+}][\mathrm{H}_{n-2}\mathrm{L}^{2^{-}}]}{[\mathrm{H}_{n-1}\mathrm{L}^{-}]}$$
(2)

$$K_{3}^{T} = \frac{f_{1}f_{3}[\mathrm{H}^{+}][\mathrm{H}_{n-3}\mathrm{L}^{3-}]}{f_{2}[\mathrm{H}_{n-2}\mathrm{L}^{2-}]}$$
(3)

where $H_{n-1}L^-$, $H_{n-2}L^{2-}$ and $H_{n-3}L^{3-}$ are the species resulting from the successive ionizations of the acid H_nL and f_1, f_2 and f_3 are the activity coefficients of uni-, bi- and tricharged ions, respectively. Unless otherwise stated activity coefficients were calculated using the Davies equation[9] viz.

$$-\log f_z = 0.5z^2 [I^{\frac{1}{2}} / (1 + I^{\frac{1}{2}}) - 0.3I]$$
⁽⁴⁾

where f_z is the activity coefficient of an ion bearing a charge of z in a solution of ionic strength, I. In the potentiometric and spectrophotometric determinations of ionization constants the ratios between the concentrations of basic species and conjugate acidic species were obtained by the methods outlined by Albert and Sarjeant[10].

Potentiometric titration of the tribasic acid 2-hydroxyphenylphosphonic acid showed the presence of two acidic groups with pK values in the regions of 2 and 6. On the basis of comparison with the other phosphonic acids studied these pK values were assigned to the successive ionizations of the phosphonic acid group. The ionization of the phenolic group is not revealed in the titration curve and is presumably outside the range of detection of the glass electrode. Spectrophotometric titration of the acid however showed that bathochromic shifts characteristic of ionization of a phenolic group were obtained with increasing pH in alkaline solutions (Fig. 1).

Values for the first two ionization constants of 2-hydroxybenzenephosphonic acid were obtained using relationships (1) and (2). The ionization constant of the weakly acidic phenolic group (K_3^T) was determined using the expression derived by Ernst and Menashi[11] for dibasic acids and later developed by Eidhin and Cinnéide[1] to include triprotic acids, viz.

$$1/(D - D_2) = 1/(D_3 - D_2) + K_w.$$

$$f_3/f_1 f_2 [OH^-](D_3 - D_2)K_3^T$$
(5)



Fig. 1. Absorption spectra of 2×10^{-4} M solutions of 2hydroxyphenylphosphonic acid: (1) pH 3·0-5·3, (2) pH 10·7, (3) 3M KOH, (4) concentrated KOH.

where D_2 , D_3 and D are the absorbancies of solutions consisting of the diionized acid HL²⁻, the fully ionized species L³⁻ and an equilibrium mixture of both these species respectively. From Eqn (5) it follows that a plot of $1/(D - D_2)$ vs $f_3/f_1f_2[OH^-]$ should be linear with a slope of $K_w/(D_3 - D_2)K_3^T$ and intercept $1/(D_3 - D_2)$. In the case of triprotic acids it may be shown[1, 11] that,

$$[OH^{-}] = [KOH] - c\{2 + (D - D_2)/(D_3 - D_2)\}$$
(6)

and

$$I = [KOH] + c + 2c(D - D_2)/(D_3 - D_2)$$
(7)

where c is total concentration of species derived from H_3L and [KOH] is the concentration of potassium hydroxide added. Since the thermodynamic ionization constant K_3^T is related to the stoichiometric ionization constant K_3^C by the relationship

$$K_3^T = K_3^c \cdot f_1 f_3 / f_2 \tag{8}$$

it follows that

$$\log K_{3}^{T} = \log K - \log f_{2} f_{1} / f_{3}$$
(9)

where $K = K_3^c f_1^2$.

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Activity coefficients may be obtained using the extended Debye Huckel equation[12], viz.

$$+\log f_z = -\{Az^2 I^{\frac{1}{2}}/(1 + Ba^0 I^{\frac{1}{2}})\} + CI$$
(10)

where a^0 is the ion size parameter (in Å) and A = 0.509 and B = 0.3286 in aqueous solutions at 25°C. Combining expressions (9) and (10) leads to the equation

$$X = \log K_3^T + CI \tag{11}$$

where $X = \log K - \{4AI^{\frac{1}{2}}/(1 + Ba^0I^{\frac{1}{2}})\}$. From Eqn (5) it then follows that

$$1/(D - D_2) = 1/(D_3 - D_2) + K_w/K[OH](D_3 - D_2).$$
 (12)

Hence a plot of $1/(D - D_2)$ vs $1/[OH^-]$ at constant ionic strength should be linear with a slope of $K_w/K(D_3 - D_2)$ and intercept $1/(D_3 - D_2)$.

Series	s No.	[<i>K</i> OH]	[KCl]	Ι	D	$1/D - D_2$	1/[OH]	— log <i>I</i>
	1	0.872	0		0.195	5.555	1.146	
	2	0.775	0.097		0.174	6.289	1.290	
A	3	0.630	0.242	0.872	0.153	7.246	1.581	14.22
	4	0.581	0.291		0.137	8.196	1.721	
	5	0.388	0.484		0.111	10.410	2.577	
В	1	1.450	0		0.364	2.865	0.690	
	2	1.289	0.161		0.343	3.048	0.777	
	3	1.047	0.403	1.45	0.297	3.546	0.955	14.62
	4	0.966	0.483		0.286	3.690	0.104	
	5	0.644	0.802		0.234	4.566	0.124	
С		1.656	0		0.358	2.915	0.604	· · · · ·
	2	1.564	0.109		0.348	3.003	0.639	
	3	1.472	0.184	1.656	0.335	3.125	0.679	14.13
	4	1.196	0.460		0.306	3.436	0.836	
	5	1.104	0.552		0.293	3.597	0.906	
D	1	1.939	0		0.496	2.079	0.517	
	2	1.724	0.216		0.479	2.155	0.580	
	3	1.401	0.539	1.94	0.448	2.309	0.714	13.80
	4	1.293	0.647		0.435	2.380	0.773	
	5	0.862	1.078		0.380	2.739	1.160	
	1	2.376	0		0.489	2.109	0.421	
	2	2.244	0.132		0.471	2.192	0.446	
E	3	2.112	0.214	2.376	0.459	2.252	0.473	14.08
	4	1.716	0.660		0.426	2.433	0.583	
	5	1.584	0.792		0.417	2.487	0.631	

Table 1. Computation of pK_3^T of 2-hydroxyphenylphosphonic acid $\lambda = 300 \text{ nm}; D_2 = 0.015; c = 1 \times 10^{-4} \text{ M}$

Five series of solutions of 2-hydroxybenzenephosphonic acid were prepared. Each series contained solutions of varying alkali concentrations but with appropriate quantities of KCl added to maintain constant ionic strength. Values of K at different ionic strengths were then obtained by a least squares method applied to Eqn (12). Values of X as a function of I were computed for different values of a^0 , and K_3^T and C then calculated using Eqn (11). The data relevant to the determination of pK_3^T of 2-hydroxyphenylphosphonic acid are presented in Table 1. The value of the ion size parameter giving the minimum deviation in K_3^T and C was found to be $3\cdot 25$ Å. The corresponding pK_3^T is 15.40.

RESULTS AND DISCUSSION

The thermodynamic ionization constants of the phosphonic acids investigated are presented in Tables 2(a) and 2(b).

pK_1 values

The order of increasing pK_1 values viz.

$$4-NO_2 < 3-NO_2 < 3-OH < H < 4-CH_3$$

< $4-OH < 4-OCH_2$

was found to correlate with the relative magnitudes of the Hammett σ values for the substituents. From the plot of pK₁ vs $-\sigma$ [Fig. 2(a)], which is a straight line represented by the equation

$pK_1 = (-\sigma) \, 0.902 + 1.83$

a Hammett ρ value of 0.902 was obtained for the first ionization step of meta and para substituted phenylphosphonic acids. An irregularity in the above order occurs in the case of the 4-OCH₃ and 4-OH substituted acids. Hence although the Hammett σ value for the 4-OH group (-0.37) is greater in magnitude than the σ value for the 4-OCH₃ group (-0.27) the acid 4hydroxybenzenephosphonic acid is surprisingly the stronger of the two acids. In previous investigations [13, 14] it was reported on the basis of kinetic results, that the greater electron releasing tendency of a para hydroxy substituent is due to a no-bond resonance mechanism where contributions from canonical structures involving the -O - group are included. However, it has also been pointed out that only in cases of high electron demand by the reaction centre does the augmenting effect ascribable to this type of electron release manifest itself; otherwise the order $-OCH_3 > -OH$ is observed. The electron withdrawing properties of the unionized phosphonic acid group have so far not been investigated. Because of its strong acidity it was not found possible to determine a σ value for this group using ionization constants of other acidic groups in the same molecule.

$X \xrightarrow{Y} Z$ PO ₃ H ₂							
X	Y	Ζ	pK ₁	p <i>K</i> ₂	pK ₃		
Н	Н	Н	1.83 ± 0.01	7.46 ± 0.01			
OH	н	н	2.00 ± 0.02	7.69 ± 0.02	10.56 ± 0.03		
н	OH	Н	1.78 ± 0.02	7.24 ± 0.02	10.03 ± 0.01		
н	н	OH	1.66 ± 0.01	6.46 ± 0.01	15.40 ± 0.02		
OCH ₃	н	н	2.10 ± 0.02	7.65 ± 0.01			
н	Н	OCH ₃	2.17 ± 0.01	7.90 ± 0.01			
CH ₃	н	Н	1.96 ± 0.02	7.65 ± 0.02			
CH ₃	CH ₃	Н	2.03 ± 0.03	7.69 ± 0.02			
NO ₂	H	Н	1.06 ± 0.04	6.50 ± 0.02			
H	NO_2	Н	1.14 ± 0.03	6.53 ± 0.02			

Table 2. (a) Thermodynamic pK values of phenylphosphonic acids

(b) Thermodynamic pK values of aminophenylphosphonic acids

$X - \bigvee_{Y = Z} - PO_{3}H_{2}$							
X	Y	Z	pK ₁	pK ₂	р <i>К</i> _{NH3+}		
NH ₂ H	H NH ₂	H H		$7.84 \pm 0.01 \\ 7.53 \pm 0.01$	$\begin{array}{r} 3.99 \pm 0.01 \\ 4.50 \pm 0.01 \end{array}$		

The increased acidity of 2-hydroxyphenylphosphonic acid relative to its *para* isomer ($\Delta p K_1 = 0.34$) may be attributed to the formation of an intramolecular hydrogen bond in which the phosphonic acid group acts as the proton acceptor [Fig. 3(a)]. A similar hydrogen bond configuration has been proposed to account for the high acidity of the $-CO_2H$ group in salicylic acid $(\Delta p K_1 = 1.54)[15]$. However, in the case of the arsonic acid analogue the phenolic group behaves as the proton acceptor in the hydrogen bond and 4-hydroxyphenyl-arsonic acid is more strongly acidic than its *ortho* isomer ($\Delta p K_1 = -0.15)[1, 4]$.

Methylation of the phenolic group in 2-hydroxyphenylphosphonic acid renders the hydrogen bond con-



Fig. 2. Plot of (a) pK_1 vs Hammett σ values and (b) pK_2 vs Hammett values for *meta* and *para* substituted phenyl-phosphonic acids.

figuration in Fig. 3(a) impossible and the alternative configuration in which the phosphonic acid group behaves as the proton donor is adopted [Fig. 3(c)]. As a result the basicity of the phosphonic acid group is increased and the order of increasing pK_1 values 2-hydroxyphenylphosphonic acid < phenylphosphonic acid < 4methoxyphenylphosphonic acid < 2-methoxyphenylphosphonic acid is obtained.

pK_2 values

The order of increasing pK_2 values for the *meta* and *para* substituted phenylphosphonic acids studied parallels the order of increasing σ values for the substituents. From the linear plot of pK_2 vs $-\sigma$ [Fig. 2(b)] a Hammett ρ value of 1.023 was calculated for the second ionization step of *meta* and *para* substituted phenylphosphonic acids.

The decreased value of pK_2 of 2-hydroxybenzenephosphonic acid relative to its *para* isomer may be attributed to intramolecular hydrogen bonding in the monoanion similar to that postulated for the unionized acid [Fig. 3(b)].

Such a hydrogen bond configuration is not possible in the case of the monoanion of 2-methoxyphenylphosphonic acid and the alternative arrangement in which the monoionized phosphonic acid group behaves as a proton donor is adopted. Consequently the pK_2 value of this acid is greater than that of its *para* isomer.

pKs of phenolic groups

The increased pK values of the phenolic groups in 3and 4-hydroxyphenylphosphonic acids relative to the pK of phenol reflects the electron donating properties of the diionized phosphonic acid group, $-PO_3^{2-}$. From the results obtained, Hammett σ values were obtained for the *meta* (-0.019) and *para* (-0.265) $-PO_3^{2-}$ substituents.



Fig. 3. Intramolecular hydrogen bonding in (a) 2-hydroxyphenylphosphonic acid, (b) mono-ionized 2-hydroxyphenylphosphonic acid and (c) 2-methoxyphenylphosphonic acid.

The very weak acidity of the phenolic group in 2hydroxyphenylphosphonic acid (pK = 15.40) is consistent with strong intramolecular hydrogen bonding in which the phenolic group acts as the proton donor. On the basis of pK values alone it may be concluded that this hydrogen bond is stronger than the corresponding hydrogen bonds in both the carboxylic (pK = 13.39) and arsonic (pK = 13.27) acid analogues. pK values of NH⁺₁ groups

The increased acidities of the $-NH_3^+$ groups in both 3- and 4-aminophenylphosphonic acids relative to the anilium ion is indicative of the electron withdrawing nature of the mono-ionized phosphonic acid group, $-PO_3H^-$. Using the pK and ρ values reported by Biggs[16] for the ionization of the anilium ion, Hammett

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 σ values of +0.036 and +0.220 were calculated for *meta* and *para* - PO₃H⁻, substituents respectively.

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