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The Acid Dissociation Constants of Aromatic Phosphonic Acids. II. Compounds with Ortho Substituents

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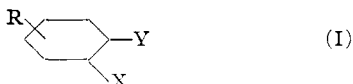
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The acid dissociation constants of sixteen *o*-substituted benzenephosphonic acids have been determined. Comparison of the observed values of the pK 's with the values expected from consideration of only the electrical effects of the ortho substituents leads to the conclusion that hydrogen bonds exist between the phosphono group ($-\text{PO}_3\text{H}_2$) and many of the ortho substituents. Further, the phosphono group acts either as the donor or the acceptor in these hydrogen bonds. Reaction constants (ρ) are calculated for series of 4- and 5-substituted 2-chloro-(or bromo)- and 2-methoxybenzenephosphonic acids, and are found to be virtually independent of the nature of the ortho substituents.

The acid dissociation constants of a series of meta and para substituted benzenephosphonic acids were reported in a recent paper from this Laboratory.¹ We have now extended this investigation to include sixteen *o*-substituted benzenephosphonic acids. The present work was undertaken for the reasons discussed below.

We previously observed that titration of *o*-carboxybenzenephosphonic,² 2-methoxy-4-aminobenzenephosphonic and *o*-biphenylphosphonic acids, with thymolphthalein as the indicator, failed to lead to the theoretical neutral equivalents.³ This fact suggested that these compounds have abnormally small dissociation constants, since other phosphonic acids which do not possess an interfering acid functional group give the theoretical neutral equivalents.⁴ Accordingly, the pK 's of these compounds were determined by potentiometric titration; several other *o*-substituted compounds were included in this study for comparison.

It has been shown recently that the Hammett equation expresses the effect of substituents (R) on the reactivity of side chains (Y) in series of compounds of type I if the ortho substituent (X) is constant throughout the series.⁵ In such reaction



series the reaction constant (ρ) was found to be virtually independent of the nature of X.⁵ Since a number of benzenephosphonic acids of type I (where X is a chloro, bromo or methoxy group) were available in this Laboratory,^{2,6} we decided to test the above relationships on these series of compounds.

Experimental

All the phosphonic acids used were prepared in this Laboratory and have been described previously^{2,4,6,7} except for the ortho and para isomers of biphenylphosphonic acid.

(1) H. H. Jaffé, L. D. Freedman and G. O. Doak, *THIS JOURNAL*, **75**, 2209 (1953).

(2) See L. D. Freedman, H. Tauber, G. O. Doak and H. J. Magnuson, *ibid.*, **75**, 1379 (1953), footnote g of Table II.

(3) The compounds were shown to be analytically pure, within experimental error, by analysis for at least two elements.

(4) G. O. Doak and L. D. Freedman, *THIS JOURNAL*, **73**, 5658 (1951), and subsequent papers.

(5) (a) H. H. Jaffé, *Science*, **118**, 246 (1953); (b) *Chem. Revs.*, **53**, 191 (1953); (c) cf. J. D. Roberts and J. A. Yancey, *THIS JOURNAL*, **73**, 1011 (1951).

(6) G. O. Doak and L. D. Freedman, *ibid.*, **75**, 6307 (1953).

(7) G. O. Doak and L. D. Freedman, *ibid.*, **74**, 753 (1952).

o-Biphenylphosphonic acid⁸ was prepared from *o*-biphenyldiazonium fluoborate by the general method described previously.⁴ Ethyl acetate was used as the reaction solvent, and cuprous chloride as the catalyst. After the reaction mixture was steam distilled, the residual liquid was filtered. The phosphonic acid was isolated from the filtrate by procedure A,⁴ and the yield was 9%; m.p. 202–203.5°.⁸

Anal. Calcd. for $\text{C}_{12}\text{H}_{11}\text{O}_3\text{P}$: C, 61.54; H, 4.73; P, 13.23. Found: C, 61.55; H, 4.72; P, 12.92.

p-Biphenylphosphonic acid was prepared from the corresponding diazonium fluoborate. The reaction was run in dioxane, and cuprous chloride was the catalyst. During the steam distillation of the reaction mixture, the phosphonic acid crystallized in the distilling flask. The crude acid was removed by filtration and dissolved in 10% sodium hydroxide solution. The alkaline solution was treated with Darco, filtered, and the hemi-sodium salt⁴ precipitated by the addition of concentrated hydrochloric acid. This salt was dissolved in a mixture of equal volumes of hot alcohol and concentrated hydrochloric acid; the crystalline acid separated when the solution was cooled. The yield was 40%; m.p. 218–220°.

Anal. Calcd. for $\text{C}_{12}\text{H}_{11}\text{O}_3\text{P}$: P, 13.23; neut. equiv., 117.1. Found: P, 13.06; neut. equiv., 117.4.

o-Biphenylarsonic acid was prepared by the Bart reaction.⁹ The pK measurements on the phosphonic acids were performed as described in the previous paper.¹ The pK 's of *o*-biphenylarsonic acid were determined by the procedure of Pressman and Brown.¹⁰

Results and Discussion

The experimental results are reported in Table I. It should be noted that the last pK 's of *o*-carboxybenzenephosphonic, 2-methoxy-4-aminobenzenephosphonic and *o*-biphenylphosphonic acids are larger than the corresponding pK 's of any of the other acids reported in this or the previous paper.¹ Comparison of the dissociation constants of these three acids with the pH at the end-point of a back-titration with thymolphthalein as indicator ($pH \sim 9.3$)¹¹ clearly shows the reason for the analytical difficulties encountered with these compounds.

In order to estimate the "ortho effects"¹² in the acids studied, it was necessary to estimate their pK 's expected on the basis of only the electrical (inductive and resonance) effects of the ortho substituents. Estimation of the expected pK , which we shall denote by pK^* , was based on the assumption that substituents exert the same resonance¹² and inductive effects from the ortho and

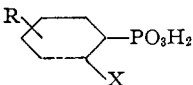
(8) Previously prepared by A. Burger and N. D. Dawson, *J. Org. Chem.*, **16**, 1250 (1951); m. p. 203–205°.

(9) G. H. Cookson and F. G. Mann, *J. Chem. Soc.*, 2895 (1952).

(10) D. Pressman and D. H. Brown, *THIS JOURNAL*, **65**, 540 (1943).

(11) W. M. Clark "The Determination of Hydrogen Ions," 2nd. Ed., Williams and Wilkins Company, Baltimore, Md., 1927, p. 78.

(12) G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1946, pp. 257–258.

TABLE I
 pK 's of 

R	X	$pK_{PO_3H_2}$		$pK_{PO_3H^-}$	
		In H ₂ O	In 50% ethanol	In H ₂ O	In 50% ethanol
H	H ^a	1.83	3.15	7.07	8.26
H	Cl	1.63	2.94	6.98	8.21
H	Br	1.64	2.91	7.00	8.22
H	F	1.64	2.84	6.80	7.99
H	I	1.74	3.06	7.06	8.40
H	C ₆ H ₅	^b	3.78	8.13	^c
H	COOH ^d	1.71	2.47	9.17 ^e	10.03 ^e
H	OCH ₃	2.16	3.62	7.77	8.87
H	NH ₂ ^f	7.29	8.34
4-NO ₂	Cl	1.12	2.18	6.14	7.31
4-NH ₂	Cl	7.33	^b
5-Cl	Cl	^b	2.55	6.63	7.84
5-NO ₂	Br	^b	^b	6.14	7.47
5-CH ₃	Br	1.81	3.04	7.15	8.35
4-NH ₂	OCH ₃	8.22	9.53
4-NO ₂	OCH ₃	1.53	2.61	6.96	7.94
4-NO ₂	OH ^g	1.22	1.95	5.39	6.59

^a From ref. 1. ^b The compound was not sufficiently soluble. ^c The sodium salt precipitated during titration. ^d pK_{COOH} , 3.78 in H₂O; 4.89 in 50% C₂H₅OH. ^e The substituent is actually COO⁻. ^f $pK_{NH_2^*}$, 4.10 in H₂O. ^g pK_{OH} , > 12 in H₂O; > 13 in 50% C₂H₅OH.

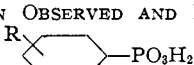
para positions. Branch and Calvin have concluded that the inductive effect from the ortho position is somewhat larger than from the para position.¹² This difference in inductive effects between the two positions was neglected, and the consequences of this neglect are examined below. We were thus able to estimate the ortho effects as $\Delta pK = pK_{observed} - pK^*$. Table II lists this difference (ΔpK) for all the compounds of Table I for which adequate reference data were available from our previous work.¹ For the mono-substituted phosphonic acids the pK^* -values are the pK 's of the corresponding para isomers. The expected pK 's of the disubstituted acids of type I were obtained from the equation

$$pK^* [2-X-5(or 4)-RC_6H_4PO_3H_2] = pK [p-XC_6H_4PO_3H_2] - pK [C_6H_5PO_3H_2] + pK [m(or p)-RC_6H_4PO_3H_2]$$

If the difference in inductive effect between ortho and para positions were included, all entries in Table II, except the value for *o*-aminobenzenephosphonic acid, would be more positive. The small inductive effect of the hydroxy group cannot greatly affect the values listed for 2-hydroxy-4-nitrobenzenephosphonic acid. All of the other ortho substituents would exhibit slightly larger "ortho effects" (see below) if the difference in inductive effect between ortho and para positions had not been neglected.

Acid dissociation constants are generally insensitive to steric hindrance,¹³ and the "ortho effects" encountered are frequently due to intramolecular hydrogen bonding between the ortho substituent and the acid function. Such hydrogen bonds affect the acid strengths by three distinguish-

(13) H. C. Brown and G. K. Barabas, *THIS JOURNAL*, **69**, 1137 (1947).

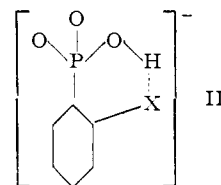
TABLE II
 THE DIFFERENCE (ΔpK) BETWEEN OBSERVED AND EXPECTED VALUES OF THE pK 'S OF 

R	X	$\Delta pK_{PO_3H_2}$		$\Delta pK_{PO_3H^-}$	
		In water	In 50% ethanol	In water	In 50% ethanol
H	COOH ^a	+0.16	-0.33	+2.28 ^b	+1.88 ^b
H	NH ₂	-0.24
H	C ₆ H ₅	+0.63 ^c	+1.06 ^c
H	Cl	-0.03	+0.01	+0.23	+0.22
H	Br	+ .03	+ .17	+ .19
4-NO ₂	Cl	+ .05	+ .06	+ .23	+ .16
4-NH ₂	Cl	+ .12
5-Cl	Cl	- .06	+ .30	+ .17
5-NO ₂	Br	+ .15	+ .29
H	OCH ₃ ^d	+ .10	+ .25	+ .49	+ .39
4-NO ₂	OCH ₃ ^d	+ .07	+ .09	+ .52	+ .21
4-NH ₂	OCH ₃ ^d	+ .48
4-NO ₂	OH ^e	- .18	- .64	-1.02	-1.06

^a ΔpK_{COOH} , -0.17 in H₂O; -0.47 in 50% C₂H₅OH. ^b The substituent is COO⁻. ^c The expected value is based on C₆H₅PO₃H₂ rather than *p*-C₆H₄C₆H₄PO₃H₂. The latter acid was not sufficiently soluble in either water or 50% alcohol to permit the determination of its pK by our standard procedure. Its second pK in water was determined by the procedure used for the arsonic acids (*cf.* ref. 10), and was found to be 7.21. ^d The pK^* -value is based on *p*-C₂H₅OC₆H₄PO₃H₂. ^e ΔpK_{OH} can be estimated to be not less than 4.

able mechanisms which will be used to interpret the data of Table II.

(1) The hydrogen atom to be removed in a dissociation process may be involved in a hydrogen bond (*cf.* formula II).



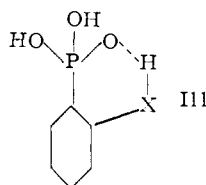
In this case the dissociation process requires, in addition to the "expected" energy, sufficient energy to break the hydrogen bond. Hence, the acid strength is appreciably less than the expected value. This effect is readily apparent in salicylic acid, in which the pK of the hydroxy group is 3.5 pH units larger than the pK of the same group in the para isomer.¹⁴ In the compounds investigated by us, this effect leads to the large positive value observed for $\Delta pK_{PO_3H^-}$ of *o*-carboxybenzenephosphonic acid, and to the much smaller positive values of $\Delta pK_{PO_3H^-}$ for the phosphonic acids with an *o*-chloro, *o*-bromo or *o*-methoxy substituent. For the *o*-chloro and *o*-bromo substituents, the effect observed barely exceeds the experimental error; however, the availability of 11 independent values of ΔpK (with an average value of 0.203 ± 0.057)¹⁵ for these two groups makes the existence of this acid weakening ortho effect quite certain. Similarly we have five independent values of ΔpK (average value 0.402 ± 0.216)¹⁵ of the *o*-methoxy group. Since the carboxylate group is negatively

(14) C. T. Abichandani and S. K. K. Jatkari, *J. Indian Inst. Sci.*, **21A**, 417 (1938); *C. A.*, **33**, 3662 (1939).

(15) The error term given is the standard error.

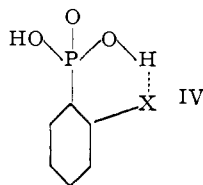
charged, it is not surprising that it forms much stronger hydrogen bonds than the uncharged chloro, bromo or methoxy groups. The same effect is also responsible for the abnormally large value of the pK of the hydroxy group in compounds containing this group as an *o*-substituent (*cf.* Table II, footnote *e*).

(2) If the phosphono group ($-\text{PO}_3\text{H}_2$) acts as the acceptor¹⁶ in a hydrogen bond (*cf.* formula III), the negative charge of the phosphoryl ($\equiv\text{P}\rightarrow\text{O}$)



oxygen atom is appreciably reduced, and hence the acid strength of the phosphono group should be increased. This effect is clearly evident in *o*-aminobenzenephosphonic acid, and in the first and second pK 's of 2-hydroxy-4-nitrobenzenephosphonic acid. Since the ortho substituent in these compounds is uncharged, hydrogen bonding with the phosphoryl group as acceptor is favored over bonding with the phosphono group as donor. An analogous effect is observed in the carboxy group of *o*-carboxybenzenephosphonic acid, and has been observed previously in the strengthening of the carboxy function of salicylic acid.¹⁴

(3) If the phosphono group acts as the donor in the hydrogen bond (*cf.* formula IV), the oxygen atom of the donor hydroxy group acquires a partial



negative charge, and therefore raises the first pK of the phosphono group.¹⁷ This effect, which can be expected to be smaller than the effect discussed under (1) above, appears to be observed in benzenephosphonic acids bearing an *o*-methoxy substituent.

In *o*-carboxybenzenephosphonic acid both the carboxy group and the phosphono group contain hydroxy groups and negative oxygen atoms, and consequently either group may act as the donor or the acceptor for the hydrogen bond. It is seen from Table II that the first pK of the phosphono group is weakened in water, but strengthened in 50% ethanol. These facts suggest that forms of type III and IV are in equilibrium, and that the equilibrium position is solvent dependent.

The great difference between the pK 's of *o*-carboxybenzenephosphonic acid and its *p*-isomer

(16) The terms acceptor and donor, as used in this paper, refer to acceptance and donation, respectively, of the bonding hydrogen atom.

(17) The effect discussed here is slightly enhanced by a "statistical factor" arising from the circumstance that a strong hydrogen bond would reduce the number of equivalent hydrogen atoms available for dissociation from 2 to 1. The magnitude of the "statistical factor" varies with the strength of the hydrogen bond between 1 and 1/2, and hence the pK 's are affected by an amount between 0 and 0.30.

contrasts markedly with the minor difference between the pK 's of the *o*- and *p*-isomers of carboxyphenylphosphate.¹⁸ Hence, it is apparent that any intramolecular hydrogen bond which exists in *o*-carboxyphenylphosphate must be quite weak. An examination of Fisher-Taylor-Hirschfelder models shows that the geometry of this compound is unfavorable for intramolecular hydrogen bonding.

The reason for the high pK 's of *o*-biphenylphosphonic acid is not obvious. An *o*-phenyl substituent is not greatly acid weakening in benzoic acid.¹⁹ Inductive, resonance and steric effects of an *o*-phenyl group are probably acid strengthening.²⁰ The only explanation which we can propose for the observed pK 's of *o*-biphenylphosphonic acid is a hydrogen bond between the phosphono group and the phenyl substituent. Such a hydrogen bond would lead to a positive value of $\Delta pK_{\text{PO}_3\text{H}}$ by the effect discussed under (1) above, and to a smaller positive value for $\Delta pK_{\text{PO}_3\text{H}_2}$ by the effect discussed under (3). Although such a hydrogen bond seems surprising, appreciable evidence exists that π -electron systems can act as acceptors for hydrogen bonds. Such evidence will now be discussed.

Hydrogen bonds involving benzene rings as acceptors have been demonstrated,²¹ but are usually rather weak. The absence of such a hydrogen bond in *o*-biphenylcarboxylic acid is not surprising since the two benzene rings and the carboxy group can approach the planar configuration favored by resonance. The geometry of this nearly planar configuration does not permit a reasonably stable hydrogen bond; the strength of a hydrogen bond with a benzene ring as acceptor can hardly be expected to overcome the resonance energy of the nearly planar configuration. However, Fisher-Taylor-Hirschfelder models show that the two rings in *o*-biphenylphosphonic acid must be almost normal to each other, and one phosphono hydrogen atom appears to be in a favorable position for hydrogen bonding with the benzene ring. A hydrogen bond to an *o*-phenyl group may also be present in *o*-phenylboric acid ($pK = 12.01$) which has a materially larger pK than its *p*-isomer ($pK = 10.80$) or phenylboric acid ($pK = 10.79$).²² Since these data refer to the first pK 's of these acids, the acid weakening would be the result of the effect discussed under (3) above. This explanation for the weakness of *o*-biphenylboric acid appears more reasonable than the interpretation proposed by Branch and co-workers.²³ Another hydrogen bond involving a π -electron system (in this case a triple bond) as the acceptor has been shown to exist in *o*-hydroxyphenylacetylene.²³

If our explanation for the weakness of *o*-biphenylphosphonic acid is correct, one would anticipate

(18) P. G. Walker and E. J. King, *Biochem. J.*, **47**, 93 (1950), report *o*- $-\text{OOC}_6\text{H}_4\text{OPO}_3\text{H}^-$, $pK = 6.11$; *p*- $-\text{OOC}_6\text{H}_4\text{OPO}_3\text{H}^-$, $pK = 6.40$.

(19) J. F. J. Dippy and R. H. Lewis, *J. Chem. Soc.*, 1423 (1937), report: *o*- $\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{COOH}$, $pK = 4.46$; J. F. J. Dippy and F. R. Williams, *ibid.*, 1888 (1934), report: $\text{C}_6\text{H}_5\text{COOH}$, $pK = 4.20$.

(20) E. Berliner and L. H. Liu, *THIS JOURNAL*, **75**, 2417 (1953).

(21) *Cf.* M. Tamres, *ibid.*, **74**, 3375 (1952); L. H. Jones and R. M. Badger, *ibid.*, **73**, 3132 (1951).

(22) D. L. Yabroff, G. E. K. Branch and B. Bettman, *ibid.*, **56**, 1850 (1934).

(23) V. Prey and H. Berbak, *Monatsh.*, **82**, 990 (1951).

that a similar hydrogen bond would be encountered in *o*-biphenylarsonic acid. Consequently, we prepared this compound and determined its pK 's. The values found ($pK_1 = 4.29$, $pK_2 = 9.33$) are much larger than the corresponding values for benzenearsonic acid ($pK_1 = 3.47$, $pK_2 = 8.48$)¹⁰; hence it appears likely that *o*-biphenylarsonic acid also contains an intramolecular hydrogen bond.

o-Carboxybenzenephosphonic acid melts at 175.5–179°, while its *m*- and *p*-isomers both melt above 300°. Similarly, *o*-aminobenzenephosphonic acid melts at 199–200°, while its *m*-isomer melts above 300°, and the *p*-isomer decomposes above 245°. The much lower melting points of the ortho compounds are consistent with the presence of strong intramolecular hydrogen bonds in these compounds.²⁴

The pK 's of the four benzenephosphonic acids with halogen atoms substituted in the ortho position are given in Table I. All four halogens are seen to be acid strengthening, and it should be noted that the effects of chlorine and bromine are identical within experimental error. In a recent paper on a correlation of substituent constants with electron densities, equal parameters (Coulomb and resonance integrals) were assigned to both bromo and chloro substituents.²⁵ This assignment is further justified by the equality of the effects of these two groups in the ortho position.

Table I further lists the pK 's of the series of phosphonic acids of type I with X = Cl (or Br) and CH₃O. Plots of these data against Hammett's substituent constants (σ) are shown in Figs. 1 and 2, where they are compared with the corresponding plots for series of compounds without an ortho

TABLE III

REACTION CONSTANTS (ρ) FOR THE ACID DISSOCIATION OF

R		X		Solvent		n^a	ρ^b	r^c	s^d	$-\log k^e$
R		X		Solvent		n^a	ρ^b	r^c	s^d	$-\log k^e$
R		X		Solvent		n^a	ρ^b	r^c	s^d	$-\log k^e$
H ^f	H ₂ O	10	0.755 ± 0.028	0.995	0.030	1.836				
Cl, Br	H ₂ O	3	.749 ± .137	.984	.090	1.697				
H ^f	50% C ₂ H ₅ OH	12	.986 ± .053	.986	.059	3.132				
Cl, Br	50% C ₂ H ₅ OH	4	.995 ± .046	.998	.031	2.942				
R		X		Solvent		n^a	ρ^b	r^c	s^d	$-\log k^e$
H ^f	H ₂ O	12	0.949 ± 0.042	0.990	0.058	6.965				
Cl, Br	H ₂ O	6	.908 ± .125	.964	.152	6.901				
OCH ₃	H ₂ O	3	.881 ± .103	.993	.105	7.685				
H ^f	50% C ₂ H ₅ OH	12	.991 ± .055 ^g	.985 ^g	.063 ^g	8.228 ^g				
Cl, Br	50% C ₂ H ₅ OH	5	1.191 ± .042	.998	.033	8.249				
OCH ₃	50% C ₂ H ₅ OH	3	1.108 ± .056	.999	.057	8.824				

^a The number of compounds on which the calculation of ρ is based. ^b The error given is the standard error of ρ . ^c The correlation coefficient (cf. ref. 5b). ^d The standard deviation from the best straight line (cf. ref. 5b). ^e The value of $-\log k$ calculated for $\sigma = 0$. ^f From ref. 1. ^g These values represent a correction of values given in ref. 1.

(24) Cf. Y. K. Syrkin and M. E. Dyatkina, "Structure of Molecules and the Chemical Bond," translated by M. A. Partridge and D. O. Jordan, Interscience Publishers, Inc., New York, N. Y., 1950, p. 282.

(25) H. H. Jaffé, *J. Chem. Phys.*, **20**, 279 (1952).

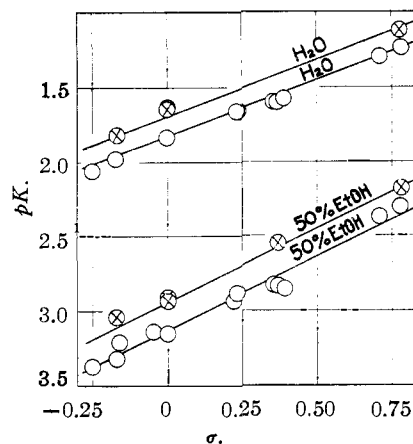


Fig. 1.—Plot of $pK_{PO_3H_2}$ against σ : O, *m*- and *p*-substituted benzenephosphonic acids; ⊗, 4- and 5-substituted 2-chloro(or bromo)-benzenephosphonic acids.

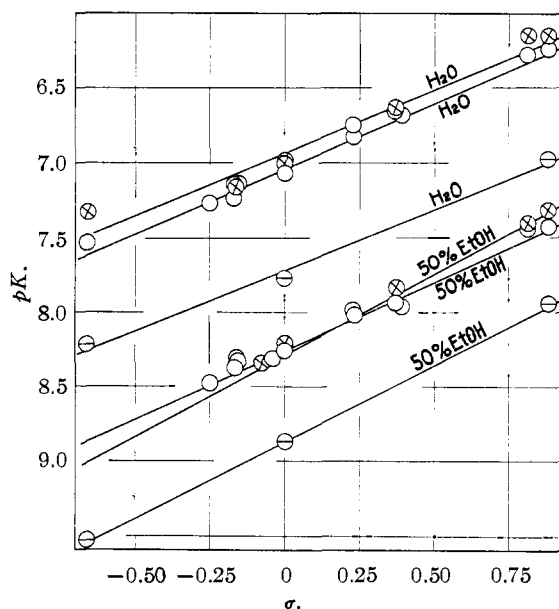


Fig. 2.—Plot of $pK_{PO_3H^-}$ against σ : O, *m*- and *p*-substituted benzenephosphonic acids; ⊗, 4- and 5-substituted 2-chloro(or bromo)-benzenephosphonic acids; ⊖, 4-substituted-2-methoxybenzenephosphonic acids.

substituent. A single straight line results for each series of compounds (compounds with X = Cl and X = Br are considered to belong to the same series), and hence the Hammett equation applies to these reaction series. The possibility of combining compounds with *o*-chloro and *o*-bromo substituents into a single series depends on the fact that both substituents equally affect the pK of benzenephosphonic acid and that the reaction constants are insensitive to the nature of the ortho substituent X.⁵ The latter fact is further illustrated by Figs. 1 and 2 and Table III, where points for comparable data define lines which are nearly parallel. The data for $pK_{PO_3H^-}$ in 50% ethanol form an exception to this generalization, since the slopes of the lines for X = CH₃O, X = Cl (or Br) and X = H differ appreciably. The degree of deviation can be seen in Table III, where the re-

action constants obtained in this paper are compared with those obtained earlier.

Reaction constants for the dissociation of series of acids have been found to increase with the alcohol concentration in mixed water-alcohol solvents.^{5b} The reaction constants reported in Table III are in agreement with this finding. The apparent exception, reported earlier,^{5b} involving the reaction

constants for the second pK 's of benzenephosphonic acids was based on an erroneous ρ -value in 50% ethanol; the corrected value is given in Table III.

Acknowledgment.—The authors wish to thank Mrs. Barbara Stanley for performing the analyses necessary for this research.

CHAPEL HILL, NORTH CAROLINA

[CONTRIBUTION FROM THE CRYOGENIC LABORATORY AND THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

Pressure-Volume-Temperature Relationships of Liquid Normal Deuterium¹

BY ABRAHAM S. FRIEDMAN, MAX TRZECIAK AND HERRICK L. JOHNSTON

RECEIVED NOVEMBER 23, 1953

Compressibility factors of liquid normal deuterium have been determined at pressures up to 100 atm. and at temperatures between the triple and critical points of D_2 . Isochores, derived from the experimental isotherms, are linear and their slopes are a linear function of the density throughout the range investigated. $(\partial P/\partial T)_V = -14.1 + (665/V)$, where the pressure is in atmospheres, the temperature is in degrees absolute, and volume is in cc. per mole.

Introduction

The compressibility of liquid deuterium at 19.71, 20.31 and 20.97°K. has been determined by Bartholomé² at pressures up to 100 atm. However, the P - V - T properties of liquid deuterium in the temperature region between the boiling point of hydrogen and the critical point of deuterium have not previously been investigated. As part of this

Laboratory's program of study of the thermal and physical properties of the isotopes of hydrogen, the data of state for liquid normal deuterium have been determined in this temperature range at pressures up to 100 atm.

Apparatus

The apparatus used in this research was the same as that employed in the earlier investigation on the compressibility of liquid hydrogen.³ It consists of a high pressure copper

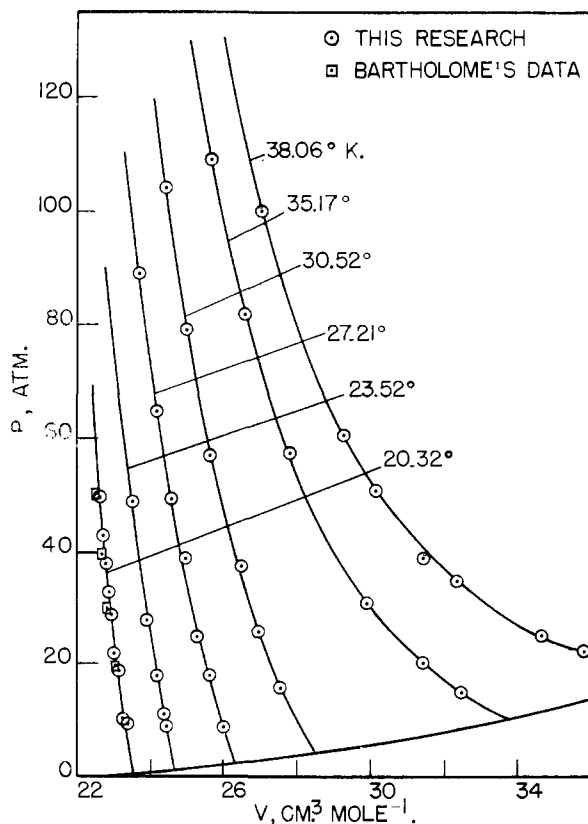


Fig. 1.— P vs. V for liquid D_2 .

(1) This work was done under the auspices of the Atomic Energy Commission.

(2) E. Bartholomé, *Z. physik. Chem.*, [B] **33**, 387 (1936).

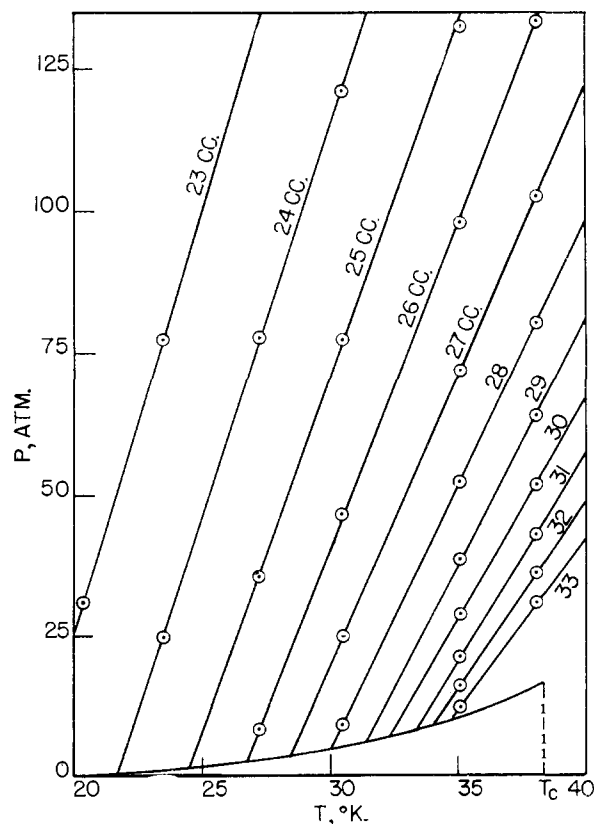


Fig. 2.—Isochores replotted from Fig. 1.

(3) H. L. Johnston, W. E. Keller and A. S. Friedman, *THIS JOURNAL*, **76**, 1482 (1954).