aries to the bands formed and "developed" in the chromatographic column.

When only one solute is present, if the adsorption isotherm is of the usual type, the front boundary of the band will be sharp and will tend constantly to sharpen itself in spite of diffusion, etc., while the rear boundary will be broad and gradual. The quantitative agreement with experimental data, at least in the case of lauric acid on charcoal, is sufficiently good to justify the assumptions made. The equations developed (equations (2), (5) and (8)) can easily be applied to a wide variety of conditions besides those ordinarily encountered. Examples are given.

The partial differential equations for multiple solutes are given (equations (20) and (21)) and the discontinuous solutions for multiple solute (equations (15) to (18)) are discussed separately, but no general solution is arrived at. Some evidence that here also the boundaries may usually tend to be sharp in front and diffuse in the rear was obtained by closer examination of a case involving two solutes, but the conclusion is not definite. In the typical two-solute case the concentration of the faster moving solute in the band where it is pure tends to be larger than in the original solution. Under similar conditions during development the concentration of the slower moving solute in the rear band where it is pure tends to be smaller than in the intermediate (overlapping) band.

It is suggested that more information about adsorption isotherms can be obtained from the diffuse boundaries of chromatograms than from the sharp ones. The chief characteristic difference is the presence of a (df/dc) in the equations for the former type in place of $(f(c_0)/c_0)$ found in the equations for the latter.

STANFORD UNIVERSITY, CALIF.

RECEIVED NOVEMBER 9, 1942

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 913]

Ionization Constants of Several Substituted Phenylarsonic Acids

BY DAVID PRESSMAN AND DAVID H. BROWN

In the course of our immunological studies[1] it became desirable to know the ionization constants of several substituted phenylarsonic acids. For this reason the constants at 22° for nineteen phenylarsonic acids were determined and are reported here. The values were obtained under identical conditions by the use of a glass electrode and are good only to about 15%. No correction for activities was made.

Experimental

Preparation of Compounds.—The arsonic acids were prepared by the methods of the references in Table I.

Potentiometric Titration of Arsonic Acids.—Solutions of the dipotassium salts (or the tripotassium salts in the cases of *p*-hydroxy- and *p*-carboxyphenylarsonic acids) were made by weighing out accurately 0.00200 mole of the acid, adding the calculated amount of carbonate-free 0.0822 *N* potassium hydroxide solution, and making up to a total volume of 100 ml. The solution was then titrated with 0.0979 *N* hydrochloric acid solution. The *p*H was measured by use of a Beckman *p*H meter after every addition of 1 to 2 ml. of the acid. The titrating system was maintained in a bath at 22.0° which was also room temperature.

In the case of some very insoluble acids, the acid precipitated before the titration was complete. This prevented the calculation of the first ionization constant in these cases. The second constant was determined in all cases.

Calculation of Ionization Constants.—The graphical point from a plot of *p*H against the volume of hydrochloric acid added which corresponds to half neutralization of the first, second, or in some cases the third hydrogen ion is taken as the ionization constant; it is good to within 0.1 *p*H unit, limiting the value of the dissociation to an error of about ±15%.

Correction was necessary in some cases for the ionization of the first hydrogen ion and for the hydrolysis of the di-ionized arsonate ion. This was done by the use of equation 1

$$K = (\mathrm{H}^+)m\left[\frac{C/2 + (\mathrm{H}^+)m - K_\mathrm{w}/(\mathrm{H}^+)}{C/2 - (\mathrm{H}^+)m + K_\mathrm{w}/(\mathrm{H}^+)}\right] \quad (1)$$

where K is the dissociation constant, C is the total

---

[1] D. Pressman, D. H. Brown and L. Pauling, THIS JOURNAL, **64**, 3015 (1942).

concentration of arsonic acid in all its forms at the half neutralization point, and $(H^+)m$ is the observed hydrogen ion concentration at that point.

Where two ionization constants are close together, as in *p*-hydroxy- and *p*-carboxyphenylarsonic acids, the method of Simms[2] was used.

There probably is an appreciable salt effect on the doubly charged ions; this was dealt with only by keeping concentrations the same for the various acids. Of course this effect is probably very large in the two cases where triply charged ions were used. The constants are listed in Table I.

TABLE I

FIRST AND SECOND IONIZATION CONSTANTS OF THE ARSONIC ACID GROUP IN PHENYLARSONIC ACIDS IN WATER AT 22°

Arsonic acid	$K_1 \times 10^4$ ±15%	$K_2 \times 10^9$ ±15%	$\sigma\rho_1$	$\sigma\rho_2$	$\sigma\rho$ Benzoic acids[l]	$\sigma\rho$ Phenylboric acids[e, 28]	Method of preparation, references
Phenyl	3.4	3.3			[21]		3
α-Naphthyl	2.2	2.2	−0.19	−0.18	+0.50[22]	−0.35	4
β-Naphthyl	[a]	3.4		+ .01	+ .03[22]	+ .12	5
o-Methylphenyl	1.5	1.4	− .36	− .37	+ .29[23]	− .89	6
m-Methylphenyl	1.5	1.5	− .37	− .34	− .07[24]	− .15	7
p-Methylphenyl	2.0[b]	2.1	− .24	− .20	− .17[24]	− .29	8
o-Nitrophenyl	4.3	2.9	+ .10	− .06	+2.03[23]	+ .45	9
m-Nitrophenyl	13.9	15.9	+ .61	+ .68	+0.71[24]	+1.54	10
p-Nitrophenyl	12.7[c]	15.9	+ .57	+ .68	+ .78[24]	+1.70	8
4-Nitro-1-naphthyl	[a]	13.5		+ .61			11
o-Aminophenyl	~100[d]	2.2		− .18[m]	− .80[25, m]	−0.36	14
m-Aminophenyl	~100[d]	2.4		− .14[m]	− .10[28]	+ .05	14
p-Aminophenyl	~100[d, e]	1.2		− .44[m]	− .72[25, m]	− .31	15
4-Amino-1-naphthyl	[a]	0.67		− .69			14
p-Chlorophenyl	4.7[f]	5.6	+ .14	+ .23	+ .22[23]	+ .50	12
p-Bromophenyl	5.6	6.5	+ .22	+ .29	+ .23[23]	+ .58	12
p-Iodophenyl	[a]	5.7		+ .24	+ .28[j, 26]		13
p-Hydroxyphenyl[h]	1.3[g]	0.09	− .42	−1.56	− .34[27]		16, 17
p-Carboxyphenyl[i]	14.0	3.6	+ .61	+0.04	+ .61(K_1)[j, k, 26] − .50(K_2)[j, k]	− .01	18

[a] Free acid precipitated. [b] Value of 1.9×10^{-4} by Erlenmeyer and Willi[19] at 18° and 1.7×10^{-4} by Breyer[20] at 18°. [c] Value of 9.1×10^{-4} by E. and W.,[19] and 8.3×10^{-4} by B.[20] [d] This value is only approximate since it was not accurately measured in the dilutions used. The values for the ionization constants of the anilinium ions $NH_3^+C_6H_4AsO_3H^-$ in the reaction, $NH_3^+C_6H_4AsO_3H^- \rightleftharpoons NH_2C_6H_4AsO_3H^- + H^+$, are 1.7, 0.9, and 0.9×10^{-4}, respectively, for ortho, meta and para compounds.[m] [e] Value of 1.0×10^{-4} by E. and W.,[19] and 0.44×10^{-4} by B.[20] [f] Value of 3.2×10^{-4} by E. and W.[19] [g] Value of 0.87×10^{-4} by B.[20] [h] Constant for phenol group is 4.3×10^{-9}. [i] Constant for carboxy group is 6.0×10^{-5}. [j] Determined in 50% methyl alcohol. [k] An entropy factor of two has been introduced. [l] All but amino acids were determined in 25% ethyl alcohol. [m] Correction not made for closeness of first and second dissociation constants. These values are not corrected for the tautomerism between amino acid and zwitter ion forms.

Discussion

For each substituent there is tabulated (Table I) the value of the product $\sigma\rho$ as defined by Hammett[29] according to Equation 2

$$\sigma\rho = \log K - \log K_0 \qquad (2)$$

where K_0 and K are the dissociation constants of the unsubstituted and substituted acids, respec-

---

(2) H. S. Simms, THIS JOURNAL, **48**, 1239 (1926).

(3) "Organic Syntheses," Vol. XV, J. Wiley and Sons, Inc., New York, N. Y., 1935, p. 59.

(4) A. E. Hill and A. K. Balls, THIS JOURNAL, **44**, 2051 (1922).

(5) H. P. Brown, *Trans. Kans. Acad. Sci.*, **42**, 209 (1939).

(6) P. Karrer, *Ber.*, **48**, 310 (1915).

(7) A. Michaelis, *Ann.*, **320**, 328 (1902).

(8) H. Bart, German Patent 250,264.

(9) J. R. Johnson, THIS JOURNAL, **45**, 1311 (1923).

(10) A. Michaelis, *Ann.*, **320**, 294 (1902).

(11) C. R. Saunders and C. S. Hamilton, THIS JOURNAL, **54**, 636 (1932).

(12) Mouneyrat, English Patent 142,947 (1919).

(13) F. Blumenthal and F. Herschman, *Chem. Zentr.*, **79**, **II**, 1618 (1908).

(14) W. A. Jacobs and M. Heidelberger, THIS JOURNAL, **40**, 1580 (1918).

(15) "Organic Syntheses," Coll. Vol. I, J. Wiley and Sons, Inc., New York, N. Y., 1932, p. 63.

(16) W. A. Jacobs and M. Heidelberger, THIS JOURNAL, **41**, 1440 (1919).

(17) W. G. Christiansen and A. J. Norton, *ibid.*, **45**, 2188 (1923).

(18) W. L. Lewis and H. C. Cheetham, *ibid.*, **43**, 2117 (1921).

(19) H. Erlenmeyer and E. Willi, *Helv. chim. acta*, **18**, 733 (1935).

(20) B. Breyer, *Ber.*, **71B**, 163 (1938).

(21) J. F. J. Dippy and F. R. Williams, *J. Chem. Soc.*, 1888 (1934).

(22) Bethmann, *Z. physik. Chem.*, **5**, 399 (1890).

(23) J. F. J. Dippy and R. H. Lewis, *J. Chem. Soc.*, 1426 (1937).

(24) J. F. J. Dippy and R. H. Lewis, *ibid.*, 644 (1936).

(25) J. Walker, *Z. physik. Chem.*, **51**, 709 (1905).

(26) R. Kuhn and A. Wasserman, *Helv. chim. acta*, **11**, 3, 31, 44 (1928).

(27) G. E. K. Branch and D. L. Yabroff, THIS JOURNAL, **56**, 2568 (1934).

(28) G. E. K. Branch, *et al.*, *ibid.*, **56**, 937, 1850, 1865 (1934); *J. Org. Chem.*, **2**, 522 (1938).

(29) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, Chapter VII.

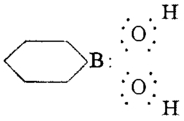
tively, ρ is the reaction constant which depends on the type of aromatic acid and σ is the substitution constant which depends only on the substituent and is independent of the type of acid. For comparison there are also listed the $\sigma\rho$ values for substituents on benzoic acid and phenylboric acid.

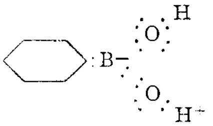
It is interesting that the value of $\sigma\rho$ for each substituent is very nearly the same for the first and second ionization constants. This shows that ρ is the same for the first ionization and second ionization.

The substitution constant has most significance for substituents in the meta and para positions. The agreement between the values of $\sigma\rho$ for substituents on the arsonic acids and benzoic acids is quite good, showing that ρ is the same for both series, for β-naphthyl, *p*-methyl, *m*- and *p*-nitro, *p*-halogen and *m*-amino.[30] The value for *m*-methyl is low compared to that for benzoic acid. $\sigma\rho$ for the *p*-carboxy group on phenylarsonic acid (K_1) compares well with the $\sigma\rho$ value in the benzoic acid series

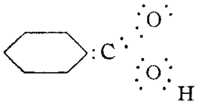
The effect of the *p*-carboxylate ion on the second dissociation constant of phenylarsonic acid compares well with the effect in phenylboric acid. This effect may not be real since the activity of the triply charged ion is probably quite affected by salt concentration.

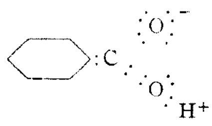
The fact that ρ is greater for phenylboric acid than benzoic acid[31] is due to the fact that the resonance brings the charge on which the



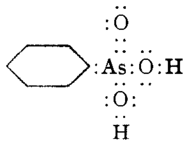


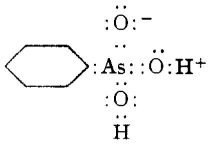
acidity depends closer to the ring where it can be affected by substitution than does the primary acidic resonance of benzoic acid



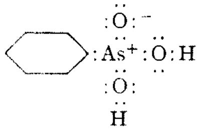


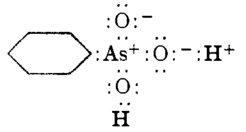
Since ρ for phenylarsonic acid is similar to that for benzoic acid, the acidic resonance of phenylarsonic acid is apparently





which is similar to that for benzoic acid while the contribution of the forms





appears small since these would place a charge the arsenic atom and the value of ρ would be like that for phenylboric acid. It is interesting that in the two important resonance forms arsenic has five electron pairs.

The *o*-nitro- and *o*-methylphenylarsonic acids resemble the corresponding phenylboric acids rather than the benzoic acids in that the dissociation constants are less for the ortho substituted acid than for the para substituted acids.[32]

The first ionization constants of the arsonic acid groups in the positive anilinium ions of the arsanilic acids $H_3N^+C_6H_4AsO_3H_2$ are high, about 10^{-2}, presumably because of the presence of the positive charge. The ionization constants of the anilinium ions $H_3N^+C_6H_4AsO_3H^-$, corresponding to conversion to $H_2NC_6H_4AsO_3H^-$, are several times that for the anilinium ion,[28] $K_A = 2 \times 10^{-5}$, although the negative charge present would be expected to cause a decrease in the value.

In the case of *p*-hydroxyphenylarsonic acid, uncertainty exists as to which of values 4.3×10^{-9} and 0.9×10^{-10} to ascribe to the ionization of the hydroxy group and to the second ionization of the arsonic acid. The value 4.3×10^{-9} gives $\sigma\rho_2$ a value of $+0.11$ which appears too large compared to the value of $\sigma\rho_1$, -0.42, since we have found in the other cases that $\sigma\rho_1$ and $\sigma\rho_2$ are practically equivalent for the effect of any one substituent. As shown above, the group AsO_3H^- increases the ionization of the anilinium ion and the same should be the case for the hydroxy

---

(30) The referee has pointed out that in the case of the ionization of *m*-aminobenzoic acid the value of -0.10 for $\sigma\rho$, corrected for tautomerism, which was obtained by Branch and Calvin[28] from the data of Cummings, compares well with our uncorrected value of -0.14 for *m*-aminophenylarsonic acid and thus suggests that the contribution of the tautomer, $H_3N^+C_6H_4AsO_3^-$, is negligible. The corrected value of $+0.08$ obtained by Branch and Calvin[28] for *m*-aminobenzoic acid would indicate, however, that the tautomer above would not be negligible, which is doubtful.

(31) G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, Chapter VI.

(32) The difference between the effects of the methyl group in the ortho and para positions is relatively small. The difference in the case of the nitro group is larger and may be due to an ortho effect (a) by hydrogen bonding of the arsonic acid group with the nitro group; or (b) by the coördination of a nitro oxygen atom with the arsenic atom, an explanation which has already been extended to *o*-nitrophenylboric acid[23]; or (c) by the steric effect of the arsonic acid group turning the nitro group from the plane of the benzene ring and thus inhibiting resonance.

group. The increase would be expected to be less than by a factor of 5 (as with anilinium ion[31]) but appears to be by a factor of forty if the constant 4.3×10^{-9} is attributed to the hydroxy group. The ionization constant of phenol[33] is 1.1×10^{-10}. This large increase may be due to salt effects on the doubly charged ion. The value of $\sigma\rho_2$ for the arsonic acid group is then -1.6 but this is due to the O$^-$ group rather than the hydroxy group. It would be expected that the O$^-$ group would decrease the ionization of the arsonic acid much more than do the hydroxy or carboxylate groups.

It is quite interesting that the group AsO$_3$H$^-$ para to a carboxy group has hardly any effect on the ionization of the carboxy group: the ionization constant of benzoic acid[21] is 6.3×10^{-5}.

The effects of a nitro or an amino group in the 4-position on the dissociation constants of α-naphthylarsonic acid are the same as for phenylarsonic acid.

This investigation was carried out with the aid of a grant from The Rockefeller Foundation. We wish to thank Dr. Linus Pauling with whom we had several helpful discussions.

Summary

An investigation was made of the first and second ionization constants of nineteen substituted phenylarsonic acids in water at 22°. It was observed that in general a given substituent changes the first and second ionization constants by the same factor. In the case of a substituent in the meta and para positions the effect is similar to that for benzoic acid and in the ortho position to that for phenylboric acid.

Received October 13, 1942

---

(33) J. Kendall, This Journal, **39**, 7 (1917).

[Contribution from the Converse Memorial Laboratory of Harvard University]

The Ester Groups in Polystyrene Made with Chloro- and Bromobenzoyl Peroxides

By Paul D. Bartlett and Saul G. Cohen[1]

There is good evidence that the polymerization of an olefinic monomer catalyzed by an acyl peroxide is neither "polymerization" nor "catalysis" in the narrow meanings of these terms. It involves the attachment of fragments from the peroxide to the double bond of the monomer with the emergence of a free radical which propagates the chain reaction by successive additions of the monomer. Although this proposition has been much debated, it yields the only satisfactory interpretation of the kinetics of polymerization.[2] There is little evidence to date as to the nature of the terminal groups which must be present in polymers prepared by acyl peroxides if this mechanism is correct. Kamenskaja and Medwedew point out that the breakdown of benzoyl peroxide can lead to both benzoate and phenyl radicals, either one of which might initiate the polymerization. They quote an unpublished observation indicating that there are benzoate fragments in polystyrene. Schulz and Husemann[3] concluded that with polystyrene of molecular weights in the usual range, the concentration of terminal groups would be so small as to escape detection readily. Price, Kell, and Krebs,[4] however, showed that a dilute solution of styrene in benzene could be polymerized at the boiling point by a relatively large amount of *p*-bromobenzoyl peroxide to a low-molecular-weight polymer containing 5.72% of bromine permanently bound.

We have utilized these conditions and have shown by suitable methods of hydrolysis that the greater part (53–64%) of the halogen permanently bound to the polymer is in the form of *p*-bromobenzoate groups, while the rest of it is evidently in the form of *p*-bromophenyl groups which cannot be removed by saponification. This substantiates the original suggestion of Kamenskaja and Medwedew and also the findings of Price and co-workers[4] to the extent that catalyst fragments are incorporated in the structure of the polymer. However, the latter authors concluded that their polystyrene contained no ester groups, since (a) the analysis for carbon, hydrogen, and halogen left no room for oxygen, and (b) boiling with 20% aqueous potassium hydroxide effected no saponification. In com-

---

(1) Pittsburgh Plate Glass Fellow.

(2) Kamenskaja and Medwedew, *Acta Physicochim. U. R. S. S.*, **13**, 565 (1940).

(3) Schulz and Husemann, *Z. physik. Chem.*, **B39**, 246 (1938).

(4) Price, Kell and Krebs, This Journal, **64**, 1103 (1942).