chloropropyl)-4-phenylpiperazine was added. Heating was resumed and the temperature was kept at 100–110° for 3 hr. After the mixture had cooled to 60°, it was poured, with stirring, into 600 ml. of ice and water. The solid was filtered, triturated with 100 ml. of water, and then dried under vacuum. Recrystallization from ethanol yielded 11.9 g. (32%) of the product, m.p. 130.5–131.5°.

The lithium amide was obtained from the Lithium Corp. of America and the trimethylene chlorobromide from the Dow Chemical Co. The amines were purchased from the Fisher Scientific Co. and were used without further purification.

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The pK_a's of Aromatic Sulfinic Acids[1]

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Received July 25, 1958

The pK_a's of six aromatic sulfinic acids have been determined by means of potentiometric titration and found to be in the vicinity of 1.8 to 2.0.

During the course of research in the laboratory of the first author, the occasion arose to determine the neutral equivalent of *p*-nitrobenzenesulfinic acid.[3] The results from this determination not only yielded the desired neutral equivalent but also indicated that the acidic group being titrated was weaker than benzenesulfinic acid.[4–7] This observation suggested that the ionization constants of aromatic sulfinic acids be reinvestigated and accordingly such a program was undertaken.

Six aromatic sulfinic acids were selected for this study: benzene-, *p*-toluene-, *p*-chlorobenzene-, *p*-bromobenzene, *m*- and *p*-nitrobenzenesulfinic acids. Each of these was prepared from the corresponding sulfonyl chloride by reduction. The identity and purity of each compound was established by means of melting point and neutral equivalent determinations (Table I).

TABLE I

MELTING POINTS AND NEUTRAL EQUIVALENTS OF SULFINIC ACIDS

Sulfinic Acid	M.P., °C. Obsd.	M.P., °C. Lit.	Neut. Equiv. Obsd.	Neut. Equiv. Theor.
Benzene	81.5–83	84[7] 85[8,9]	144.6	142.2
p-Toluene	84–85	84[10] 84–85[11] 86–87[8,9,12]	160.1	156.2
p-Chlorobenzene	98.5–99.5	93–94[13] 98–99[10] 99[14] 100–102[15]	179.7	176.7
p-Bromobenzene	113–114	114[10] 114–115[13] 115[16]	229.8	221.1
m-Nitrobenzene	94.5–96	95–96[17] 98[18]	190.4	187.2
p-Nitrobenzene	s. 125 m. 152–154	s. 136[19,20] m. 159[19] 160[20] 120[21,22]	195.5	187.2

(1) Supported in part by the Faculty Research Fund, Kansas State University and National Science Foundation Grant No. P-2670.

As a means of comparing the values obtained for benzenesulfinic acid with the values reported earlier in the literature two methods of sample preparation (A and B) were used. In method A the samples were dried *in vacuo* prior to use, while in method B the samples were used immediately after preparation. The pK_a's and other data related to the potentiometric titrations are given in Table II.

With the exception of the value of 1.29 which Rumpf and Sadet report[7] for benzesulfinic acid there is reasonable agreement among the values reported in Table II and the earlier literature. Loven, for example, has reported that the dissociation

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(3) Unpublished data taken by Harry A. Smith, deceased.

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TABLE II

pK_a'S FOR SULFINIC ACIDS (25°)

Sulfinic Acid	Method of Sample Prep.	No. of Titrations	Mean pK_a (Corr.)	Ave. Dev.
Benzene	A	2	1.84	0.07
	B	2	2.16	0.05
p-Toluene	A	2	1.99	0.04
p-Bromobenzene	A	2	1.89	0.09
p-Chlorobenzene	A	2	1.81	0.01
m-Nitrobenzene	A	3	1.88	0.07
p-Nitrobenzene	A	5	1.86	0.08

constants for benzene- and *p*-toluenesulfinic acids are 3.5×10^{-2} and 2.5×10^{-2}, respectively.[4] Coats and Gibson have recalulated Loven's data to obtain very similar values and have also reported that the dissociation constant for *o*-toluenesulfinic acid is near 3.4×10^{-2}.[5] Fieser and Fieser state that the pK_a for benzenesulfinic acid is 1.80.[6]

It should be pointed out that two methods have been used for the determinations reported previously in the literature. Loven (and presumably Coats and Gibson) performed conductance experiments on freshly prepared samples of sulfinic acids. Rumpf and Sadet, in contrast, performed potentiometric titrations on dried samples of benzenesulfinic acid and its sodium salt. Since this latter method was also used by the authors of this paper it is quite surprising to find such great disagreement. The reasons for this are not apparent. However, from the brief description of the experimental procedure employed by Rumpf and Sadet it seems likely that there could have been appreciable differences between the two titration procedures.

A likely source of error in either type of measurement arises from the instability of sulfinic acids. Due to oxidation varying amounts of sulfonic acid might contaminate a solution of sulfinic acid. Loven used freshly prepared samples of sulfinic acid in order to minimize this source of error. Rumpf and Sadet, on the other hand, used dried samples. In this paper both types of samples were used in the case of benzenesulfinic acid and it was found that the pK_a for the freshly prepared acid was slightly higher than for the dried acid. This difference could have been caused by oxidation of the sulfinic acid during drying and suggests that the true pK_a's for sulfinic acids are probably higher than reported.

EXPERIMENTAL

Preparation of sulfinic acids. Each sulfinic acid was prepared from the corresponding sulfonyl chloride by zinc or sodium sulfite reduction.[23-26]

Sample preparation and titration. Two methods of sample preparation (A and B) were used. In method A the sample of sulfinic acid was dried *in vacuo* over Drierite after recrystallization. Then a weighed, dry sample of acid was added to water, heated briefly on a steam cone to affect solution, cooled, and made up to volume. Aliquots of this solution were then titrated with standardized sodium hydroxide by use of a microburet and a Model H-2 Beckman *p*H meter.

Method B was patterned after that of Loven in that the acid was isolated and then recrystallized once from boiling water as rapidly as possible. An unweighed, wet sample of the acid was then placed in a titration vessel containing a known volume of water and titrated with standardized NaOH by use of a microburet and a Model G Beckman *p*H meter equipped with external electrodes.

In both methods the water which was used had previously been boiled and gassed with nitrogen during cooling. Also in both cases nitrogen was bubbled through each titration vessel during titration in order to exclude oxygen and affect stirring. The temperature of each titration vessel was maintained at 25° by use of a constant temperature bath. Each *p*H meter was standardized before use by checking against buffers of known *p*H. The author who used method A determined the end point of each titration by the parallelogram method. The authors who used method B determined each end point by plotting $\Delta p\mathrm{H}/\Delta \mathrm{V}$ versus V.

Evaluation of pK_a. The calculation of the pK_a for each acid was achieved by the use of an IBM 650 computer. A program was devised[27] by which the data for each experimental point (up to the equivalence point) of a titration curve could be fed into the computer and from these data calculate a pK_a for each experimental point and a mean pK_a for each titration. The equations which the computer solved are derived below.

A solution of an acid (HA) when being titrated contains at at any point i (up to the equivalence point) the species H^+, A^-, and HA whose concentrations at point i can be expressed as follows: $[H^+]_i$ equals the concentration of the hydrogen ion due to ionization of the untitrated acid; the total concentration of A^- equals that formed by titration, $[A^-]_i$, plus that formed by ionization of the untitrated acid, $[H^+]_i$; the total concentration of HA equals the untitrated acid, $[HA]_i$, minus that lost due to ionization, $[H^+]_i$. Thus at any point i on a titration curve the ionization constant for HA (using concentration terms) can be given by Equation 1.

$$k_i = \frac{[H^+]_i \{[A^-]_i + [H^+]_i\}}{[HA]_i - [H^+]_i} \qquad (1)$$

Each of the quantities in Equation 1 can be expressed in terms of data taken during titration:

$$[H^+]_i = 10^{-x_i}$$

$$[A^-]_i = \frac{V_i N}{V_0 + V_i}$$

$$[HA]_i = \frac{(V_f - V_i)N}{V_0 + V_i}$$

where x_i is the *p*H at point i, N is the normality of the base used to titrate HA, V_0 is the volume of water used to dissolve the sample of sulfinic acid, V_i is the volume of base added up to point i, and V_f is the volume of base needed to reach the equivalence point.

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Making these substitutions into Equation 1, one can obtain Equation 2 from which k_i can be calculated at point i on the titration curve (up to the equivalence point).

$$k_i = \frac{10^{-x_i}\left\{\frac{V_iN}{V_o + V_i} + 10^{-x_i}\right\}}{\frac{(V_f - V_i)N}{V_o + V_i} - 10^{-x_i}} \qquad (2)$$

While Equation 2 corrects for the ionization of the untitrated acid and the volume change at each point on the titration curve, it does not correct for ionic strength. Accordingly, a correction term was then derived from the limiting equation of Debye and Huckel for the mean activity coefficients of strong electrolytes. The use of this limiting equation was considered valid since the ionic strengths involved were all in the vicinity of 0.01.

The correction which should be applied to any experimental pK_i is equal to $-2 \log f_i$ where f_i is the mean activity coefficient at point i. At 25° this correction is equal to $1.011 (u_i)^{\frac{1}{2}}$, where u_i is the ionic strength at that point and is given by the equation

$$u_i = \frac{1}{2}\{[H^+]_i + [A^-]_i + [Na^+]_i\}$$

Using the symbols introduced above, u_i can be expressed by Equation 3.

$$u_i = \left\{10^{-x_i} + \frac{V_iN}{V_o + V_i}\right\} \qquad (3)$$

Thus by use of Equations 2 and 3 it is possible to calculate a corrected pK_a for each point on the titration curve (up to the equivalence point) and hence a mean corrected pK_a for each titration.

Calculation by computer was deemed necessary since the denominator of Equation 1 may become very small because the solubilities of the sulfinic acids are limited and their extends of ionization are appreciable. With the aid of the computer, the pK_a's were conveniently calculated from a sufficient number of points to permit statistical treatment.

It should further be pointed out that near the equivalence point the first term in the denominator of Equation 2 becomes very small. Experimental data on the steeply rising portion of the titration curve close to the end point were generally found to be less reliable than those on the more horizontal portion. Accordingly, experimental points in this region were not analyzed by the computer. The number of experimental points analyzed in each titration averaged 22, but ranged from a low of 12 to a high of 58 depending on the sample size and the experimentor.

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Polyol Complexes and Structure of the Benzeneboronate Ion

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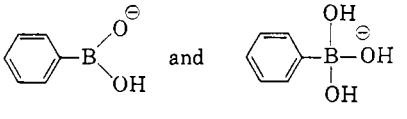
Received September 11, 1958

The complexing equilibria of aqueous benzeneboronate ion with several polyols have been studied and the measured constants compared with those of borate. The results indicate that the anion has the formula $C_6H_5B(OH)_3^-$ with tetrahedral coordination about boron; this is consistent with a steric effect, previously cited, on the acid-base equilibria of *ortho* substituted benzeneboronic acids. Examination of the data on complexing equilibria requires modification of an earlier assumption that only anionic complexes are formed.

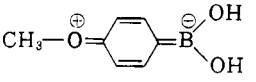
Following the recent elucidation of the structure of the borate ion in aqueous medium,[2] a study of the structure of aqueous benzeneboronate has been made, using quite different methods. Borate was previously thought to be either a trigonal Brönsted base form, $H_2BO_3^-$, or a tetrahedral Lewis acid-base adduct, $B(OH)_4^-$. The present case, likewise, offered a choice between



for the anion of benzeneboronic acid, $C_6H_5B(OH)_2$. The borate ion was studied by infrared and Raman spectroscopy, its behavior being found analogous to fluoborate, BF_4^-, because of the symmetry about boron. Such evidence was believed inapplicable to benzeneboronate because of the loss of symmetry and larger number of spectral bands.

Three different methods of attack were, however, available. The first two will be mentioned briefly, since the first proved inconclusive and the second has been previously cited. It was the third method for which complexing equilibria were experimentally studied.

Method A consisted of comparing *meta* and *para* substituted benzeneboronic acids[3] with benzoic acids[4] through their acid dissociation constants, using a plot of pK_a for $X\text{-}C_6H_4B(OH)_2$ *vs.* Hammett's σ values. It was thought that, if the tetrahedral form prdeominated, a curvature might be observed at negative values because of the presence of a resonance form,



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