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ULTRAVIOLET SPECTRA AND DISSOCIATION CONSTANTS OF *p*-HYDROXYBENZOIC ACID, METHYL, ETHYL, *n*-BUTYL, AND BENZYL *p*-HYDROXYBENZOATE AND POTASSIUM *p*-PHENOLSULFONATE

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ABSTRACT

The apparent first and second dissociation constants of *p*-hydroxybenzoic acid, the constants for the phenol group of methyl, ethyl, *n*-butyl, and benzyl *p*-hydroxybenzoate, and potassium *p*-phenolsulfonate have been determined from ultraviolet spectral data. The compounds have wide absorption bands located in the region of 200 to 400 mμ, and the differences between the transmittancy curves for their ionic and molecular forms are great enough to permit the measurement of several intermediate steps in the transformation at various pH values. The buffers used to control the dissociation were acetates, phosphates, and borates, all of low ionic strengths. Esterification of the carboxyl group of *p*-hydroxybenzoic acid apparently increases the dissociation of the phenol, and pK* decreases from 9.3 for the second dissociation of the acid to 8.3 for the esters. The thermodynamic dissociation constants are estimated.

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I. INTRODUCTION

The dissociation constants of many organic compounds have been determined by electromotive-force and conductivity methods. The

constants of several indicators have also been calculated from spectrophotometric measurements, by the use of quantitative changes in color in the visible part of the spectrum, corresponding to known changes in hydrogen-ion concentration of the indicator solutions.

Colorless compounds transmit light completely in the visible region of the spectrum but have absorption bands in the ultraviolet, the positions of which have been reported by various investigators. Most of the published data were obtained by spectrographic methods, which involve density measurements of photographic plates. The experimental errors of such determinations are acknowledged to be large. In a recent spectrophotometric study of a buffer compound [1] [1] it was shown that measurements in the ultraviolet from 200 to 400 mμ can be obtained by means of a photoelectric spectrophotometer [2] with sufficient accuracy to calculate the dissociation constant. The behavior of *p*-phenolsulfonic acid, its primary potassium salt, and its secondary potassium-sodium salt was illustrated by the spectral data. The change in the absorption index with variation in the hydrogen-ion concentration was of the same order of magnitude as encountered with indicators in the visible portion of the spectrum. By employing other buffers, such as phosphates and borates, whose absorption bands are not in the same region of the spectrum, the degree of transformation was controlled and measured quantitatively.

In many cases the use of ultraviolet spectrophotometry in the study of electrolytic solutions possesses decided advantages. One may obtain the limiting curves for the ionic or the molecular form of a compound in acid, in alkali, or in buffers of known pH, and thus shed light upon the behavior of the molecule. A large number of organic and inorganic compounds have been investigated by this means, and transmittancy curves have been obtained for various concentrations in water, hydrochloric acid, sodium hydroxide, and in buffers.

The spectrophotometric method is the only known means of determining the dissociation constants of many difficultly soluble compounds whose saturated solutions have concentrations less than approximately 10^{-3} molar.[2] For the more soluble compounds, the electromotive-force and conductance methods may often be supplemented advantageously by the spectrophotometric study and a measurement of the concentrations of the ion and mole forms obtained.

The data presented in this paper illustrate the application of the method to calculations of the first and second dissociation constants of *p*-hydroxybenzoic acid and of the dissociation constant of the phenol group of methyl, ethyl, *n*-butyl, and benzyl *p*-hydroxybenzoate, and potassium *p*-phenolsulfonate. The dissociation of the two groups of *p*-phenolsulfonic acid has also been recently studied by electromotive-force methods [3, 4]. The esters of *p*-hydroxybenzoic acid are representative of compounds difficulty soluble in water. Their dissociation constants have not been reported by any one of the three methods mentioned above. Several of the substituted benzoic acids have been studied and reported [5]. The value of the spectrophotometric method is well illustrated by the data for *p*-hydroxybenzoic acid, where the two steps in the dissociation can be differentiated by a study of the spectral transmittancies.

[1] Figures in brackets indicate literature references at the end of this paper.
[2] The symbol *M* will hereafter be used to designate "molar."

II. MATERIALS

The compounds investigated were obtained from commercial firms, and were further purified in some cases when the melting points and spectrophotometric curves indicated the presence of impurities. Before use, the white crystalline compounds were dried to constant weight in a vacuum oven at about 3- to 5-mm pressure and at temperatures ranging from 30° to 60° C.

The *p*-hydroxybenzoic acid, after two recrystallizations from distilled water, had a melting point of 211° to 213° C. The methyl and ethyl *p*-hydroxybenzoate were used without further purification. Their melting points were 125° to 126° C and 115.5° to 116° C, respectively. The *n*-butyl and benzyl *p*-hydroxybenzoate were each recrystallized once from water, and their melting points were 70° and 112° C, respectively. The potassium *p*-phenolsulfonate was purified by several recrystallizations from water. Its purity was found to be 100.03 percent by bromometric assay, as described in an earlier publication [1]. The solubilities of the different compounds were not determined.

The phosphate buffers were prepared from disodium hydrogen phosphate and sodium dihydrogen phosphate of known purity [6]. The borate buffers [7] were prepared from recrystallized boric acid, recrystallized borax, and 0.1-*M* sodium hydroxide, prepared free from carbonate. The acetate buffers were prepared from reagent-grade acetic acid and sodium hydroxide. Solutions of hydrochloric acid were prepared by dilution of material of reagent grade.

III. EQUIPMENT

1. SPECTROPHOTOMETRIC EQUIPMENT

All the spectrophotometric measurements were made over a spectral range of 200 to 400 mμ with a quartz photoelectric spectrophotometer [2]. The cell compartment was remodeled so that absorption cells previously constructed for indicator studies [8] could be used. The cells consisted of Pyrex tubing, 3.8 cm in diameter and 1-, 2-, and 5-cm in length. The ends were polished and fitted with removable quartz plates. Cells and end plates were held tightly together by metal holders. For the measurement of the transmittancies of solutions, two absorption cells of the same length were used. One contained the solvent alone and the other contained the compound under investigation, dissolved in the solvent. A special slide in the cell compartment of the spectrophotometer permitted movement of the cells into positions axial with the light beam.

Balance of the spectrophotometer was accomplished by adjusting the slit-width for the entrance and exit of the light beam, with the solvent cell in the beam. This setting corresponded to a transmission reading of 100 percent. The slit-width was small (less than 1 mm) for most wavelengths, and changes in slit-width caused no appreciable error in the values for the wide absorption bands characteristic of these solutions. When a balance of the needle was obtained for the solvent cell, the other cell was moved to the same position in the beam, and a measurement of the transmittancy of the unknown compound was made. Inasmuch as the absorptions of the four crystalline quartz end plates differed slightly at the lower wavelengths, the pair showing the least absorption was always used for the solvent cell.

All the equipment was used in a room maintained at 25° C. In order to eliminate a rise in temperature of the solutions because of the proximity of the light source, the cell compartment of the spectrophotometer was fitted with an inlet and an outlet tube, through which a slow stream of air was drawn from the constant-temperature room. The temperature of the solutions thus remained at 25° to 26° C. For some of the measurements, an especially designed water-jacketed hydrogen arc [3] was used. This source of light was sufficiently intense for use at wavelengths as low as 200 mμ.

2. ELECTROMETRIC EQUIPMENT

The pH measurements were made at 25° C with commercial glass-electrode assemblies. The pH meter was calibrated with a 0.05-*M* solution of potassium acid phthalate, the pH of which is 4.008 at 25° C [9]. Frequent checks were made with a phosphate buffer, pH 7.01, and a borax buffer, pH 9.18. These standard pH values were computed on the activity basis, and the measured pH is therefore assumed to represent the negative of the logarithm of the activity of hydrogen ion. Although most of the buffers used in this work had ionic strengths less than 0.05, a few experiments were made with additional phthalate buffers of 0.01-, 0.02-, and 0.10-*M* concentrations. The glass-electrode readings agreed with the calculated values [9] within the error of the instrument (0.01 pH unit). The readings are considered to be reasonably free from errors which might be attributed to liquid-junction potentials and are believed to be correct within ±0.02 pH unit.

IV. EXPERIMENTAL PROCEDURE

1. PROVISIONAL TRANSMITTANCY MEASUREMENTS

The procedure found to be the most useful was to measure first the absorption of a 10^{-2}-*M* aqueous solution of the compound with the 1-cm absorption cells. This measurement served to locate the "cutoff" position of the band nearest the visible region, in which the transmittancies varied from 0 to 100 percent within a wavelength range of about 10 to 20 mμ. For difficultly soluble compounds, it was necessary to use lower concentrations and longer absorption cells. When concentrations as low as 10^{-4} to 10^{-5} *M* were used, all bands were usually located by a series of dilutions in approximately tenfold steps.

The limiting spectral curves that represent the ionic and molecular forms of the compound were next determined by employing buffers that covered a wide pH range, or a 0.1-*M* solution of strong acid and a 10^{-3}-*M* solution of strong alkali. When the absorption bands remained unchanged over a considerable range of pH (1 or more units), it was assumed that the spectral curves were those of the limiting forms. A few additional experiments at intermediate pH values resulted in a set of intersecting curves that gave a rough spectral pattern of the behavior of the compound. From the transmittancy values at a given wavelength, calculations of the amount of the molecular form transformed to the ionic form, or vice versa, were made, and these values were plotted as a function of pH. From these data, the pH steps and corresponding buffers to cover the range were

[3] Made by Austin G. Nester, Swarthmore, Pa.

selected. The solutions required to obtain the necessary spectrophotometric curves were then prepared.

2. SELECTION OF BUFFERS

The selection of buffers for spectrophotometric work in the ultraviolet presents a more complicated problem than does the choice of buffers suitable for the visible region. Not only must a wider pH range be covered, which usually requires more than one buffering system, but the choice is limited to buffers whose absorption bands do not lie in the same spectral region as the bands of the compounds under study. The "cutoff" positions of many buffer compounds of about 0.01-*M* concentration have already been determined in 1-cm absorption cells.[4]

In order to prevent distortion of the spectrophotometric curves by specific salt errors, it is desirable to keep the ionic strength of each buffer as low as possible, without sacrifice of buffering capacity. In earlier published work on the acid range of metacresolsulfonphthalein in the visible region [8], it was shown that the intermediate and complete transformation of this indicator could be accomplished simply by the use of solutions of hydrochloric acid of concentrations ranging from about 10^{-3} to 2 *M*. Provisional measurements of several other indicators in the visible and in the ultraviolet have now been obtained by use of phthalates, benzoates, citrates, phosphates, and phenolsulfonates, in addition to hydrochloric acid and sodium or potassium hydroxide. With buffers of ionic strength of about 0.01, transmittancy measurements may be made above 220 mμ with the acetates, above 230 mμ with the citrates, and above 280 to 300 mμ with the benzoates, phenolsulfonates, and phthalates. Hydrochloric acid in concentrations up to 2 *M* satisfactorily transmits wavelengths greater than 200 mμ. The phosphates and borates of low ionic strengths transmit at wavelengths longer than 205 mμ. Sodium and potassium hydroxide transmit above about 215 mμ. The lower limit depends upon the concentration of the hydroxyl ion. There was considerable evidence of adverse influence of phosphate buffers on the transmittancies of potassium phenolsulfonate in the ultraviolet and of metacresolsulfonphthalein in the visible. Other buffers such as the acetates or borates may also have some specific effect and should be studied. The poor isosbestic points in many of the series of curves for the transformation of indicators may be attributable to the use of buffers of high ionic strengths.

3. GENERAL PROCEDURE

The solutions were prepared at 25° C in a constant-temperature room by volumetric methods. For both the spectrophotometric and the pH measurements, 100 ml of each solution was sufficient. It was convenient to use 10 ml of stock solution of the compound under investigation with 90 ml of buffer. For the comparison solution, 10 ml of water and 90 ml of buffer were used.

Before a series of spectrophotometric measurements was started, the two pairs of end plates were carefully cleaned, the cells assembled and filled with water, and a calibration was made over the spectral range to be covered. This was accomplished by measuring the transmission of the solution cell against the transmission of the sol-

[4] Unpublished work of E. E. Sager, M. R. Schooley, A. S. Carr, and S. F. Acree. A preliminary report appeared in the March 1944 issue of the NBS Technical News Bulletin.

vent cell, which was set at 100 percent. Any differences may be attributed to differences in absorption of the pairs of end plates. As there were differences at the shorter wavelengths in the crystal quartz end plates used in these experiments, the end plates were marked and the same pair were always used for the same cell. The transmission of the solution cell was 95 percent of that of the solvent cell at 200 mμ. The transmissions approached equality at about 225 mμ, and the cells were considered to be clean if they "balanced" within 0.2 percent transmittancy at wavelengths longer than 225 to 230 mμ. To make the calibration, readings were taken at 1, 2, or 5 mμ from 200 to 225 mμ and at intervals of 10 mμ from 225 to 400 mμ. The same procedure was followed at the end of each series of measurements or at the end of the day, to assure that no film adhered to the end plates during the measurements. A calibration curve for the water was drawn, from which the corrections to be made to the transmittancy values of the solutions could readily be obtained. The absorption cells were reassembled daily.

For each spectral curve, one cell was filled with the desired concentration of the compound in the chosen solvent medium and the other was filled with the solvent. In all cases the solvent consisted of water, acid, alkali, or buffer solution. Before the transmittancy measurements were made progessively over the desired wavelength range, a few readings were made at selected wavelengths. Readings for the entire curve were then made, at intervals of 2 mμ. Near the maxima and minima of the bands, readings were usually made at intervals of 1 mμ. The selected wavelengths were checked in the reverse order. If agreement in these transmittancies was within the experimental error, it was assumed that no change had taken place in the solution during the time required for the readings. The reproducibility of the transmittancies at a given wavelength was usually ±0.001 from 230 to 400 mμ and ±0.005 from 200 to 230 mμ, where the precision in setting the dials of the spectrophotometer is least. About 20 to 30 minutes is required for an experienced operator to make measurements over the ultraviolet range alone.

V. CALCULATIONS FROM THE SPECTROPHOTOMETRIC DATA

1. APPLICATION OF BEER'S LAW

A pure compound in solution has a characteristic spectral-absorption curve, and at any given wavelength the molar absorption index, k, is calculated by eq 1, derived from Beer's law:

$$k=\frac{-\log_{10} t}{dM}, \tag{1}$$

in which t is the transmittancy of the solution, d is the thickness of the absorbing layer in centimeters (cell length), and M is the molar concentration of the compound. The value for k at any selected wave length should be the same, unless impurities are present or some reaction, such as dissociation or hydrolysis, is taking place. In order to determine the validity of Beer's law, one may compare the values of k, measuring several different concentrations of the compound in a cell of the same depth or by use of the same concentration in cells of different lengths. For each compound reported in this paper, Beer's law was found valid. The experiments included either

two or more concentrations in the 1-cm absorption cells, or the same concentration in cells of 1-, 2-, and 5-cm lengths. The data for all of the compounds are too extensive for publication. However, to demonstrate their accuracy, the data for potassium *p*-phenolsulfonate are given. The transmittancies and the corresponding molar absorption indices are shown in table 1. The resulting ratios of the indices for three concentrations are given for several wavelengths.

TABLE 1.—*Beer's law applied to potassium p-phenolsulfonate in 0.1-M* HCl, *a borate buffer, and 0.001-M* NaOH

[Comparison of the molar absorption indices of three concentrations in 1-cm absorption cells]

Wavelength	A, 2.999×10^{-5} *M*		B, 4.003×10^{-5} *M*		C, 5.000×10^{-5} *M*		Ratios	
	Transmittancy	k_A	Transmittancy	k_B	Transmittancy	k_C	k_B/k_A	k_B/k_C
				IN 0.1-*M* HCl, pH 1.04				
mμ								
220	0.610	7158	0.516	7179	0.439	7151	1.003	1.004
222	.554	8552	.456	8520	.374	8543	0.996	0.997
224	.504	9922	.402	9888	.320	9898	.997	.999
226	.461	11213	.359	11115	.278	11120	.991	1.000
228	.432	12154	.329	12062	.250	12042	.992	1.002
229	.423	12459	.320	12363	.242	12325	.992	1.003
230	.420	12562	.318	12431	.239	12433	.990	1.000
231	.421	12527	.319	12397	.240	12397	.990	1.000
232	.428	12289	.326	12161	.248	12112	.990	1.004
234	.458	11307	.356	11206	.275	11214	.991	0.999
236	.513	9665	.412	9621	.334	9526	.995	1.010
238	.592	7591	.501	7499	.422	7494	.988	1.001
240	.693	5310	.619	5204	.548	5225	.980	0.996
							avg 0.992	avg 1.001
				IN BORATE BUFFER, pH 8.98				
244	0.630	6690	0.540	6686	0.463	6689	0.999	1.000
246	.611	7134	.520	7095	.443	7073	.995	1.003
248	.586	7739	.491	7718	.413	7682	.997	1.005
250	.565	8267	.465	8308	.387	8246	1.005	1.007
251	.558	8448	.455	8544	.376	8497	1.011	1.006
252	.550	8657	.449	8688	.370	8637	1.004	1.006
253	.548	8710	.445	8785	.364	8779	1.009	1.001
254	.545	8789	.444	8810	.364	8779	1.002	1.004
255	.550	8657	.447	8736	.368	8684	1.009	1.006
256	.557	8474	.453	8592	.377	8474	1.014	1.014
258	.582	7838	.481	7941	.406	7830	1.013	1.014
260	.622	6876	.524	7012	.448	6975	1.020	1.005
262	.672	5756	.581	5892	.512	5815	1.024	1.013
							avg 1.008	avg 1.006
				IN 0.001-*M* NaOH, pH 11				
244	0.435	12053	0.327	12128	0.250	12042	1.006	1.007
246	.383	13897	.278	13890	.202	13894	0.999	1.000
248	.341	15579	.237	15620	.168	15494	1.003	1.008
250	.310	16959	.209	16985	.142	16955	1.001	1.002
251	.299	17482	.200	17462	.134	17459	0.999	1.000
252	.290	17925	.193	17849	.130	17722	.996	1.007
253	.287	18075	.191	17962	.126	17993	.994	0.998
254	.288	18025	.190	18019	.128	17857	1.000	1.009
255	.290	17925	.192	17905	.130	17722	0.999	1.010
256	.300	17434	.198	17571	.135	17394	1.008	1.010
258	.330	16054	.227	16088	.160	15918	1.002	1.011
260	.381	13973	.273	14086	.201	13937	1.008	1.010
262	.450	11563	.343	11610	.263	11601	1.004	1.001
							avg 1.001	avg 1.006

In calculating numerical quantities from spectral data, one should remember that the experimental transmittancy values may easily be in error by 0.001 to 0.002. However, it is the error in the logarithm ($-\log t$) that is significant. When transmittancies below 0.1 and above 0.9 are used, additional errors are involved. The ratios given in table 1, therefore, include all experimental errors, such as dilution error or temperature effects, as well as instrumental errors in the spectrophotometric measurements.

2. CALCULATION OF THE "APPARENT" DISSOCIATION CONSTANTS

The molar absorption indices, k, are calculated from the transmittancies at any wavelength by eq 1. The indices k_m, k_i and k_α are those of the molecular form, the ionic form, and a mixture of the two, respectively. From the indices at a given wavelength, α is calculated by eq 2:

$$\alpha=(k_\alpha-k_m)/(k_i-k_m). \tag{2}$$

α represents the amount of the electromeric forms of the acid or ester transformed to the electromeric forms of the salt or of the acid or acid salt to the neutral salt. From the values of α at one or more wavelengths, the apparent [5] dissociation constant, K^*, can then be calculated by the relationship

$$pK^*=pH-\log[\alpha/(1-\alpha)]. \tag{3}$$

At each step in the transformation, the calculated value of α should be the same for all wavelengths over the entire spectral range, if the reaction is merely one of dissociation. The best results, however, will be obtained at wavelengths in the middle of the absorption bands, and also in the regions where the transmittancy curves for the limiting ionic and molecular forms are widely separated. The spectral regions used for the calculations will therefore vary with the particular compound under investigation. Transmittancy values on steep slopes or near isosbestic points should be used with caution.

The values of α are averaged for several wavelengths. The average is then used for each intermediate stage of the ionization, and the pK^* values are easily computed from eq 3 with the use of measured pH values of the buffered mixtures.

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[5] This apparent dissociation constant has been termed the "incomplete" (unvollständig) dissociation constant by Bjerrum and Unmack [10]. It is defined by the equation $K^*=a_H\ (c_A/c_{HA})$, where a and c represent activity and concentration, respectively. It differs, therefore, from the classical constant, which involves the concentrations of reactants and products, and from the thermodynamic constant, which involves their activities.

VI. PRESENTATION OF THE DATA

1. DISSOCIATION OF *p*-HYDROXYBENZOIC ACID

The spectral transmittancies are plotted as a function of wavelength in figures 1 and 2. The curves represent, progressively, the two stages in the dissociation of 4×10^{-5}-*M* *p*-hydroxybenzoic acid. The dissociation of the carboxyl group is represented by the six curves in figure 1. The second stage, that of the phenol group of the carboxylate salt, is shown by the 12 curves in figure 2. In the first series, the solutions used for the limiting forms and the intermediate steps

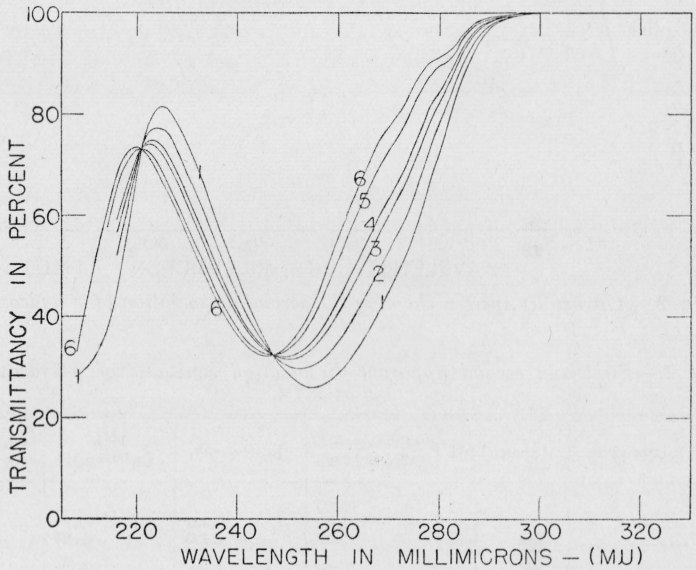

FIGURE 1.—*Ultraviolet spectra showing the first dissociation of p-hydroxybenzoic acid.*

in the transformation were 0.1-*M* hydrochloric acid (curve 1), a phosphate buffer (curve 6), and four intermediate acetate buffers (curves 2, 3, 4, 5). Although the latter were low in ionic strength, measurements could not be made below 216 mμ, because the acetate itself cut out light at lower wavelengths. Many experiments at pH values near 7 were performed before the limiting curve, No. 6, was found. The intersecting curves 1 and 6 are not widely separated, and the slopes of the bands are rather steep. However, the values of α calculated at 2-mμ intervals between 254 and 286 mμ, inclusive, are consistent. These 17 values for each step are averaged and given in table 2, column 3. The pK^* values are then calculated by use of eq 3, and the measured pH values of each buffered solution. For the dissociation of the carboxyl group at 25° C, pK^* is 4.5_1.

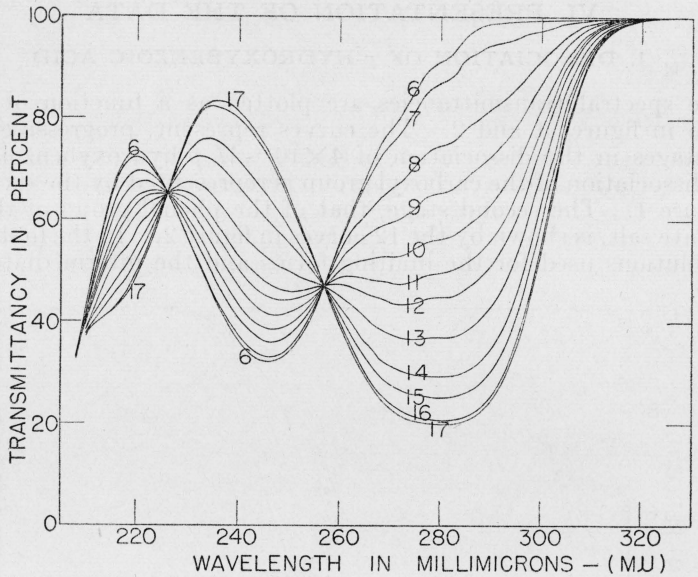

FIGURE 2.—*Ultraviolet spectra showing the second dissociation of p-hydroxybenzoic acid.*

TABLE 2.—*First and second apparent dissociation constants of p-hydroxybenzoic acid at 25° C*

Figure 1, curve No.	Measured pH	Average α_1 (λ254 to λ286)	$[\alpha_1/(1-\alpha_1)]$	$\log_{10}[\alpha_1/(1-\alpha_1)]$	$pK^*_1=pH-\log_{10}[\alpha_1/(1-\alpha_1)]$
1	1.12	0.000			
2	4.17	.302	0.432	−0.36	4.53
3	4.58	.529	1.123	+.05	4.53
4	4.73	.629	1.698	+.23	4.50
5	5.32	.876	7.091	+.85	4.47
6	7.01	1.000			

Figure 2, curve No.	Measured pH	Average α_2 (λ264 to λ294)	$[\alpha_2/(1-\alpha_2)]$	$\log_{10}[\alpha_2/(1-\alpha_2)]$	$pK^*_2=pH-\log_{10}[\alpha_2/(1-\alpha_2)$
6	7.01	0.000			
7	7.96	.031			
8	8.54	.131	0.151	−0.82	9.36
9	8.79	.218	.279	−.55	9.34
10	8.99	.317	.465	−.33	9.32
11	9.15	.402	.671	−.17	9.32
12	9.28	.468	.879	−.06	9.34
13	9.48	.594	1.460	+.16	9.32
14	9.79	.745	2.925	+.47	9.32
15	10.03	.843	5.353	+.73	9.30
16	10.84	.969			
17	11.93	1.000			

The second series of curves, shown in figure 2, represents the second dissociation. The data for this series, curves 6 to 17, inclusive, were obtained by use of the same phosphate buffer used in the first series, several borate buffers, and 10^{-3}-M sodium hydroxide. The intersecting curves for the limiting forms, curves 6 and 17, have a wide spread and values of α were calculated at 17 wavelengths, 264 to 294

mμ, inclusive, at intervals of 2 mμ. The average α for each step is shown in column 3, table 2. For the second dissociation at 25° C, pK^*_2 is 9.3_3.

2. DISSOCIATION OF METHYL *p*-HYDROXYBENZOATE

The partial neutralization of the phenol group of 4×10^{-5}-*M* methyl *p*-hydroxybenzoate was accomplished by the use of borate buffers. The molecular form was obtained in 0.1-*M* hydrochloric acid and the ionic form in 10^{-3}-*M* sodium hydroxide. The values of α were calculated as above from the 12 curves as shown in figure 3.

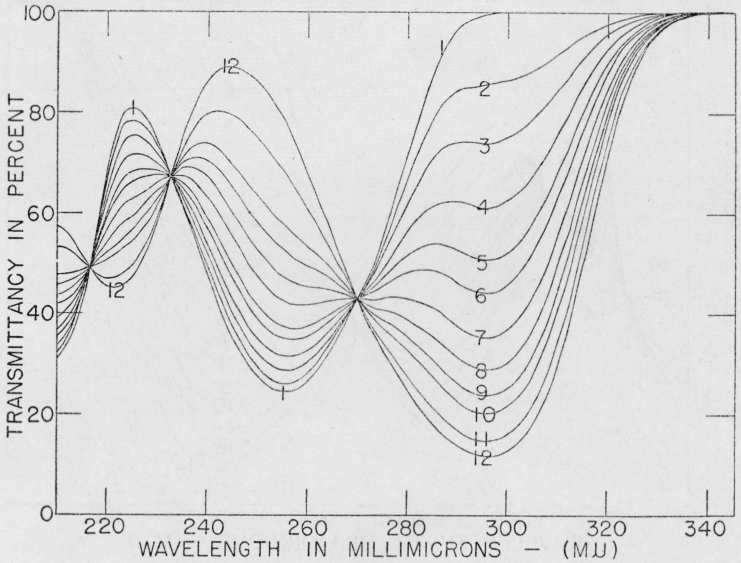

FIGURE 3.—*Ultraviolet spectra showing the dissociation of methyl p-hydroxybenzoate.*

The transmittancies at 2-mμ intervals between wavelengths 280 and 312 mμ, inclusive, were used. Averages of the α values obtained are given in table 3, column 3. An average pK^* of 8.3_4 at 25° C was obtained.

TABLE 3.—*Apparent dissociation constant of methyl p-hydroxybenzoate at 25° C*

Figure 4, curve No.	Measured pH	Average α (λ280 to λ312)	$\alpha/(1-\alpha)$	$\log_{10}[\alpha/(1-\alpha)]$	$pK^*=pH-\log_{10}[\alpha/(1-\alpha)]$
1	1.06	0.000			
2	7.22	.070			
3	7.54	.137	0.159	−0.80	8.34
4	7.82	.227	.293	−.53	8.35
5	8.01	.314	.457	−.34	8.35
6	8.14	.378	.608	−.22	8.36
7	8.33	.485	.941	−.03	8.36
8	8.47	.578	1.370	+.14	8.33
9	8.62	.667	2.007	+.30	8.32
10	8.80	.743	2.886	+.48	8.34
11	9.20	.889	7.993	+.90	8.30
12	11.23	1.000			
Average					8.34

3. DISSOCIATION OF ETHYL *p*-HYDROXYBENZOATE

The ethyl ester of *p*-hydroxybenzoic acid was studied in somewhat more detail, with the use of three concentrations: 10^{-5} *M*, 2.5×10^{-5}*M*, and 5×10^{-5} *M*, in the 1-cm absorption cells. The series of curves for each concentration covered a different portion of the transmittancy scale, and thus a comprehensive analysis of the spectrophotometric data could be made. For brevity, however, the spectral data for only one concentration, namely, 5×10^{-5} *M*, are shown in the 14 curves given in figure 4.

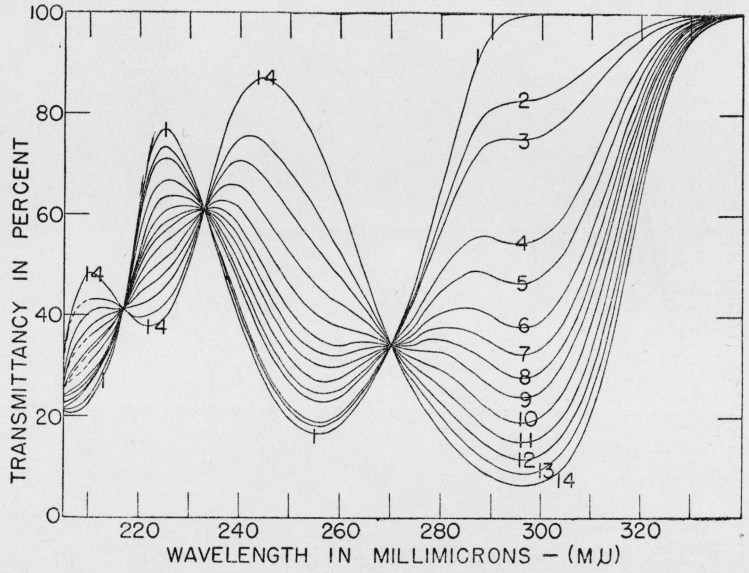

FIGURE 4.—*Ultraviolet spectra showing the dissociation of ethyl p-hydroxybenzoate*

For the limiting forms, 0.1-*M* hydrochloric acid and 10^{-3}-*M* sodium hydroxide (curves 1 and 14) were used. For the 12 intermediate curves, Nos. 2 to 13, inclusive, borate buffers pH 7.3 to 9.2 were used. The values of α were calculated between wavelengths 280 to 312 mμ, inclusive, for each pH step. The average α for each series of the three concentrations is given in columns 3, 4, and 5 of table 4. Calculations were also made across the broader parts of the other two overlapping bands at the lower wavelengths, and the agreement was as good as experimental errors would allow. For the reasons previously stated, however, only the spectral data for the bands nearest the visible were used for final calculations. The average pK^* for ethyl *p*-hydroxybenzoate at 25° C is 8.3_7.

TABLE 4.—*Apparent dissociation constant of ethyl p-hydroxybenzoate at 25° C*

Figure 4, curve No.	Measured pH	Average α's (λ 280 to λ 312)			Average $[\alpha/(1-\alpha)]$	$\log_{10}[\alpha/(1-\alpha)]$	$pK^*=pH-\log_{10}[\alpha/(1-\alpha)]$
		10^{-5} *M*	2.5×10^{-5} *M*	5×10^{-5} *M*			
1	1.08	0.000	0.000	0.000			
2	7.27	.068	.067	.068			
3	7.42	.107	.101	.102	0.115	−0.94	8.36
4	7.84	.219	.220	.222	.282	−.55	8.39
5	7.94	.287	.279	.280	.392	−.41	8.35
6	8.11	.362	.351	.355	.552	−.26	8.37
7	8.23	.416	.417	.411	.709	−.15	8.38
8	8.29	.463	.467	.466	.870	−.06	8.35
9	8.42	.522	.516	.521	1.082	+.03	8.39
10	8.54	.612	.605	.607	1.552	+.19	8.35
11	8.71	.698	.688	.695	2.264	+.35	8.36
12	8.92	.787	.785	.786	3.669	+.56	8.36
13	9.21	.886	.874	.884	7.446	+.87	8.34
14	11.24	1.000	1.000	1.000			
Average							8.37

4. DISSOCIATION OF *n*-BUTYL *p*-HYDROXYBENZOATE

Although the *n*-butyl ester of *p*-hydroxybenzoic acid is difficultly soluble in water, a 5×10^{-4}-*M* stock solution was prepared. Solutions containing the ester in 2.5×10^{-5}-*M* concentration were used for the spectrophotometric measurements. The spectral transmittancies are plotted in figure 5, and the calculations are given in table 5. The solutions used were 0.1-*M* hydrochloric acid, borate buffers, and 10^{-3}-*M* sodium hydroxide. For this ester, pK^* was found to be 8.3_4 at 25° C.

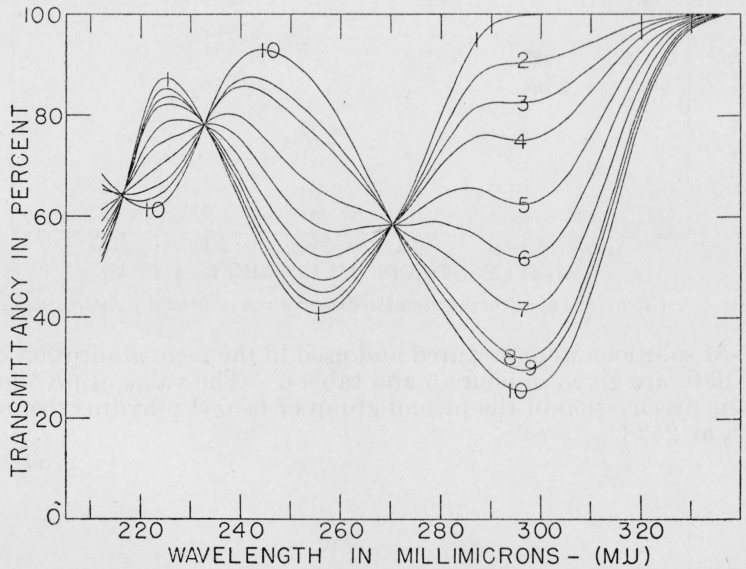

FIGURE 5.—*Ultraviolet spectra showing the dissociation of n-butyl p-hydroxybenzoate.*

TABLE 5.—*Apparent dissociation constant of n-butyl p-hydroxybenzoate at 25° C*

Figure 5, curve No.	Measured pH	Average α (λ282 to λ310)	$[\alpha/(1-\alpha)]$	$\log_{10}[\alpha/(1-\alpha)]$	$pK^*=pH-\log_{10}[\alpha/(1-\alpha)]$
1	1.12	0.000			
2	7.28	.071	0.077	−1.11	8.39
3	7.60	.139	.161	−0.79	8.39
4	7.81	.207	.261	−.58	8.39
5	8.11	.342	.521	−.28	8.39
6	8.27	.482	.930	−.03	8.30
7	8.52	.642	1.794	+.25	8.27
8	9.00	.832	4.942	+.69	8.31
9	9.23	.892	8.294	+.92	8.31
10	11.56	1.000			
Average					8.34

5. DISSOCIATION OF BENZYL *p*-HYDROXYBENZOATE

Benzyl *p*-hydroxybenzoate is also very slightly soluble in water. A stock solution, 10^{-4} *M* in the ester, was made up, from which

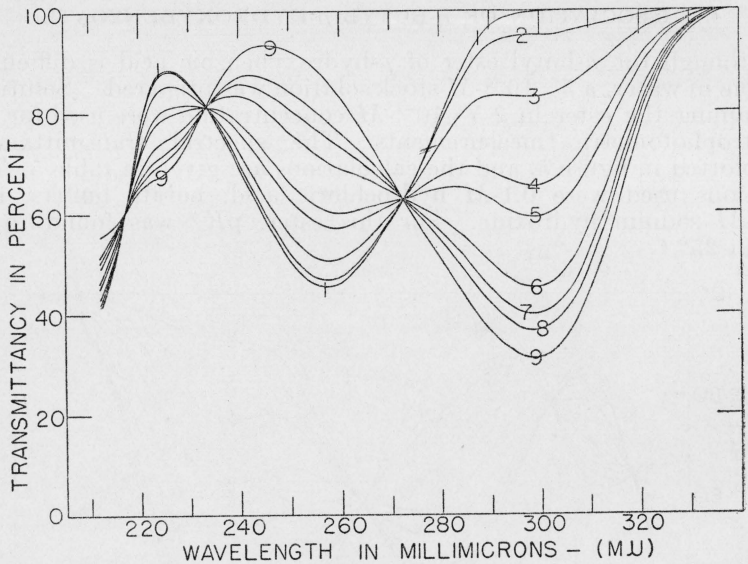

FIGURE 6.—*Ultraviolet spectra showing the dissociation of benzyl p-hydroxybenzoate.*

10^{-5}-*M* solutions were prepared and used in the 2-cm absorption cells. The data are given in figure 6 and table 6. The value of pK^* found or the dissociation of the phenol group of benzyl p-hydroxybenzoate s 8.2_8 at 25° C.

TABLE 6.—*Apparent dissociation constant of benzyl p-hydrozybenzoate at 25° C*

Figure 6, curve No.	Measured pH	Average α (λ282 to λ310)	$[\alpha/(1-\alpha)]$	$\log_{10}[\alpha/(1-\alpha)]$	$pK^*=pH-\log_{10}[\alpha/(1-\alpha)]$
1	1.03	0.000			
2	6.91	.039	0.040	−1.39	8.30
3	7.55	.156	.185	−0.73	8.28
4	8.05	.359	.561	−.25	8.30
5	8.21	.445	.803	−.10	8.31
6	8.57	.676	2.089	+.32	8.25
7	8.83	.783	3.600	+.56	8.27
8	9.04	.855	5.901	+.77	8.27
9	11.63	1.000			
Average					8.28

6. DISSOCIATION OF POTASSIUM *p*-PHENOLSULFONATE

Potassium *p*-phenolsulfonate is fairly soluble in water. Preliminary curves were given for the primary and secondary salts in an earlier publication [1].

The spectral transmittancy curves, shown in figure 7, represent some of the steps in the transformation of the *p*-phenosulfonic acid

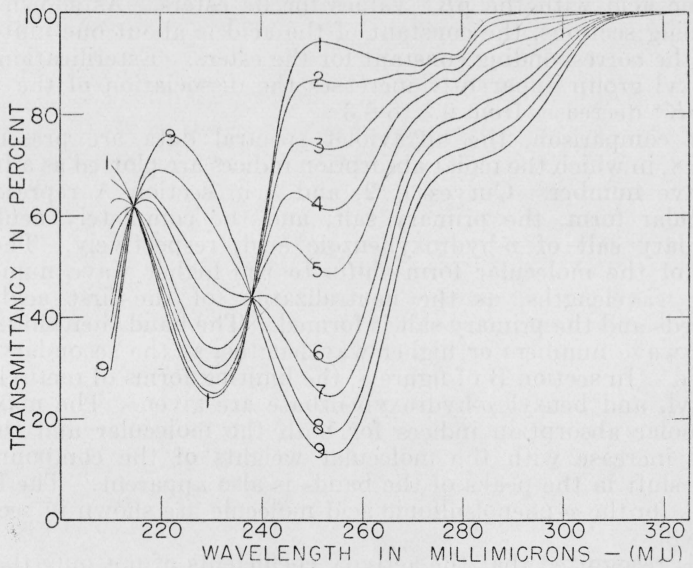

FIGURE 7.—*Ultraviolet spectra showing the second dissociation of p-phenolsulfonic acid.*

to the fully neutralized secondary potassium salt. Solutions containing potassium *p*-phenolsulfonate at a concentration of 5×10^{-5} *M* in a phosphate buffer, in several borate buffers, and in 10^{-2}-*M* potassium hydroxide were studied. The absorption bands occur at lower wavelengths and are not as broad as those of the hydroxybenzoates. The α values were calculated for wavelengths from 244 to 264 mμ, inclusive, and the averages of the different values at each pH are given in table 7. Calculations were made as described previously. A pK^* of 8.9$_0$ at 25° C was obtained.

TABLE 7.—*Apparent dissociation constant of potassium-p-phenolsulfonate at 25° C*

Figure 7, Curve No.	Measured pH	α $10^{-4}M$ λ244 to λ264	α $5\times10^{-5}M$ λ244 to λ264	Average $[\alpha/(1-\alpha)]$	$\log_{10}$ $[\alpha/(1-\alpha)]$	$pK^*=pH-\log_{10}[\alpha/(1-\alpha)]$
1	1.08	0.0000	0.0000			
2	7.38	.045	.043			
Not drawn	7.66	.077	.076			
Do	7.85	.106	.104	0.117	−0.93	8.78
3	8.05	.124	.125	.143	−.85	8.90
4	8.33	.212	.214	.271	−.57	8.90
5	8.57	.325	.329	.486	−.31	8.88
6	8.98	.556	.552	1.243	+.09	8.89
7	9.20	.668	.670	1.623	+.30	8.90
8	9.66	.848	.844	5.489	+.74	8.92
9	11.20	1.000	1.000			

VII. DISCUSSION

The dissociation of the esters of *p*-hydroxybenzoic acid and the dissociation of the unsubstituted acid from spectrophotometric studies are demonstrated in the foregoing data. It is of interest to compare the value of the apparent second dissociation constant of *p*-hydroxybenzoic acid with the pK^* values for its esters. As shown in the foregoing sections, the constant of the acid is about one unit higher than the corresponding constant for the esters. Esterification of the carboxyl group apparently increases the dissociation of the phenol, and pK^* decreases from 9.3 to 8.3.

For comparison, the ultraviolet spectral data are presented in figure 8, in which the molar absorption indices are plotted as a function of wave number. Curves 1, 2, and 3 in section A represent the molecular form, the primary salt, and the completely neutralized secondary salt of *p*-hydroxybenzoic acid, respectively. The main band of the molecular form shifts to the higher wave numbers or lower wavelengths, as the neutralization of the first acid group proceeds and the primary salt is formed. The band then shifts to the lower wave numbers or higher wavelengths, as the secondary salt is formed. In section B of figure 8, the limiting forms of methyl, ethyl, *n*-butyl, and benzyl *p*-hydroxybenzoate are given. The maxima in the molar absorption indices for both the molecular and the ionic forms increase with the molecular weights of the compounds. A slight shift in the peaks of the bands is also apparent. The limiting curves for the *p*-phenolsulfonic acid molecule are shown in section C, figure 8.

It is recognized that the activity coefficients of not only the buffer ions but also of the compounds themselves must be considered in order to determine the thermodynamic ionization constants. All the buffers were dilute and of practically the same ionic strengths. It is not feasible at present to make a more extensive study with buffers of many different concentrations. When a wide range of buffers of accurately known pH is available and further refinements in control of temperature of the spectrophotometric absorption cells have been made, the measurements can be extended to furnish data from which calculations of the true thermodynamic constants can be made.

If measurements of the type described here were made with buffers of widely different concentrations, it would be possible to determine

pK_a, the negative of the logarithm of the thermodynamic dissociation constant, by the extrapolation of measured values of pK^*, to zero ionic strength, where the activity-coefficient correction becomes zero by definition and the apparent and true dissociation constants are identical. In general, it can be expected that pK_a for the second dis-

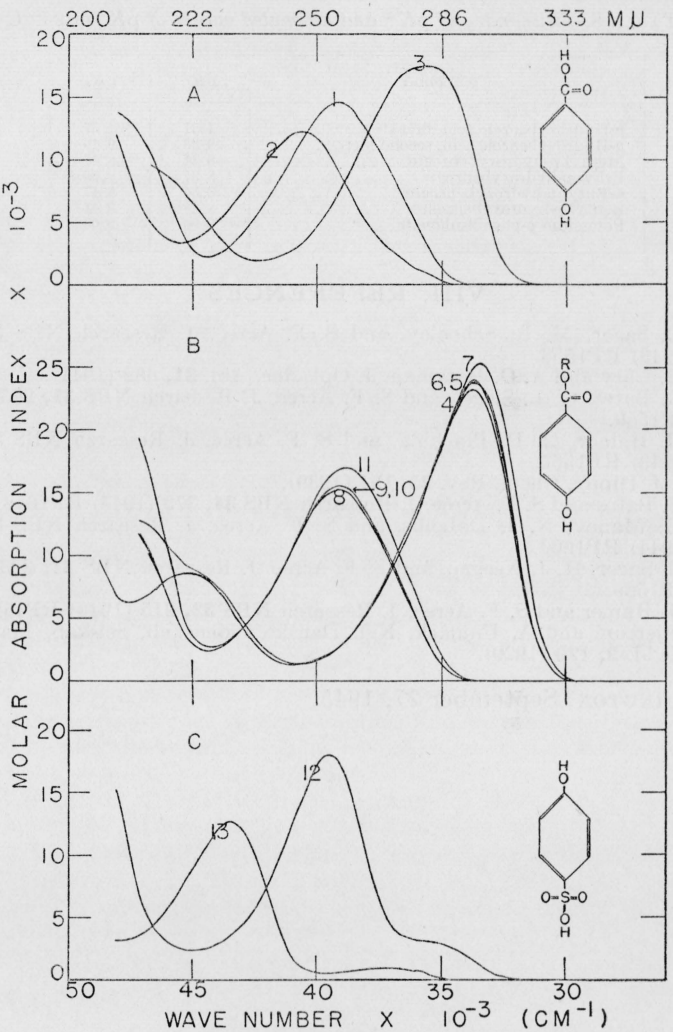

FIGURE 8.—*Limiting spectral absorption curves for p-hydroxybenzoic acid, A, menthyl, ethyl, n-butyl, and benzyl p-phydroxybenzoate, B and potassium p-phenolsulfonate, C.*

sociation of *p*-hydroxybenzoic acid would be about 0.18 higher than the pK^* value obtained at an ionic strength of 0.02. For the same ionic strength, the pK_a for the first dissociation of this acid and for the dissociation of the esters would be about 0.06 higher than the pK^* values listed. Inasmuch as borate buffers approximately 0.01 in ionic strength were used, for the most part, in obtaining pK^* for potassium

p-phenolsulfonate, the correction for activity coefficients amount to about 0.13 unit. The value of pK_a thus becomes 9.03, or slightly lower than 9.053 found by emf methods at 25° C [3]. The pK^* values found by spectrophotometric methods are listed in table 8, together with the estimated values for pK_a.

TABLE 8.—*Summary of* pK^* *and estimated values of* pK_a *at 25° C*

Compound	pK^*	pK_a
p-Hydroxybenzoic acid, first step	4.51	4.57
p-Hydroxybenzoic acid, second step	9.33	9.46
Methyl *p*-hydroxybenzoate	8.34	8.47
Ethyl *p*-hydroxybenzoate	8.37	8.50
n-Butyl *p*-hydroxybenzoate	8.34	8.47
Benzyl *p*-hydroxybenzoate	8.28	8.41
Potassium *p*-phenolsulfonate	8.90	9.03

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WASHINGTON, September 27, 1945.