

# Ionization Constants of Substituted Benzoic Acids in Ethanol-Water\*

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The thermodynamic ionization constants of meta and para substituted allyl- and propenylbenzoic acids were determined potentiometrically in aqueous ethanol of varying ethanol concentration. The  $pK$  values increase with increasing ethanol content. The relative acid strength does not vary with change in solvent concentration. The  $\Delta pK/\Delta$  percent ETOH increases with ethanol content of the medium until a maximum is reached around 40 weight-percent ethanol. A plot of  $pK + \log [H_2O]$  versus the reciprocal of the dielectric constant of the solvent gives a nearly linear relationship to about 44 weight-percent ethanol. From  $pK$  values found in the literature a similar linear relationship exists for other benzoic acids. With the exception of the *p*-propenylbenzoic acid the  $\sigma$ -substituent constants of the Hammett equation do not change greatly with ethanol concentration. This behavior may be indicative that the solvation shell surrounding the *p*-propenyl-acid differs from that of other benzoic acids.

Key Words: Allyl- and propenylbenzoic acids, change of  $pK$  with dielectric constant, Hammett sigma constants, ionization constants,  $pK$  values in ethanol-water, sigma constants in ethanol-water, substituted benzoic acids.

## 1. Introduction

Previous results [1]<sup>1</sup> have shown that a relationship exists between the reactivity and the presence of substituent groups in phenols. This relationship applies to the ionization constants of substituted *o*-methoxyphenols (substituted guaiacols) as well as to the rate of the setting reaction of 4-allyl-2-methoxyphenol (eugenol) and 5-allyl-2-methoxyphenol (chavibetol) with zinc oxide. One of the objectives of this study was to determine the ionization constants of meta- and para-allyl- and propenylbenzoic acids. These constants were determined in aqueous ethanol solutions of varying ethanol content to study the effect of the composition of the solvent medium on ionization constants, relative acid strength, solvent-solute interaction, and the free energy of ionization. Data from this and other investigations were used to examine the validity of existing relationships between the dielectric constant of the solvent and ionization constants, and to calculate ion size-parameters.

Another aim of this study was to obtain accurate values for the substituent constants of the Hammett equation for allyl ( $-CH_2-CH=CH_2$ ) and propenyl

( $-CH=CH-CH_3$ ) groups. These constants may be very valuable in predicting rate or equilibrium parameters such as chelate stability constants of aromatic compounds containing allyl or propenyl groups. The results of this and previously published works were also used to calculate the substituent constants of various functional groups in aqueous ethanol solutions.

## 2. Experimental Procedures

### 2.1. Materials

The benzoic acid and potassium acid phthalate were standard samples of the National Bureau of Standards.

The allyl- and propenylbenzoic acids were synthesized as previously described [1]. In addition, *p*-propenylbenzoic acid was prepared by isomerization from *p*-allylbenzoic acid. To 15 ml of a saturated solution of KOH in 90 percent ethanol, 0.1 g of *p*-allylbenzoic acid was added in a 50 ml flask. The solution was saturated with argon and refluxed for 48 hr, cooled and neutralized with 6*N* HCl solution. The precipitate was filtered, washed with water, decolorized with activated charcoal, and recrystallized repeatedly from a 30 percent ethanol-water solution. Yield: 0.04 g (40%) of *p*-propenylbenzoic acid, mp = 215 °C.

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<sup>2</sup>Figures in brackets indicate the literature references at the end of this paper.

## 2.2. Procedures

The thermodynamic ionization constants at  $25.0 \pm 0.2$  °C were determined potentiometrically in an inert atmosphere with a carbonate-free aqueous ethanol solution of sodium hydroxide in the buffer region where the degree of ionization is between 25 percent and 75 percent. Further pH values were obtained in the vicinity of the end point. A Radiometer pH meter with scale expander was used. Before each titration the instrument was standardized with 0.05 M potassium acid phthalate (pH=4.008) and 0.025 M  $\text{KH}_2\text{PO}_4 - \text{Na}_2\text{HPO}_4$  (pH=6.865).

A 40 ml ethanol-water solution of the acid ( $2$  to  $4 \times 10^{-3}M$ ) was used in the titrations with the exception of *p*-propenylbenzoic acid, where 100 ml of a nearly saturated solution was employed.

A slow stream of nitrogen or argon saturated with the solvent used in the titration was passed through the liquid in the reaction vessel for at least 10 min. The inert gas was also passed through the solution before each pH reading. All solutions were protected from carbon dioxide contamination by sodium hydroxide-asbestos absorbent. Details of the experimental procedures are given by Brauer, Argentar, and Durany [1]. The precise end point was obtained by plotting  $\Delta\text{pH}/\Delta$  ml or its reciprocal versus milliliters of NaOH added and taking as the end point the number of milliliters of NaOH at which  $\Delta\text{pH}/\Delta$  ml is a maximum or  $\Delta$  ml/ $\Delta$  pH is a minimum [2]. From the law of mass action and assuming (1) the validity of the Debye-Hückel equation, (2) that the activity coefficient of the unchanged, undissociated acid molecule is unity, and (3) that the hydroxyl ion concentration may be neglected, the following equation that was employed to calculate pK values can be derived.

$$\text{pK} = \text{pH} + \log \frac{C_A - ([\text{Na}^+] + [\text{H}^+])}{[\text{Na}^+] + [\text{H}^+]} + \frac{A\sqrt{[\text{Na}^+] + [\text{H}^+]}}{1 + B\sqrt{[\text{Na}^+] + [\text{H}^+]}} \quad (1)$$

where  $C_A = [\text{HA}] + [\text{A}^-]$  = total concentration of all acid species,

$[\text{HA}]$  = concentration of the undissociated acid, and

$[\text{A}^-]$  = concentration of anion of the acid.

The constants  $A$  and  $B$  which are dependent on the solvent composition were calculated from the expressions by Bates, Paabo, and Robinson [3]  $A = 1.825 \times 10^6 (\epsilon T)^{-3/2}$  and  $B = 1.5 (78.3/\epsilon)^{1/2}$  where  $T$  = absolute temperature and  $\epsilon$  = dielectric constant of the solvent, obtained by interpolation from the values given by Åkerlöf [4]. The calculations were made using the National Bureau of Standards Omnitab program [5].

## 3. Results and Discussion

### 3.1. Ionization Constants

The apparent thermodynamic pK values of benzoic acid and the substituted benzoic acids in 0 to 64.8 weight percent (0 to 70 volume percent) aqueous ethanol solutions (including the number of runs and the standard error of the mean of the pK values) are given in table 1. The pK values were corrected for liquid junction potential and medium effect by graphic interpolation of the average values of  $\delta = (\bar{E}_j - \log_m \gamma_H)$  from data of Gutbezahl and Grunwald [6] and Bates, Paabo, and Robinson [3] where  $\bar{E}_j$  is the liquid junction potential expressed in pH units and  $m\gamma_H$ , the medium effect, measures the difference in the standard free energy of the proton in water and aqueous ethanol. The estimated standard deviations for pK values obtained during one run were about 0.004 pK units. With increasing ethanol concentration the pK values increase markedly from around 4.2 in water to 6.4 for the 64.8 weight percent ethanol solution. As has been shown by Grunwald [6]  $\Delta\text{pK} = \log m\gamma_H + \log (\gamma_{A^-}/\gamma_{\text{HA}})$  where  $m\gamma_H$ ,  $\gamma_{A^-}$  and  $\gamma_{\text{HA}}$  are the degenerate activity coefficients of the proton, anion, and undissociated acid referred to the infinitely dilute aqueous state. Since  $\Delta\text{pK}$  is a function of both solvent and acid structure and  $\log \gamma_H$  is a function of solvent only,  $\log \gamma_{A^-}/\gamma_{\text{HA}}$  must be a function at least of the acid structure and possibly of the solvent. On increasing the ethanol concentration the nature of the ionization equilibrium is changed, partially because the ethanol-solvated carboxylate moiety differs from the corresponding water-solvated group.

TABLE 1. pK Values of substituted benzoic acids in aqueous ethanol solution

Temperature =  $25.0 \pm 0.2$  °C.

Substituent	Weight percent ethanol in solution																			
	0.0				12.2				25.2				44.1				64.8			
	<i>n</i> <sup>a</sup>	<i>pK</i> <sub>app.</sub>	<i>S</i> / $\sqrt{n}$ <sup>b</sup>	<i>pK</i> <sub>cor.</sub> <sup>c</sup>	<i>n</i>	<i>pK</i> <sub>app.</sub>	<i>S</i> / $\sqrt{n}$	<i>pK</i> <sub>cor.</sub>	<i>n</i>	<i>pK</i> <sub>app.</sub>	<i>S</i> / $\sqrt{n}$	<i>pK</i> <sub>cor.</sub>	<i>n</i>	<i>pK</i> <sub>app.</sub>	<i>S</i> / $\sqrt{n}$	<i>pK</i> <sub>cor.</sub>	<i>n</i>	<i>pK</i> <sub>app.</sub>	<i>S</i> / $\sqrt{n}$	<i>pK</i> <sub>cor.</sub>
Hydrogen.....	17	4.210	0.002	4.210	14	4.444	0.002	4.46	16	4.918	0.003	4.89	8	5.692	0.004	5.55	15	6.424	0.012	6.21
<i>m</i> -Allyl.....	9	4.266	.004	4.266	8	4.514	.007	4.53	4	5.035	.010	5.01	5	5.808	.003	5.66	4	6.532	.009	6.32
<i>p</i> -Allyl.....	9	4.326	.004	4.326	8	4.563	.003	4.58	5	5.061	.007	5.04	3	5.811	.003	5.67	3	6.537	.013	6.32
<i>m</i> -Propenyl.....	5	4.248	.006	4.248	7	4.485	.007	4.50	4	4.972	.001	4.95	7	5.763	.008	5.62	2	6.478	.008	6.26
<i>p</i> -Propenyl.....	4	4.487	.003	4.487	3	4.785	.039	4.80	4	5.154	.016	5.13	2	5.854	.014	5.71	6	6.614	.028	6.40

<sup>a</sup> *n* = number of runs.

<sup>b</sup> Standard error of the mean =  $\frac{S}{\sqrt{n}}$

Estimated standard deviation =  $\sqrt{\frac{n\sum x^2 - (\sum x)^2}{n(n-1)}}$

<sup>c</sup> *pK*<sub>cor.</sub> is corrected for liquid junction potential and the medium effect for hydrogen ion; *pK*<sub>cor.</sub> = *pK*<sub>app.</sub> -  $\delta$ .

Figure 1 shows the  $pK$  values as a function of the ethanol-water composition. For the *m*- and *p*-allyl- and propenylbenzoic acids, the relative acid strength does not vary with solvent composition and the  $pK$  versus ethanol content curves have the same general shape. Ion solvating power is the dominant factor in the dissociation of the acids. Increases in the ion solvating power should favor the creation and concentration of charge [7]. Kilpatrick [8] has pointed out that estimation of acid strength in mixed solvents such as water-ethanol is difficult since two bases are competing for the proton and two solvated protons may be formed. In addition, the solvent dipoles will be oriented differently around the ions and solute molecules. Thus, it is conceivable that a local unmixing of the solvent may occur.

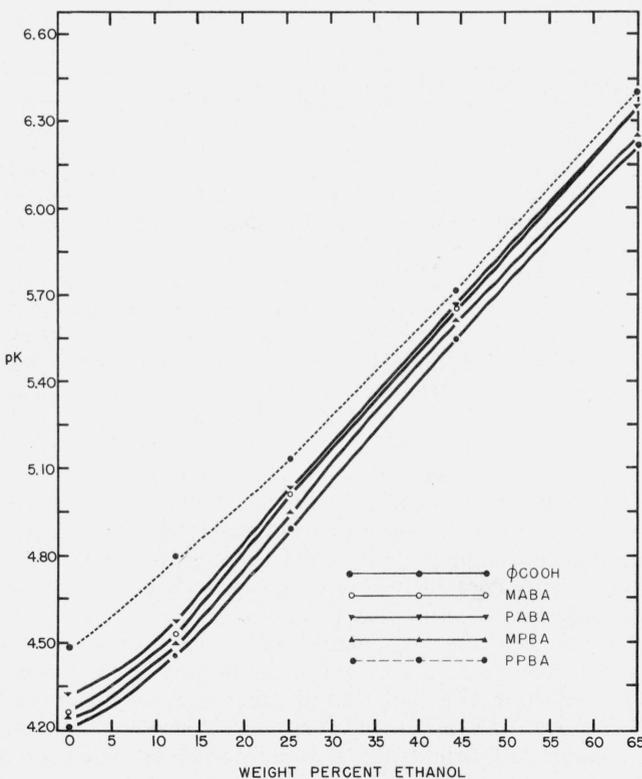


FIGURE 1. Change of ionization constants of benzoic acid with change in ethanol content of the solvent.

The change in free energy,  $\Delta G$ , is likely to be a measure of the relative affinity of ion-solvent interaction arising mainly in the primary solvation zone. The  $pK$  values are directly proportional to the free energy change in the ionization reaction at any given temperature. In table 2,  $\Delta G$ , the change in free energy of ionization for the benzoic acids, calculated from their  $pK$  values, are tabulated. The  $\Delta G$  values increase with the increasing ethanol concentration.

In table 3, the rates of change of  $pK$  with change in solvent composition are given. The  $\Delta pK/\Delta$  (percent EtOH) increases with ethanol content of the medium

TABLE 2.  $\Delta G$  values for the dissociation of substituted benzoic acids in aqueous ethanol solutions

Temperature =  $25.0 \pm 0.2$  °C

Wt. % Ethanol	$\Delta G$ in cal/mole				
	Substituent				
	<i>H</i>	<i>m</i> -Allyl	<i>p</i> -Allyl	<i>m</i> -Propenyl	<i>p</i> -Propenyl
0	5740	5820	5900	5790	6120
12.2	6080	6180	6240	6140	6540
25.2	6670	6830	6870	6750	6990
44.1	7570	7720	7730	7660	7790
64.8	8470	8620	8620	8540	8730

TABLE 3. Rate of change of  $pK$  values of substituted benzoic acids with change in solvent composition

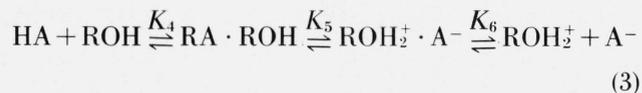
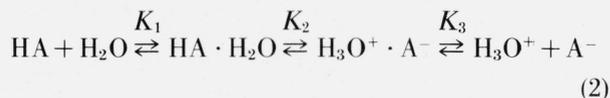
Substituent	$(\Delta pK)/\Delta$ (percent EtOH)			
	0-12.2%	12.2-25.2	25.2-44.1	44.1-64.8
Hydrogen.....	$1.92 \times 10^{-2}$	$3.65 \times 10^{-2}$	$4.10 \times 10^{-2}$	$3.54 \times 10^{-2}$
<i>m</i> -Allyl.....	$2.03 \times 10^{-2}$	$4.01 \times 10^{-2}$	$4.09 \times 10^{-2}$	$3.50 \times 10^{-2}$
<i>p</i> -Allyl.....	$1.94 \times 10^{-2}$	$3.83 \times 10^{-2}$	$3.97 \times 10^{-2}$	$3.57 \times 10^{-2}$
<i>m</i> -Propenyl.....	$1.94 \times 10^{-2}$	$3.75 \times 10^{-2}$	$4.19 \times 10^{-2}$	$3.45 \times 10^{-2}$
<i>p</i> -Propenyl.....	$2.43 \times 10^{-2}$	$2.84 \times 10^{-2}$	$3.70 \times 10^{-2}$	$3.68 \times 10^{-2}$

until a maximum is reached around 40 weight-percent ethanol. This maximum appears to be in the vicinity of the solvent composition where the nature of the interaction of the binary components of the medium may be altered (so that the benzoate ion becomes more soluble in ethanol than in water) as indicated by the change in the slope of the  $pK + \log [H_2O]$  versus the reciprocal of the dielectric constant (see next paragraph) and where the differential heats of dilution for ethanol reach a minimum [9].

### 3.2. Ion Size Parameters

The change of free energy,  $\Delta G$ , on transfer of ions from one solvent medium to another results from a change in the type of solvation shell. The electrostatic part of the free energy change can be estimated by the Born equation [10], if the ions are treated as spheres of finite radius  $r$  immersed in a continuum of uniform dielectric constant  $\epsilon$ . Plots of  $pK$  versus the reciprocal of the dielectric constant are not linear since the Born equation does not take into account the specific interaction between ions and the solvent which must contribute significantly to the nonelectrostatic part of the free energy change. Yasuda [11] showed that linearity of the  $pK$  versus  $1/\epsilon$  plot is improved for partially aqueous solvents by the addition of a water concentration term to account for the variation of the amount of water in the mixed solvent. With the exception of media containing high concentrations of organic solvents the acids investigated by Yasuda had relatively almost the same dissociation constants in various mixed solvents with the same dielectric constant.

Shedlovsky [12] assumes that in mixed solvents, such as ethanol-water, on dissolving a weak organic acid the following competitive reactions take place:



where  $K_1$  to  $K_6$  are the corresponding mass action constants. The overall constants for each solvent are  $K_H$  and  $K_R$  where

$$K_1 K_2 K_3 = \frac{[\text{H}_3\text{O}^+][\text{A}^-]f^2}{[\text{HA}][\text{H}_2\text{O}]} = K_H \quad (4)$$

$$K_4 K_5 K_6 = \frac{[\text{ROH}_2^+][\text{A}^-]f^2}{[\text{HA}][\text{ROH}]} = K_R \quad (5)$$

Assuming that the concentrations of all the electrically neutral species can be taken as their activities and that the last step in the ionic dissociation is controlled by simple coulombic forces, then

$$K_H = B_H e^{-b} \quad (6)$$

and

$$K_R = B_R e^{-b} \quad (7)$$

where  $B_H$  and  $B_R$  are empirical constants;  $b = e^2/\epsilon kT a$  in which  $e$  is the electronic charge,  $k$  is the Boltzmann constant,  $T$  is the temperature in degrees K. The parameter,  $a$ , may be interpreted as the distance between the centers of charge in the ion-pairs. It can be shown [13] that if  $B_H \gg B_R$  and hence  $K_H \gg K_R$  then the observed ionization constant is given by the following equation

$$pK + \log [\text{H}_2\text{O}] + \log B_H = \frac{1}{2.303} \frac{e^2}{kT a} \left( \frac{1}{\epsilon} \right); \quad (8)$$

thus a plot of  $pK + \log [\text{H}_2\text{O}]$  against  $1/\epsilon$  should be linear (at least in the water-rich region of solvent composition) and the ion size parameter,  $a$ , can be obtained from the slope. For acetic acid in water-ethanol, the linear relationship applies up to nearly 50 weight percent (28 mole percent) ethanol [12].

On plotting  $pK + \log [\text{H}_2\text{O}]$  versus  $1/\epsilon$  for the benzoic acids investigated, a nearly linear relationship was obtained from 0 to about 44 weight percent ethanol. The values of  $a$  and  $-\log B_H$  (the intercept on the ordinate when  $1/\epsilon = 0$ ) and their estimated standard deviations were obtained by the method of least squares and are given in table 4. With the exception of *p*-propenylbenzoic acid, the ion size parameter and

the  $-\log B_H$  values for the benzoic acids are the same within experimental error. Unexpectedly, the ion size parameter for acetic acid is 2.56 Å [12] which is considerably larger than the values obtained for benzoic acid in this study. It is conceivable that the larger ratio of charge to mass of the acetate ion compared to the benzoate ion may lead to an increase in hydration.

TABLE 4. Ion size parameters and values of  $-\log B_H$  for benzoic acids

Substituent	Ion size parameter		$-\log B_H$	
	Å			
Hydrogen.....	1.25	0.10 <sup>a</sup>	3.46	0.17 <sup>b</sup>
<i>m</i> -Allyl.....	1.19	0.07	3.40	0.18
<i>p</i> -Allyl.....	1.25	0.07	3.57	0.17
<i>m</i> -Propenyl.....	1.22	0.06	3.43	0.15
<i>p</i> -Propenyl.....	1.44	0.10	4.10	0.18

<sup>a</sup> Estimated standard deviation calculated from the estimated variance of the slope of the  $pK + \log [\text{H}_2\text{O}]$  against  $1/\epsilon$  plot using the method given in reference 22.

<sup>b</sup> Estimated standard deviation calculated from the estimated variance of the intercept using the method given in reference 22.

To check further validity of the  $pK + \log [\text{H}_2\text{O}]$  versus  $1/\epsilon$  relationship, literature values of the ionization constant of benzoic acid in aqueous ethanol were collected. The values of Bright and Briscoe [13] were corrected by eq (1) where  $pH$  was taken as the observed  $pH$  and the second term was omitted since it was found to be negligible. The value of  $[\text{Na}^+]$  was 0.01 mol/l and the  $[\text{H}^+]$  terms were neglected. The volume percent ethanol was converted to weight percent for the  $pK$  values of Bright and Briscoe [13] and Tabagua [14]. The values of Grunwald and Berkowitz as given in reference 5 were also plotted in figure 2. The earlier values given in the literature [15, 16] were not used since it was either impossible to calculate the exact weight percentage of ethanol or not enough data were available to calculate the thermodynamic ionization constants. Up to about 44 weight percent ethanol, the thermodynamic  $pK$  values of the different investigators are seen to be in quite good agreement despite the fact that in this work and that of Grunwald, glass electrodes were used, whereas Tabagua and Bright and Briscoe employed hydrogen-AgCl and hydrogen-calomel electrodes, respectively. At concentrations exceeding 80 weight-percent alcohol the differences in the  $pK$  values are considerable. A possible cause for this discrepancy is that the glass electrode may not always measure hydrogen ion activity accurately at high ethanol concentrations. The nearly linear relationship of  $pK + \log [\text{H}_2\text{O}]$  versus  $1/\epsilon$  up to 44 weight-percent ethanol is clearly seen from figure 2. A similar relationship should exist for anisic acid (*p*-methoxybenzoic acid) (also plotted in fig. 2) the  $pK$  of which was accurately determined by Sager and Bower [17] and for the eight substituted benzoic acids studied by Bright and Briscoe [13]. The approximately linear relationship up to around 45 weight-percent is not unexpected since the molar concentration of water in this region is always much

larger than that of ethanol. In view of the larger dipole moment of water compared to ethanol, preferential hydration of the substituted benzoate ions should occur and, therefore, their effective diameter should be practically constant over a considerable concentration range. On increasing the ethanol concentration, substitution of water by ethanol in the solvent cloud surrounding the substituted benzoate ion takes place. It would be interesting to determine if a transition from the hydrated ion to an ethanol solvated complex takes place around 45 weight-percent ethanol.

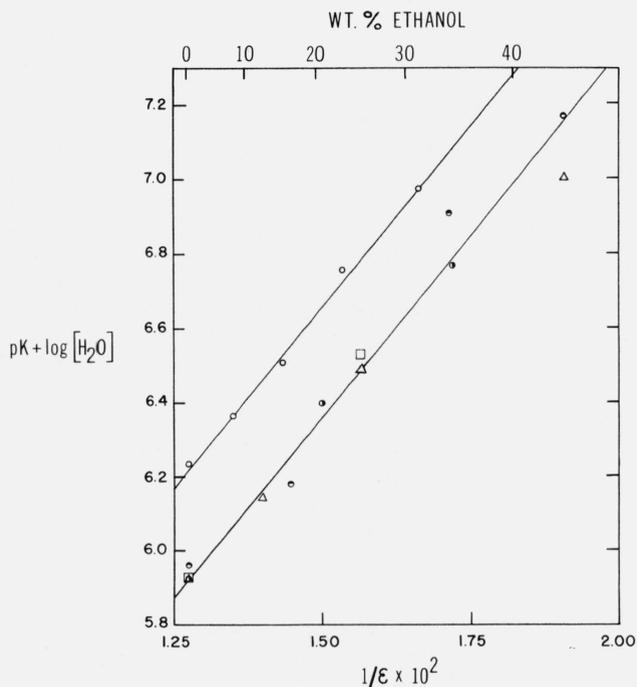


FIGURE 2. Plot  $\log pK + \log [H_2O]$  versus  $1/\epsilon$ .

Benzoic acid:  $\Delta$  this study,  $\bullet$  Grunwald and Berkowitz [6],  $\circ$  Bright and Briscoe [13],  $\square$  Tabagua [14]. Anisic acid:  $\circ$  Sager and Bower [17].

### 3.3. Hammett Sigma Constants

Among the linear free energy relationships, the equation first proposed by Hammett has been very successful for correlating rate and equilibrium constants. This equation describes the effect of a meta or para substituent on the rate or equilibrium constant of an aromatic side chain reaction provided that the resonance interaction between the substituent and the reaction center is either small or proportional to the polar effects.

For acid dissociation equilibria, the Hammett equation may be written

$$pK_0 - pK = \sigma\rho \quad (9)$$

where  $pK_0$  and  $pK$  are the negative logarithms of the ionization constants for the corresponding unsubstituted compound and the meta or para substituted benzene derivative respectively;  $\sigma$  is a substituent

constant which is a measure of the ability of the substituent to donate or withdraw electrons; and  $\rho$  is the solvent-dependent reaction constant characteristic of the reaction under consideration. The reaction constant  $\rho$  has been defined as unity for the acid dissociation equilibrium of benzoic acid in water at 25 °C so that  $\sigma$  can be defined as the difference between the logarithm of the ionization constant in water of the substituted benzoic acid and benzoic acid itself.

Only limited data are available on the change of  $\sigma$  or  $\rho$  with solvent. For ethanol-water systems Grunwald and Berkowitz [6] showed that

$$\rho = \rho^w + \beta Y_- \quad (10)$$

where  $\rho^w$  is the reaction constant which by definition is 1.000 for benzoic acids and its derivatives in water,  $Y_-$  is a solvent-dependent activity function and the parameter  $\beta = 0.628$ . By interpolation of the data given in reference 6 values at the respective weight concentrations of ethanol were found and the corresponding  $\rho$  values were calculated. These  $\rho$  values are in reasonably good agreement with other values given in the literature for the ethanol concentrations investigated [18–20].

It is interesting to note that up to 45 percent ethanol content the product of  $\rho$  and  $\epsilon$  is constant within  $\pm 2.3$  percent. According to Bowden [21]

$$\rho = (A + B/\epsilon)/RT \quad (11)$$

where the constants  $A$  and  $B$  respectively describe the susceptibility of the reaction to polar effects independent of and dependent on the medium. If  $A$  is negligible compared to  $B/\epsilon$  then  $\rho$  is inversely proportional to  $\epsilon$ . In the 0–45 weight-percent ethanol range where the reaction constant varies inversely with the dielectric constant of the medium any effect caused by preferential solvation of the anion or the undissociated acid by the two solvents appears to be negligible.

Using the calculated  $\rho$  values, the  $\sigma$  values of the Hammett equation were obtained and are tabulated in table 5 and plotted in figure 3. With the exception of the *p*-propenylbenzoic acid the  $\sigma$  values do not change greatly with change in ethanol concentration.

TABLE 5. Hammett sigma constants

Ethanol concentration	$\rho^a$	Sigma constant							
		<i>m</i> -Allyl		<i>p</i> -Allyl		<i>m</i> -Propenyl		<i>p</i> -Propenyl	
Wt %									
0	1.000	-0.056	0.004 <sup>b</sup>	-0.116	0.004 <sup>b</sup>	-0.038	0.006 <sup>b</sup>	-0.277	0.023 <sup>b</sup>
12.2	1.128	-0.062	.006	-0.105	.003	-0.036	.006	-0.302	.035
25.2	1.266	-0.092	.008	-0.113	.006	-0.043	.002	-0.187	.013
44.1	1.465	-0.079	.003	-0.081	.003	-0.048	.006	-0.111	.009
64.8	1.578	-0.068	.010	-0.072	.011	-0.034	.009	-0.121	.019

<sup>a</sup> Calculated from  $\rho = 1.000 + 0.628 Y_-$ , where  $Y_-$ , which is a characteristic parameter of carboxylate-carboxylic acid equilibria, was obtained by interpolation of the values given by Grunwald and Berkowitz [6].

<sup>b</sup> Standard error of the mean  $\frac{\sqrt{S_{\rho}^2 + S_{\sigma}^2}}{\rho}$  where  $S_{\rho}$  is the standard error of the mean for benzoic acid and  $S_{\sigma}$  is the corresponding value for the substituted benzoic acid.

It is possible that the solvation shell surrounding the *p*-propenylbenzoic acid differs from that of the other benzoic acids.

To check further the effect of solvent composition on  $\sigma$  the corrected *pK* values of Bright and Briscoe [13] and  $\rho$  constants obtained by the equation given by Grunwald and Berkowitz [6] were used to calculate  $\sigma$  for ten substituents. These data including the estimated standard deviation of the  $\sigma$  values for all ethanol concentrations are given in table 6. Only for the NH<sub>2</sub>, OH and NO<sub>2</sub> groups, where the electron distribution is altered because of solvation of the substituent is the substituent constant markedly dependent on solvent. For these substituents, the dependence of  $\sigma$  on solvent is of the same order of magnitude as that found for the *p*-propenyl group in this study.

The ionization constants for benzoic acids are recommended for calculating primary Hammett substituent constants [19]. This is especially true for the *p*-propenyl group since *p*-propenylphenol is not very stable in basic media. A comparison of the secondary  $\sigma$  constants determined previously from the *pK* values in water of guaiacol and substituted guaiacols [1], and the primary constants obtained from the respective benzoic acids are given in table 7. These values for the allyl groups agree within  $\pm 0.02$ . For the *m*-propenyl group the  $\sigma$  constant decreases by 0.08 when benzoic

acids are used instead of guaiacols. The greatest change in  $\sigma$  occurs for the *p*-propenyl group ( $\sigma$  values are 0.05 and  $-0.28$  as calculated from the *pK*'s of guaiacols and benzoic acids, respectively). This difference may be explained by noting that in *p*-propenylguaiacols the propenyl group is in direct conjugation with the acidic OH while in the corresponding benzoic acid any resonance effect of the propenyl group would likely be transmitted to the para carbon atom of the ring and the acidic OH group by induction.

#### 4. Summary

The thermodynamic *pK* values of allyl- and propenylbenzoic acids in aqueous ethanol increase with increasing ethanol content the *pK* values are dependent on the dielectric constant of the medium. For mixed solvents up to 44 percent water an approximately linear relationship between *pK* + log [H<sub>2</sub>O] and the reciprocal of the dielectric constant exists. The Hammett substituent constant,  $\sigma$  for the *m*- and *p*-allyl and *m*-propenyl groups do not vary greatly with composition of the solvent. However, for the *p*-propenyl group the  $\sigma$  constant is affected by the medium.

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TABLE 6. Sigma constants for various substituents<sup>a</sup>

Wt % ETOH	$\rho$	Sigma constants									
		<i>m</i> -CH <sub>3</sub>	<i>p</i> -CH <sub>3</sub>	<i>m</i> -NH <sub>2</sub>	<i>p</i> -NH <sub>2</sub>	<i>m</i> -OH	<i>p</i> -OH	<i>m</i> -Cl	<i>p</i> -Cl	<i>m</i> -NO <sub>2</sub>	<i>p</i> -NO <sub>2</sub>
0	1.00	-0.07	-0.19	-0.61	-0.74	0.14	-0.32	0.37	0.14	0.72	0.78
16.5	1.17	-0.12	-0.31	-0.42	-0.64	-0.05	-0.42	.....	.....	.....	.....
34.4	1.36	-0.04	-0.11	-0.13	-0.55	0.05	-0.30	0.38	.....	1.13	1.04
44.1	1.46	-0.05	-0.11	-0.13	-0.54	0.02	-0.29	0.36	0.30	0.77	0.88
64.8	1.58	-0.10	-0.08	-0.13	-0.60	-0.08	-0.35	0.33	0.27	0.75	0.85
75.9	1.60	-0.09	-0.08	.....	-0.62	-0.08	-0.39	0.34	0.30	0.71	0.81
87.7	1.61	-0.14	-0.11	.....	-0.66	-0.12	-0.47	0.33	0.26	0.67	0.77
93.7	1.62	.....	.....	.....	.....	.....	.....	.....	.....	0.82	0.90
100*	1.63	+0.14	-0.14	.....	-0.66	-0.13	-0.48	0.34	0.28	0.86	0.96
Average....		-0.09	-0.14	-0.29	-0.63	-0.03	-0.38	0.35	0.26	0.80	0.87
Estimated standard deviation.		0.04	0.08	0.21	0.06	0.09	0.07	0.02	0.06	0.15	0.09

\*From extrapolated *pK* values.

\*\*Uncorrected *pK* values using quinhydrone electrode for benzoic acid and substituted benzoic acids.

<sup>a</sup>Calculated from Bright and Briscoe [13].

TABLE 7. Sigma values of allyl and propenyl groups in water

Substituent	Sigma	
	Primary <sup>a</sup>	Secondary <sup>b</sup>
<i>m</i> -Allyl.....	-0.056	-0.02
<i>p</i> -Allyl.....	-0.116	-0.10
<i>m</i> -Propenyl.....	-0.038	+0.04
<i>p</i> -Propenyl.....	-0.277	+0.05

<sup>a</sup>From benzoic acids.

<sup>b</sup>From guaiacols.