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An Extended Table of Hammett Substituent Constants Based on the Ionization of Substituted Benzoic Acids

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It is recommended that a return be made to the use of the dissociation constants of substituted benzoic acids as a basis for evaluating Hammett substituent constants. A survey of the available data has been made and the substituent constants have been tabulated. The approximate precision of these values is discussed.

More than twenty years ago Hammett pointed out certain parallelisms between the magnitude of reaction rate constants in a homologous series and equilibrium constants of various substituted compounds in other homologous series.* Using the ionization of benzoic acids as a standard reaction, he expressed this relationship in the now well known form:

$$\log \frac{k}{k^\circ} = \rho\sigma \quad (1)$$

where k = a rate (or equilibrium) constant for a *meta* or *para* substituted aromatic compound (2)

k° = the rate (or equilibrium) constant for the unsubstituted aromatic compound (3)

ρ = a constant for the specific reaction and taken as unity for the ionization of benzoic acids (4)

σ = a constant for a given substituent $\equiv \log K - \log K^\circ$ where K is the ionization constant for a substituted benzoic acid in water at 25° C and K° is the ionization constant for benzoic acid itself. (5)

The choice of the standard reaction was dictated by the relative availability of numerous and highly accurate values, largely by Dippy and his co-workers, for the ionization constants of substituted benzoic acids. Fortunately, σ values for most of the more common substituents could thus be directly established. Some σ values, however, were obtained by indirect means. After a ρ value for a particular reaction had been established, based upon the σ values obtained from the ionization of benzoic acids, it was possible to calculate σ values for groups whose rate constants (or equilibrium constants) for that particular reaction were known, even though the ionization constants for the corresponding benzoic acids were not known. The σ values calculated in this manner might be considered to be "secondary standards" or "secondary" σ values. When these "secondary" σ values were used in calculating ρ values for other reactions, and further σ values obtained from these reactions, the σ values so derived (which might be termed "tertiary" σ values) were found to be dependent on the precise order in which the process of establishing ρ values and secondary σ values was carried out. Partially to circumvent this difficulty Jaffé proposed a redefinition of the substituent constant as "the value of σ which best fits the entire body of experimental data." (The ρ value would presumably still be set as 1.000 for the ionization of the benzoic acids.)

Jaffé himself has pointed out the shortcomings of his redefinition. "It makes substituent constants dependent on the body of knowledge available at the time of their evaluation, and implies that they should be revised at frequent intervals. Moreover, the evaluation of such substituent constants requires the formidable task of fitting the entire available data by some suitable statistical procedure. Such computation is not feasible without the use of electronic computing equipment."

Both Hammett and Jaffé include such "secondary" and "tertiary" values in their compilations. In some cases relatively large discrepancies have been shown to exist between these derived σ constants and those based upon more recently available dissociation constants. In other cases the values listed exhibit relatively large differences between very similar, closely related groups.

Our attention was drawn to this problem in the course of our efforts to extend the Hammett treatment to electrophilic reactions through the development of a set of electrophilic (σ^+) substituent constants.[21,65] Excellent agreement had been observed previously between the σ_m^+ and the σ_m values.[21] However, in extending our determination of σ^+ values to additional groups, we observed a number of discrepancies between the σ_m values listed in the compilations of Hammett[40] and of Jaffé[47] and the experimental σ_m^+ values. In almost every case where a major discrepancy was encountered the σ_m value proved to be a "secondary" or "tertiary" constant. In large part the discrepancies could be eliminated by re-evaluating the σ_m values, utilizing dissociation constants now available in the literature.

As a result of our experience, we wish to recommend a return to Hammett's original definition for σ, *i.e.*, the difference in pK_a values of benzoic acid

* Because of the large number of references to which attention must be called repeatedly throughout the paper, it has appeared more convenient to list them together at the end of the paper.

and a substituted benzoic acid. The ambiguity inherent in the development of "secondary" and "tertiary" σ values may be avoided by using for the establishment of ρ values only σ values obtained from the thermodynamic dissociation constants of benzoic acids in water at 25°. This does not rule out the evaluation and consideration of "secondary" σ values, but it would eliminate their use in determining ρ or in evaluating further σ values.

Jaffé's proposed redefinition of the σ constant would be useful in applying the Hammett equation primarily as an empirical tool for the correlation of rate and equilibrium data. However, recently, there has been evidenced considerable interest in examining the inductive and resonance components of the Hammett substituent constants in an effort to attain a better theoretical understanding of the influence of structure on chemical behavior.[65,86] For such theoretical studies, it appears more desirable that unambiguous values of the σ constants be available, together with a realistic estimate of the probable precision with which the individual constants are established by the experimental measurements. The availability of such data should facilitate both an understanding of the factors controlling the observed effects of the substituents and of the theoretical basis for deviations from the Hammett equation which lie outside the precision of the experimental measurements.

In a recent publication we had surveyed the literature on the effects of structure on the dissociation of acids and bases.[20] Consequently, with this preliminary survey available, it appeared desirable to gather together all of the available data to provide the basis for a critical appraisal of unambiguous values for the σ constants.

THE σ VALUES

The pK_a values of benzoic acid as determined by various investigators are given in Table I.

TABLE I

pK_a VALUES OF BENZOIC ACID AT 25°

Classical and Apparent	Conductance (Thermodynamic)	Potentiometric (Thermodynamic)
4.222[5,36]	4.200[19]	4.213[16]
4.164[97]	4.203[34]	4.228[18]
4.165[79]	4.203[35]	4.202[51]
4.183[83]	4.185[46]	4.175[55]
4.177[a,93]	4.215[76]	4.175[57]
4.174[10]	4.201[78]	4.202[35]
4.16, 4.15[90]	4.196[49,91]	4.188[35]
3.995[b,94]	4.205[53]	4.202[36]
Average	4.201 ± 0.005	4.198 ± 0.012

[a] μ = 0.03. [b] μ = 0.1 at 20°.

The constants listed under the heading of classical or apparent pK_a values are those determined from the Ostwald dilution law,[67] or from the midpoint of a pH titration[39] or by other methods which do not adequately take into account the activity, rather than concentration, of the species present. As has been noted by Dippy,[26] these pK values tend to be lower than the thermodynamic values, approaching the latter at high dilution. Since there is often a variation in the dilution at which the different substituted benzoic acids have been measured, the σ values calculated from the classical constants will reflect this variation. Of perhaps even greater importance is the failure of many early workers to establish the purity of their compounds.[26]

Inspection of the thermodynamic pK_a values in Table I indicates that the precision of the conductance method is slightly greater than the various potentiometric methods.* Furthermore, it is usually recognized as desirable to have a single set of values from one laboratory since procedural or systematic errors may to some extent cancel when σ values are obtained by Equation 5. The dissociation constants obtained by Dippy and co-workers are the most extensive set available and these values were obtained by conductance methods.[26-34] Accordingly, it appears reasonable to continue to use values obtained by Dippy and co-workers where such values are available. Thermodynamic dissociation constants obtained by other workers may be used as a check on the reliability of the data.

In Table II are listed the original σ values, based upon the dissociation constants of Dippy and co-workers, as well as a comparison with other values based upon both thermodynamic and classical dissociation constants. Agreement with other thermodynamic values at 25° is seen to be approximately ±0.01 unit, while the average deviation of the remaining data is ± 0.04.

Table III gives additional σ values, based upon data of Dippy *et al.* Also given in this Table are σ values from other data on ionization of benzoic acids in water and values of σ from Hammett and from Jaffé. These values of Hammett were not based on benzoic acid ionization, while the values of Jaffé represent assignments from all reactions of that particular substituent known to him at the time.

Major discrepancies are apparent between Jaffé's values and those based on Dippy's measurements for p-C_6H_5O and m-OH. The value due to Dippy *et al.* of σ for p-OH appears to be slightly low (by comparison with other thermodynamic data at 25°) and a value of −0.37 might reasonably be assigned to this group. For the p-CN group good agreement is found among the thermodynamic data and a σ value of 0.660 may be safely assigned to this group. With the m-CN group there is a surprising disagreement in thermodynamic values; an average value of 0.56 will be adopted.

The σ-constants in Tables II and III which were derived from the thermodynamic dissociation constants of the benzoic acids may be considered to be accurate to within ~0.02 units. Only these values, of those reported in this survey, should be used to establish ρ values.

SECONDARY SIGMA VALUES

Within recent years a large amount of data has become available on the ionization of substituted benzoic acids in 50% (by volume) ethanol measured with the glass electrode.† Using the σ values from Tables II and III, the data of Roberts and his co-workers (H, 5.80;[74] p-CH_3, 6.00;[74] p-CH_3O, 6.12;[74] p-Br, 5.35;[72] m-Br, 5.22;[72] m-OH, 5.61;[73] m-NO_2, 4.66;[72] p-NO_2, 4.53;[72] p-CN, 4.70[71]) and the data of Bordwell and Cooper (m-CH_3CO, 5.21;[14] p-CH_3CO, 5.10[14]), a value of ρ of 1.522 was calculated for the ionization of benzoic acid in 50% aqueous ethanol, with log K° = 5.761. (The calculations were made assuming σ to be more pre-

* It is of interest to note that some of the variation in the values obtained by the conductance method lies in the value assigned to the limiting mobility of the hydrogen ion.[91]

† The pK values obtained with a quinhydrone or hydrogen electrode in 50% alcohol appear to be significantly lower than those obtained with the glass electrode.[17]

TABLE II

σ VALUES ORIGINALLY DERIVED FROM THE DISSOCIATION CONSTANTS OF BENZOIC ACIDS

Group	Substituent Constants, σ			
	Hammett's values[43]	Derived from thermodynamic data at 25°	Derived from thermodynamic data, not at 25°	Derived from classical and apparent data
p-CH_3O	−0.268[34]		−0.22,[22] −0.29[52]	−0.28,[94] −0.27,[66] −0.25[90] −0.31,[79] −0.26[68]
p-*t*-C_4H_9	−0.197[27]			−0.194[83]
p-CH_3	−0.170[31]			−0.18,[79] −0.20,[92] −0.07[66] −0.19,[10] −0.20[90]
p-*i*-C_3H_7	−0.151[27]			−0.11[10]
p-C_2H_5	−0.151[27]			
m-CH_3	−0.069[31]			−0.08,[79] −0.09[92] −0.07,[66] −0.08,[90] −0.20[90]
p-F	0.062[33]		0.16[58]	
m-CH_3O	0.115[31]		0.12[52]	0.14,[68] 0.15 to 0.24[90]
p-Cl	0.227[33]	0.227,[16] 0.203[78]		0.06,[84] 0.20,[94] 0.16[90]
p-Br	0.232[33]	0.211[16]		0.23[90]
m-F	0.337[31]		0.35[58]	
m-I	0.352[31]			0.31,[79] 0.37[90]
m-Cl	0.373[33]	0.386,[16] 0.379[78]		0.36,[84] 0.46[90]
m-Br	0.391[31]	0.395[16]		0.25,[84] 0.38[90]
m-NO_2	0.710[31]			0.72,[79,10] 0.76,[66,90] 0.80[90]
p-NO_2	0.778[31]	0.771[16]		0.82,[66] 0.76,[90] 0.73[94] 0.78,[10] 0.80[64]

TABLE III

NEW σ VALUES BASED ON THE IONIZATION OF BENZOIC ACIDS

Group	Substituent Constants, σ					
	Hammett's values[a,4]	Jaffé's values[a,47]	Values based on Dippy's data	Derived from other thermodynamic data at 25°	Derived from thermodynamic data not at 25°	Derived from classical and apparent data
p-C_6H_5O		−0.028	−0.320[32]			
p-OH		−0.357	−0.327[29]	−0.369[16] −0.37[77]	−0.28[58] −0.32[22] −0.39[52] −0.41[62] 0.09[1]	−0.32[66,90] −0.37[95] −0.38[92]
3,4$(CH)_4$[b]	0.170		0.042[30]			0.053[8] 0.051[59] 0.024[25]
m-OH		−0.002	0.121[29]		0.04[52] 0.14[58] 0.30[1]	0.07,[92] 0.00[84] 0.03,[95] 0.16[66] 0.05 to 0.22[90]
m-C_6H_5O			0.252[32]			
m-CH_3CO	0.306		0.376[28]			
p-CH_3CO		0.516	0.502[28]			
m-CN	0.678			0.615[16] 0.520[54]		0.52[66] 0.60[93]
p-CN		0.628		0.662[16] 0.651[54] 0.666[55,89]		0.66[93]

[a] Not derived from benzoic acid ionization data. [b] β-Naphthyl.

cisely known than *p*K′. The correlation coefficient is 0.995.) Using these values in Equation 1, the σ values given in Table IV have been calculated. The σ values of Hammett and of Jaffé have been listed for comparative purposes, many of the σ values of the latter have been based in part on the ionization data in 50% alcohol.

The variation of *p*K′ values of benzoic acid itself in 50% alcohol obtained with the use of the glass electrode, *i.e.*, 5.70 (at 20°)[36] 5.73,[14] 5.75,[72] 5.80,[74] is probably typical of the precision of these data. Direct comparison of the σ values derived from the *p*K′ in 50% alcohol with those obtained in water using the glass electrode may be made in the cases of the groups $(CH_3)_3Si$, PO_3H^-, and CH_3SO_2. Such comparison indicates that the σ values in Table IV are probably reliable to approximately ±0.1 unit. Solvation effects may be the source of some difference in σ in water and 50% alcohol.

Ionization data for substituted benzoic acids in other concentrations of aqueous alcohol may be used to obtain σ values for other groups. Thus Chatt and Williams[23] have shown that in the *para* position the groups $(CH_3)_3Si$, $(C_2H_5)_3Si$, $(CH_3)_3Ge$, $(C_2H_5)_3Ge$, $(CH_3)_3Sn$, and $(C_2H_5)_3Sn$ have *p*K′ values within ±0.03 of that of benzoic acid itself

TABLE IV

σ-VALUES CALCULATED FROM THE APPARENT DISSOCIATION CONSTANTS AT 25° OF BENZOIC ACID IN 50% (BY VOLUME) ETHANOL

Group	Substituent Constants, σ			
	Hammett's values[43]	Jaffé's values[47]	Derived from pK′ values in 50% alcohol	Derived from classical and apparent pK_a values in water
p-$(CH_3)_3SiCH_2$			−0.210[a,36]	
m-$(CH_3)_3SiCH_2$			−0.157[a,36]	
m-$(CH_3)_3Si$		−0.121	−0.157[74]	−0.04[5]
p-$(CH_3)_3Si$		−0.072	−0.026[74]	−0.07[5]
p-CH_3S	−0.047		0.014,[14] −0.026[b,4]	
p-C_2H_5S			0.034[b,4]	
p-CH_3CONH		−0.015	0.053[12]	−0.06[66]
p-i-C_3H_7S			0.067[b,4]	
m-CH_3S		0.144	0.152[14]	
p-PO_3H^-		0.238	0.263[48]	0.25[48]
m-CH_3CONH			0.270[12]	0.15[66]
m-PO_3H^-			0.309[48]	0.17[48]
p-CH_3CO_2			0.309[12]	−0.16[66]
m-$C_2H_5O_2C$		0.398	0.369[73]	
m-CH_3COS			0.388[12]	
m-CH_3CO_2		0.315	0.395[12]	0.22,[66] 0.31[84]
m-CF_3		0.415	0.428[75]	0.41[85]
p-CH_3COS			0.441[12]	
p-$C_2H_5O_2C$		0.522	0.451[73]	
p-CH_3SO		0.567	0.493[13]	
m-CH_3SO		0.551	0.520[13]	
p-SCN		0.699	0.520[12]	
p-CF_3		0.551	0.540[75]	
m-CN	0.678		0.598[71]	See Table III
m-CH_3SO_2		0.647	0.645,[14] 0.658[56]	0.56[56]
p-CH_3SO_2		0.728	0.710,[14] 0.756[56]	0.68[56]
p-$(CH_3)_3N^+$		0.859	0.881[70]	0.77[60]
m-$(CH_3)_3N^+$		0.904	1.012[70]	0.75[24]

[a] 18°. [b] 32°.

TABLE V

σ VALUES ESTIMATED FROM DISSOCIATION OF BENZOIC ACID IN AQUEOUS ALCOHOL AT VARIOUS CONCENTRATIONS

Group	Substituent Constants, σ			Concentration of Ethanol
	Hammett's values[43]	Jaffé's values[47]	Estimated values	
m-NH_2	−0.161		−0.07 to −0.20	55:45 Ethanol-water and 50(vol)% ethanol
m-C_2H_5		−0.043	−0.07	55:45 ethanol-water
p-$(C_2H_5)_3Si$			0.0	60.1 wt. % ethanol
p-$(CH_3)_3Ge$			0.0	60.1 wt. % ethanol
p-$(C_2H_5)_3Ge$			0.0	60.1 wt. % ethanol
p-$(CH_3)_3Sn$			0.0	60.1 wt. % ethanol
p-$(C_2H_5)_3Sn$			0.0	60.1 wt. % ethanol
p-CH_3Se			0.0	30 (vol.) % ethanol
m-CH_3Se			0.10	30 (vol.) % ethanol
p-SH			0.15	48.9% ethanol
m-SH			0.25	48.9% ethanol
p-C_6H_5	+0.009		−0.01	50% butylcellosolve[a]
m-C_6H_5	+0.218		0.06	50% butylcellosolve[a]

[a] Ionic strength 0.05 in lithium chloride.

in 60.1 weight % ethanol. Accordingly all of these groups may be assigned a σ value of 0.0 ± 0.1. Likewise, the data of Baker, Barrett, and Tweed[3] show that in 30% by volume aqueous alcohol the pK′ of CH_3S and CH_3Se substituted benzoic acids lie within 0.01 unit of each other. Accordingly, the σ value assigned to m-CH_3Se should be the same as that assigned to m-CH_3S and likewise the σ of p-CH_3Se should be the same as p-CH_3S. The data of Baker *et al.* further indicate that the σ value for m-CH_3O should be greater than m-CH_3S (by ~0.02 units), *i.e.*, the σ value for m-CH_3S in Table IV is probably high by ~0.05 units.

From the pK′ values of Schwarzenbach and Rudin[80] for the isomeric hydroxy and mercapto benzoic acids in 48.9% alcohol the σ value of the p-SH group should be about 0.03 unit greater than that of m-OH. From this σ for p-SH may be set at ~0.15 ± 0.1. The σ value for m-SH

TABLE VI

σ VALUES FROM CLASSICAL AND APPARENT IONIZATION CONSTANTS OF BENZOIC ACIDS IN WATER

Group	Substituent Constants, σ		
	Hammett's values[43]	Jaffé's values[47]	Derived from classical ionization constants
p-$(CH_3)_2N$	−0.205	−0.600	−0.83[50]
p-CH_3NH		−0.592	−0.84[50]
p-NH_2	−0.660		−0.66 to −0.70,[90] −0.70,[81] −0.62,[2] −0.73[45] −0.72,[50] −0.6,[44] −0.66,[61] −0.98[92]
p-C_2H_5O	−0.25		−0.07,[68] −0.57,[52] −0.24[22]
p-n-C_3H_7O		−0.268	−0.55,[52] −0.25[22]
p-n-C_4H_9O		−0.320	−0.32[22]
p-i-C_3H_7O		−0.286	−0.45[52]
p-n-$C_5H_{11}O$		−0.340	−0.34[22]
m-t-C_4H_9		−0.120	−0.10[83]
m-CO_2^-		0.104	−0.05 to −0.14,[90] +0.021,[63] −0.10,[9] −0.10[88] 0.075[87]
p-CO_2^-		0.132	0.16 to −0.05,[90] −0.05,[95] +0.04[88]
p-AsO_3H^-		−0.019	−0.02[69]
m-SO_3^-			0.05[96]
p-SO_3^-		0.381	0.09[96]
p-I	0.276		0.18[90]
m-C_2H_5O	0.150		0.186,[68] 0.05[52]
m-n-C_3H_7O			0.03[52]
m-i-C_3H_7O			0.08[52]
m-n-C_4H_9O			−0.02[52]
m-CO_2H	0.355		0.38,[66] 0.46,[99] 0.28,[88] 0.18,[87] 0.42[63]
p-CO_2H	0.728		0.66,[90] 0.51,[58] 0.36[88]
m-NH_2SO_2			0.46[97]
p-NH_2SO_2		0.621	0.62,[82] 0.53[97]
m-IO_2		0.70	0.70[15]
p-IO_2		0.76	0.76[15]
p-$(CH_3)_2S^+$			0.90[11]
m-$(CH_3)_2S^+$			1.00[11]

should be about 0.1 higher, giving a σ value for this group of ~0.25 ± 0.1.

Beringer and Sands[6] report the same pK' value for m-C_2H_5 and m-CH_3 benzoic acid in 55:45 ethanol-water, hence the σ value for m-C_2H_5 may be set at −0.07. Beringer and Sands also report a pK' for m-aminobenzoic acid of about the same magnitude as m-methylbenzoic acid, while in 50 volume % alcohol Bright and Briscoe[17] report a pK' for m-aminobenzoic acid which is slightly more than that of p-methylbenzoic acid.* From these data the σ value of m-NH_2 should lie in the range −0.07 to −0.20. Hammett's value of −0.161 (derived from ester hydrolysis at 30° in 87.83% alcohol) is within this range.[43]

Finally, from the pK' values at 25° of benzoic acid (5.65), m-phenyl- (5.57) and p-phenylbenzoic acids (5.66) in 50% aqueous butylcellosolve, ionic strength 0.05 in lithium chloride (ρ = 1.32), the σ values of m-C_6H_5 and p-C_6H_5 can be estimated as +0.06 and −0.01 respectively. These estimates are summarized in Table V.

VALUES FROM CLASSICAL IONIZATION CONSTANTS

The σ values presented in Table VI are based on classical and apparent pK values of the benzoic acids in water, or on thermodynamic values at temperatures other than 25°. The reliability of the data varies widely.

There are two sets of thermodynamic pK_a values of the p-n-alkoxybenzoic acids at 20° available. Those of Cavil, Gibson, and Nyholm[22] have been used by Jaffé to establish the σ values of the n-C_4H_9O and n-$C_5H_{11}O$ groups. The precision of the pK data was given as ±0.1. The data of Jones and Speakman[52] give σ values which differ considerably from those of Cavil *et al.* and which give σ values for the higher p-n-alkoxy groups which differ considerably from that of p-CH_3O. Accordingly, it is believed that the data of Cavil *et al.* are to be preferred. For the *meta* alkoxy groups Jones and Speakman indicate greater precision, but again the rather wide variation of values from that for m-CH_3O indicates that the σ values for these derivatives are probably questionable. An approximate σ value of 0.1 is assigned to these groups.

Thermodynamic pK_a data for p-aminobenzoic acid give a value of −0.66 for the p-NH_2 group in excellent agreement with the value assigned to this group by Hammett. This may be somewhat fortuitous, since Willi and Meier estimate that 9.5% zwitterion exists in this system.[94] For the p-$NHCH_3$ and p-$N(CH_3)_2$ groups the classical data of Johnson[50] has been used to obtain σ values. Comparison of the value assigned to p-NH_2 from Johnson's calculations on Winkelbleck's data makes it appear that these values are probably larger than they should be by 0.05 to 0.10 units.

The excellent agreement of the σ-value for p-t-C_4H_9 (see Table II) from the conductance data of Shoesmith and Mackie[83] with that of Dippy *et al.* makes it seem reasonable to place limits of ±0.03 on the σ value of m-t-C_4H_9 in Table VI.

Comparison of the numerous values in Tables II and III from the data of Vandenbelt *et al.* with those of Dippy *et al.* indicates a probable limit of ±0.1 in the accuracy of the σ value for p-I.

* The pK value of m-aminobenzoic acid in water is not used here in assigning a σ value since in water the "neutral" species exists to a large extent as the zwitterion. According to Ebert[37] the ratio of zwitterion to uncharged species is given by $K_1/K_E - 1$ where K_1 is the first acid dissociation constant of the amino acid and K_E is the ionization constant of an alkyl ester of the amino acid. From the data of Cumming[24] the ratio of zwitterion to uncharged species in water is thus approximately 2.2. In alcoholic solution the pK of the amino group decreases while that of the carboxyl group increases, greatly reducing the ratio of zwitterion to uncharged species.

TABLE VII

SUMMARY OF HAMMETT SUBSTITUENT CONSTANTS, σ, BASED ON IONIZATION OF SUBSTITUTED BENZOIC ACIDS[a]

	Meta			Para		
Group	σ	Estimated limits of uncertainty	Table	σ	Estimated limits of uncertainty	Table
—CH_3	**−0.069**	0.02	II	**−0.170**	0.02	II
—CH_2CH_3	−0.07	0.1	V	**−0.151**	0.02	II
—$CH(CH_3)_2$				**−0.151**	0.02	II
—$C(CH_3)_3$	−0.10	0.03	VI	**−0.197**	0.02	II
—C_6H_5	0.06	0.05	V	−0.01	0.05	V
—3,4$(CH)_4$				**0.042**	0.02	III
—CF_3	0.43	0.1	IV	0.54	0.1	IV
—CN	**0.56**	0.05	III	**0.660**	0.02	III
—$COCH_3$	**0.376**	0.02	III	**0.502**	0.02	III
—$CO_2C_2H_5$	0.37	0.1	IV	0.45	0.1	IV
—CO_2H	(0.37)	0.1	VI	(0.45)	0.1	VI
—CO_2^-	−0.1	0.1	VI	0.0	0.1	VI
—$CH_2Si(CH_3)_3$	−0.16	>0.1	IV	−0.21	>0.1	IV
—$Si(CH_3)_3$	−0.04	0.1	IV	−0.07	0.1	IV
—$Si(C_2H_5)_3$				0.0	0.1	V
—$Ge(CH_3)_3$				0.0	0.1	V
—$Ge(C_2H_5)_3$				0.0	0.1	V
—$Sn(CH_3)_3$				0.0	0.1	V
—$Sn(C_2H_5)_3$				0.0	0.1	V
—NH_2	−0.16	0.1	V	−0.66	0.1	VI
—$NHCH_3$				−0.84	0.1	VI
—$N(CH_3)_2$				−0.83	0.1	VI
—$NHCOCH_3$	0.21	0.1	IV	0.00	0.1	IV
—$N(CH_3)_3^+$	0.88	>0.2	IV	0.82	>0.2	IV
—NO_2	**0.710**	0.02	II	**0.778**	0.02	II
—PO_3H^-	0.2	>0.1	IV	0.26	>0.1	IV
—AsO_3H^-				−0.02	>0.1	VI
—OCH_3	**0.115**	0.02	II	**−0.268**	0.02	II
—OC_2H_5	0.1	0.1	VI	−0.24	0.1	VI
—$O(CH_2)_2CH_3$	0.1	0.1	VI	−0.25	0.1	VI
—$OCH(CH_3)_2$	0.1	0.1	VI	−0.45	0.1	VI
—$O(CH_2)_3CH_3$	0.1	0.1	VI	−0.32	0.1	VI
—$O(CH_2)_4CH_3$	0.1	0.1	VI	−0.34	0.1	VI
—OC_6H_5	**0.252**	0.02	III	**−0.320**	0.02	III
—OH	**0.121**	0.02	III	**−0.37**	0.04	III
—$OCOCH_3$	0.39	0.1	IV	0.31	0.1	IV
—SCH_3	0.15	0.1	IV	0.00	0.1	IV
—SC_2H_5				0.03	0.1	IV
—$SCH(CH_3)_2$				0.07	0.1	IV
—SH	0.25	0.1	V	0.15	0.1	V
—$SCOCH_3$	0.39	0.1	IV	0.44	0.1	IV
—SCN				0.52	0.1	IV
—$SOCH_3$	0.52	0.1	IV	0.49	0.1	IV
—SO_2CH_3	0.60	0.1	IV	0.72	0.1	IV
—SO_2NH_2	0.46	0.1	VI	0.57	0.1	VI
—$S(CH_3)_2^+$	1.00	>0.1	VI	0.90	>0.1	VI
—SO_3^-	0.05	>0.1	VI	0.09	>0.1	VI
—$SeCH_3$	0.1	0.1	V	0.0	0.1	V
—F	**0.337**	0.02	II	**0.062**	0.02	II
—Cl	**0.373**	0.02	II	**0.227**	0.02	II
—Br	**0.391**	0.02	II	**0.232**	0.02	II
—I	**0.352**	0.02	II	0.18	0.1	VI
—IO_2	0.70	0.1	VI	0.76	0.1	VI

[a] Values in bold faced type are σ constants based on thermodynamic constants in water at 25°. It is recommended that the reaction constants, ρ, be based on these σ constants.

The σ values for the *m*- and *p*-IO_2 groups are from the data of Bothner-By and Medalia[15] obtained at 50°. The original authors indicate a ρ for dissociation at this temperature of 1.09 and report σ values of 0.63 and 0.69 respectively for the meta and para substituents. The original authors' values are probably better assignments of σ, but the ρ is probably due more to systematic errors rather than a real change (*cf.* Briegleb's data[16] and the variation of ρ with T assigned by Jaffé[47]). From the precision of Bothner-By and Medalia, limits of ±0.06 may be assigned to their values of σ or of $\sim \pm 0.12$ to the values in Table VI.

In similar fashion, the σ values for *m*- and *p*-NH_2SO_2 given in Table VI are 0.09 units lower than those reported by Zollinger and Wittwer.[97] Since the measurements were made in a medium of ionic strength of 0.1, and the ρ value apparently differs from unity, the values assigned by the original authors may be more accurate than those given in Table VI.

There is considerable variation in the σ values assigned to the m- and p-CO_2H groups on the basis of pK data (corrected for a statistical factor of 2 in K_a). Accordingly it seems reasonable to assign values to these groups by resorting to the practice of assuming the electrical effects of the carboxyl group are approximately equal to those of carbalkoxy groups. Hammett's value for m-CO_2H thus receives support from Table IV (σ for m-$C_2H_5O_2C$ is 0.37); however, his value for p-CO_2H may be questioned (σ for p-$C_2H_5O_2C$, 0.45).

Again, for the m- and p-CO_2^- groups there is considerable variation, however the average σ for m-CO_2^- is -0.1 while that of p-CO_2^- group is 0.0. The σ value of these groups, as well as those of the remaining groups which bear a charge, are subject to large activity corrections and accordingly limits of somewhat larger than 0.1 appear reasonable.

SUMMARY

Hammett σ values have been compiled from the literature data of the ionization of benzoic acids. Hammett's original values given in Table II and further values from the data of Dippy *et al.* in Table III (with the exception of p-OH) are probably reliable within approximately 0.02 unit. The values in Table IV are based on ionization of benzoic acids in 50% ethanol and approximate limits of ± 0.1 have been set here. Table V contains estimates of σ from ionization data in various concentrations of ethanol and the limits may be set somewhat in excess of 0.1. Table VI contains σ values from classical ionization data with widely varying limits of error to the values assigned to σ.

For convenience in utilization, the individual σ values have been summarized in Table VII, together with an estimate of the probable uncertainty. Reference is given to the particular table which lists both the individual measurements and the literature references. The σ values based on thermodynamic data are shown in bold faced type. According to the recommendation advanced here, only these values should be used for the calculation of ρ. All other σ constants are derived values.

It is apparent from this survey that additional precise thermodynamic dissociation constants for the ionization of substituted benzoic acids are greatly to be desired.

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Kinetics of the Reaction between a Vinyl Fluoride and Sodium Ethoxide

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The synthesis of 1,1-diphenyl-2-fluoroethylene is reported. This vinyl fluoride is converted to 1,1-diphenyl-2-ethoxyethylene by sodium ethoxide in ethanol. At 99.75° the kinetics are second-order, first-order with respect to each reactant, and the rate is 270 times faster than that of 1,1-diphenyl-2-chloroethylene. The results are consistent with an addition-elimination mechanism.

The unexpectedly high reactivity of fluorine attached to unsaturated carbon atoms toward nucleophilic substitution has been observed by a number of workers.[1-6] For example, piperidine reacts with 2,4-dinitrofluorobenzene more rapidly than with the other 2,4-dinitrohalobenzenes.[1] Also, the vinylic fluorine atoms of perfluorocyclobutene can be replaced by ethoxide more readily than the allylic ones.[2] These observations probably rule out an S_N2 displacement mechanism that

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