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WORKING PARTY ON STRUCTURE-REACTIVITY PARAMETERS AND EQUATIONS†

COMPILATION AND CRITICAL EVALUATION OF STRUCTURE-REACTIVITY
PARAMETERS AND EQUATIONS: PART I.

VALUES OF σ_m AND σ_p BASED ON THE
IONIZATION OF SUBSTITUTED BENZOIC ACIDS
IN WATER AT 25°C

(Technical Report)

Prepared for publication by

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Compilation and critical evaluation of structure-reactivity parameters and equations. Part 1. Values of σ_m and σ_p based on the ionization of substituted benzoic acids in water at 25°C (Technical Report)

Abstract - Data have been compiled for the pK_a values in water at 25°C of about 60 *meta*- or *para*-substituted benzoic acids, with a view to proposing recommended values of Hammett substituent constants, σ . The number of substituents covered is about one-half of this number, but for certain substituents data are not available for both the *meta* and the *para* position. The amount and the reliability of the data vary greatly from one acid to another. Critical appraisal leads to the classification of the substituents and their σ values as belonging to a First Division (with more reliable data) or a Second Division (with less reliable data). The substituents in the former category are: Me, NO₂, OMe, F, Cl, and Br (each in both the *meta* and the *para* position). Recommended values of σ are tabulated for substituents in each Division, but for certain members of the Second Division there are *caveats* because the data show discrepancies.

INTRODUCTION

Various linear free energy relationships were discovered in the early 1930s for the side-chain reactions of *meta*- or *para*-substituted benzene derivatives. Hammett's signal contribution [Hammett (1937)] lay essentially in recognizing the value of taking one reaction as a standard process, with which all other relevant reactions could be compared. Much information on reactivity could thereby be summarized in terms of a very simple mathematical equation, with its characteristic constants. The concept of the 'standard reaction series' has dominated the development of correlation analysis in organic chemistry. As the subject has expanded to take in a wider variety of data and as the analysis has been made more precise, the number of standard processes has grown.

Equations (1) and (2) show the basic form of the Hammett equation:

$$\begin{aligned}\log k &= \log k^\circ + \rho \sigma & (1) \\ \log K &= \log K^\circ + \rho \sigma & (2)\end{aligned}$$

in which k or K is the rate or equilibrium constant, respectively, for a side-chain reaction of a *meta*- or *para*-substituted benzene derivative. The symbol k° or K° denotes the statistical quantity (intercept term) approximating to k or K for the 'parent' or 'unsubstituted' compound. The *substituent constant*, σ , measures the polar (electronic) effect of replacing H by a given substituent (in the *meta*- or *para*-position) and is, in principle, independent of the nature of the reaction. The *reaction constant*, ρ , depends on the nature of the reaction (including conditions such as solvent and temperature) and measures the susceptibility of the reaction to polar effects. Hammett chose the ionization of benzoic acids in water at 25°C as the standard process. For this, ρ is defined as 1.000, and the value of σ for a given substituent is then $\log(K/K^\circ)$, where K_a is the ionization constant of the substituted benzoic acid and K°_a that of benzoic acid itself.

Hammett's choice of standard reaction appears to have been considerably influenced by the availability of fairly accurate values for the ionization constants of substituted benzoic acids, largely measured in the mid-1930s by J.F.J. Dippy and his co-workers [Dippy (1939)]. These were obtained by conductance measurements and were claimed to be 'thermodynamic' constants, i.e. all the necessary corrections had been made to ensure that the values were based on 'activities' rather than 'concentrations'. (Ionization constants essentially based on the latter may be described as 'apparent' or 'classical' constants.) It should be noted, however, that even in Hammett's publications [Hammett (1937,1940)] only a minority of the

σ values tabulated were based directly on the ionization of substituted benzoic acids in water at 25°C. In the Table in Chapter 7 of Hammett (1940) the proportion is 17 entries out of 44. Most of the σ values given depended on first applying the Hammett equation to various reactions (e.g. the rates of alkaline hydrolysis of ethyl benzoates in 87.83% ethanol-water at 30°C) by using the data relating to substituents for which σ values based on the ionization of substituted benzoic acids were available, and then applying the established ρ values to the relevant experimental results for other substituents. Thus, right from the start, as pointed out by McDaniel and Brown (1958), there was but a limited number of 'primary' σ values; there were a larger number of 'secondary' σ values, and even some which might be termed 'tertiary', the last-mentioned being based on correlation equations which had been established by using a mixture of primary and secondary σ values. This situation, in fact, led McDaniel and Brown (1958) to suggest that secondary σ values should as far as possible be based on ionization constants of benzoic acids in aqueous organic solvents such as 50% ethanol-water, rather than on rate or equilibrium measurements for a wider range of systems.

Since the late 1930s there have been many studies of the ionization of substituted benzoic acids in water, some of them of rather greater accuracy than those of Dippy and co-workers. The range of substituents studied has also increased, although limitations imposed by insolubility in water and the sensitivity of certain substituents to water still apply. Compilations of ionization constants of organic acids in water have twice been made in publications under IUPAC auspices.

The first of these was by Kortüm, Vogel, and Andrussov (1961). In this publication the descriptive text was given in both an English and a German version, but the Tables were in German only. The text was mainly a detailed critical survey of the various methods of measurement, occupying some 20 pp. in each language. In the Tables the various determinations for each acid were summarized, with indications of experimental and calculation methods (referring back to the earlier text), experimental conditions (temperature, concentration, ionic strength, etc.), the numerical results (the values tabulated usually being those of thermodynamic constants), and a 'Kritik' of the reliability of the constants tabulated. The last-mentioned was in the following terms:

"sehr zuverlässig" (*s. zuv.* = very reliable): estimated uncertainty of some tenths of a percent in K_a ; $\Delta pK_a \approx \pm 0.0005$.

"zuverlässig" (*zuv.* = reliable): estimated uncertainty of ca. 1 percent in K_a ; $\Delta pK_a \approx \pm 0.005$.

"relativ zuverlässig" (*rel. zuv.* = approximate): estimated uncertainty of several percent in K_a ; $\Delta pK_a \leq \pm 0.04$.

"unsicher" (= uncertain): estimated uncertainty of more than 10 percent in K_a ; $\Delta pK_a \geq \pm 0.04$.

The second compilation was by Serjeant and Dempsey (1979). This work was entirely in English and used the same general approach and arrangement as in the earlier publication. The experimental results were, however, expressed as pK_a values, and not as simple values of K_a as was done in the earlier work. Further, a distinction between "very reliable" and "reliable" in the critical assessment was no longer made, the two categories being subsumed under "reliable" ($\Delta pK_a \leq \pm 0.005$). A further category of "very uncertain" was introduced, "where the uncertainty cannot be estimated but is likely to be very great". The volume contains a useful combined index to entries in both volumes.

In making the present compilation of σ values based on the ionization constants of benzoic acids in water, extensive use has been made of the above volumes, but the more important original papers referred to therein have often been consulted. A number of relevant studies have been published subsequently to 1979. These include studies in aqueous organic solvents containing only a small percentage ($\leq 10\%$ v/v) of the organic component. Such studies may permit the calculation, by appropriate extrapolation, of σ values proper to behaviour in water.

BACKGROUND INFORMATION FOR TABLES AND NOTES

Experimental data for ionization constants in water at 25°C (in the main thermodynamic constants) are available for about sixty *meta*- or *para*-substituted benzoic acids. The number of substituents covered is about one-half of this number, but for certain substituents data are not available for both *meta*- and *para*-positions. The amount of data varies enormously from one acid to another. Thus for *para*-nitrobenzoic

acid, determinations by five different research groups require consideration; for *para*-fluorobenzoic acid there are three determinations, while for *para*-carbamoylbenzoic acid and for *meta*-ethoxybenzoic acid the data comprise solitary determinations. Only data regarded in the IUPAC compilations as Reliable or Approximate are normally considered (data classified as Very Reliable in the first volume are subsumed under the category Reliable). In the case of data not appearing in the IUPAC volumes, the present author has essayed an assessment along the same lines. The whole body of data falls roughly into two groups. On the one hand there are acids for which there are several determinations (usually involving more than one type of experimental method), of which at least one is assessed as Reliable, and which are reasonably concordant. On the other hand there are acids for which there is only a very limited number of determinations, perhaps involving only one type of experimental method, of which most if not all are classified as Approximate, and which may show some striking lack of mutual agreement. Thus it is possible to classify the substituents and corresponding σ values as belonging to the First Division or Second Division respectively. (It has been possible to avoid classifying a given substituent X in one division for *m*-X and the other for *p*-X).

The σ values for the First and the Second Division are shown in Tables 1 and 2 respectively. It has seemed convenient to number the entries in Table 2 to follow on from those of Table 1. In each Table the substituents are presented in the same order in which they appear in the Tables in the compilation of substituent constants by Exner (1978). To facilitate comparisons, the ordinal number in Exner's Tables is repeated in our Tables. In this system the substituents are arranged according to the 'first atom', i.e. that bonded to the benzene ring: H, C, and then others in a sequence according to the Groups of the Periodic System; in each Group, the arrangement proceeds according to the 'next atoms', with single-bonded 'next atoms' preceding multiple-bonded ones.

Following Hammett (1937, 1940) values of σ have often been given to three places of decimals, even though the reliability of the experimental results does not really justify this (see below). The calculations as detailed in the Notes keep three places of decimals (unless the data are restricted to two places), but the resulting mean values are rounded up or down to two decimal places for Table 1 and 2. (Manipulations of σ values should be done with the unrounded σ values in the Notes.)

The calculations of mean values include a weighting factor of 2 for Reliable data and of 1 for Approximate data. This choice of weighting factors is arbitrary but does bear a sensible relationship to the reliability of the data in question. (Often the weighted mean differs little from a straightforward mean, but it seems proper to pay such attention to the differing reliabilities of data.)

The assessment of the reliability of individual σ values in numerical terms is a difficult matter. The number of determinations is usually too small for any formal treatment of errors to be applicable. McDaniel and Brown (1958) attempted to deal with this problem in terms of a 'limit of uncertainty', which was not too clearly defined. Exner (1978) adopted the same practice. It is the kind of procedure which is often adopted in chemistry to express the feeling, based on the reproducibility of a given result, that a particular numerical value "is good to within a certain number of units". We have essentially adopted this practice here. When there are several determinations of the pK_a value, the spread and distribution of values gives a guide to the reliability of the mean σ value. It is usually accepted that most of the uncertainty in a given σ value lies in the pK_a value of the substituted benzoic acid, that for benzoic acid itself being known much more precisely. When the experimental data are meagre, we base our assessment on an uncertainty of 0.01 for a σ value from a Reliable value of pK_a and of 0.02 for one from an Approximate value. (It seems likely that for many Approximate values of pK_a , the reliability is rather better than suggested by the $\Delta pK_a \leq \pm 0.04$.) Sometimes rather great uncertainty is attributed to the σ value because of discrepant data. Naturally when a σ value depends on a solitary determination, an estimate of its reliability is of very limited significance. Notice has also been taken of particular authors' views as to the reliability of σ values determined by them.

The values given in Tables 1 and 2 are thus the best values which can at present be provided for σ constants based on the ionization of benzoic acids in water at 25°C. Readers who require such values but do not wish to examine carefully the considerations which underlie them may use them with some confidence. The detailed considerations are given in the Notes for those who wish to examine them.

TABLE 1. Values of σ_m and σ_p based on the ionization of substituted benzoic acids in water at 25°C. First Division.

Entry and Note Number	Exner Number	Substituent	σ_m	Limit of uncertainty	σ_p	Limit of uncertainty
				\pm		\pm
1	1	H	0.00	—	0.00	—
2	3	Me	-0.06	0.01	-0.16	0.01
3	346	NO ₂	0.73	0.02	0.78	0.01
4	390	OMe	0.11	0.01	-0.29	0.02
5	490	F	0.34	0.01	0.05	0.01
6	491	Cl	0.37	0.01	0.22	0.01
7	492	Br	0.40	0.01	0.23	0.02

TABLE 2. Values of σ_m and σ_p based on the ionization of substituted benzoic acids in water at 25°C. Second Division.

Entry and Note Number	Exner Number	Substituent	σ_m	Limit of uncertainty	σ_p	Limit of uncertainty
				\pm		\pm
8	4	Et	-0.06	0.02	-0.15	0.02
9	7	Pr ⁱ	-0.08	0.02	-0.15	0.02
10	11	Bu ^t	-0.07	0.02		See Note 10
11	19	CH:CH ₂	0.08	0.03	-0.08	0.03
12	30	cyclopropyl	-0.07	0.02	-0.21	0.02
13	103	CH ₂ OH	0.07	0.02	—	—
14	132	CF ₃	0.44	0.03	—	—
15	181	CHO		See Note 15		
16	182	COMe	0.37	0.02	0.49	0.02
17	189	CONH ₂	—	—	0.31	0.02
18	194	CO ₂ H		See Note 18		
19	195	CO ₂ Me	0.33	0.02	0.45	0.02
20	203	CN	0.62	0.02	0.67	0.02
21	251	SiMe ₃		See Note 21		
22	285	NH ₂	0.00	?	-0.62	0.02
23	287	NMe ₂	—	—	-0.69	0.02
24	297	NHAc	0.17	0.02	-0.06	0.02
25	375	PO(OMe) ₂	0.42	0.03	0.55	0.03
26	389	OH	0.10	0.04	-0.36	0.03
27	391	OEt	0.10	0.02	—	—
28	395	OPh	0.26	0.02		See Note 28
29	424	SH	0.25	0.02	—	—
30	425	SMe	—	—	0.01	0.02
31	453	SOMe	—	—	0.53	0.02
32	461	SO ₂ Me	0.68	0.02	0.72	0.02
33	472	SO ₂ NH ₂	0.53	0.02	0.58	0.02
34	493	I	0.35	0.02	0.23	0.04

THE STRUCTURE OF THE NOTES

Each note usually contains certain information in a standard form, together with some textual comment as applicable to the given entry.

The standard form involves the listing of the individual determinations which contribute to the tabulated weighted mean σ value, followed by the appropriate literature citation. Then in square brackets we give the entry number in the IUPAC compilation, where applicable (Nos. in the range 1 - 1056 are in Kortüm *et al*; those in the range 2001 - 6521 are in Serjeant and Dempsey), the pK_a value (K_a values in Kortüm *et al* are converted to pK_a), the experimental method (S = spectrophotometric; C = conductance; EH = electrometric with hydrogen electrode; EG = electrometric with glass electrode; SE = a combination of spectrophotometric and electrometric methods) and assessment of reliability (R = Reliable; A = Approximate). (See the summary below of the paper by Matsui *et al* for the special position of this paper in the matter of assessment of reliability.)

Summaries of the more important source papers are given after the Notes.

NOTES FOR TABLES 1 AND 2

Note 1: H

The most reliable determinations of the thermodynamic pK_a of benzoic acid in water at 25°C are cited by Serjeant and Dempsey (entry 3388) as follows:

Fischer, Mann, and Vaughan (1961): 4.205 (conductance)

King and Prue (1961): 4.205 (electrometric, glass electrode)

Bolton, Fleming, and Hall (1972): 4.204 (spectrophotometric and electrometric)

In calculating values of σ_m and σ_p we have used 4.205 for the pK_a value of benzoic acid, unless the authors concerned have determined their own value (or sometimes cited a special value) as standard. Thus pK_a values for benzoic acid have been taken as follows in connection with the principal papers involved:

Saxton <i>et al</i> (1934)	4.201 (Kortüm <i>et al</i> entry 404)
Dippy (1939) and later papers of this author	4.203 (Kortüm <i>et al</i> entry 404)
Briegleb <i>et al</i> (1951)	4.213 (Kortüm <i>et al</i> entry 404)
Fischer <i>et al</i> (1961)	4.205 (Serjeant <i>et al</i> entry 3388)
Humffray <i>et al</i> (1965)	4.20
Wilson <i>et al</i> (1967, 1970)	4.202 (Serjeant <i>et al</i> entry 3388)
Bowden <i>et al</i> (1971)	4.20
Bolton <i>et al</i> (1972)	4.204 (Serjeant <i>et al</i> entry 3388)
Matsui <i>et al</i> (1974)	4.205
Ludwig <i>et al</i> (1986)	4.21
Hoefnagel <i>et al</i> (1989)(1990)	4.21

<u>Note 2: Me</u> σ_m =	-0.069 Dippy (1939)	[406,4.272,C ,A]
	-0.072 Wilson <i>et al</i> (1967)	[3983,4.274,S ,A]
	-0.050 Bolton <i>et al</i> (1972)	[3983,4.254,SE,R]
	-0.047 Matsui <i>et al</i> (1974)	[- ,4.252,- ,]
	-0.06 Hoefnagel <i>et al</i> (1989)	[- , - ,EG,A]

Mean = -0.058

σ_p =	-0.170 Dippy (1939)	[407,4.373,C ,A]
	-0.165 Wilson <i>et al</i> (1967)	[3984,4.367,S ,A]
	-0.169 Bolton <i>et al</i> (1972)	[3984,4.373,SE,R]
	-0.157 Matsui <i>et al</i> (1974)	[- ,4.362,- , -]
	-0.16 Hoefnagel <i>et al</i> (1989)	[- , - ,EG,A]

Mean = -0.165

The values from Hoefnagel *et al* (1989) are by extrapolation from measurements in 4 and 2% v/v EtOH-H₂O mixtures.

<u>Note 3: NO₂</u> σ_m =	0.710 Dippy (1939)	[465,3.493,C ,A]
	0.732 Fischer <i>et al</i> (1961)	[3575,3.473, C,A]
	0.742 Bolton <i>et al</i> (1972)	[3575,3.462, S,R]
	0.745 Matsui <i>et al</i> (1974)	[- ,3.460, -,-]

Mean = 0.734

σ_p =	0.778 Dippy (1939)	[466,3.425,C ,A]
	0.771 Briegleb <i>et al</i> (1951)	[466,3.442,EH,R]
	0.783 Fischer <i>et al</i> (1961)	[3576,3.422,C ,A]
	0.778 Bolton <i>et al</i> (1972)	[3576,3.426, S,R]
	0.781 Matsui <i>et al</i> (1974)	[- ,3.424,- , -]

Mean = 0.777

<u>Note 4: OMe</u> σ_m =	0.115 Dippy (1939)	[481,4.088,C ,A]
	0.119 Fischer <i>et al</i> (1961)	[4005,4.086,C ,A]
	0.109 Bolton <i>et al</i> (1972)	[4005,4.095,SE,R]
	0.112 Matsui <i>et al</i> (1974)	[- ,4.093,- , -]
	0.12 Hoefnagel <i>et al</i> (1989)	[- , - ,EG,A]

Mean = 0.114

σ_p =	-0.268 Dippy (1939)	[482,4.471,C ,A]
	-0.306 Fischer <i>et al</i> (1961)	[4006,4.511,C ,A]
	-0.292 Bolton <i>et al</i> (1972)	[4006,4.496,SE,R]
	-0.282 Matsui <i>et al</i> (1974)	[- ,4.487,- , -]

Mean = -0.288

<u>Note 5: F</u> σ_m =	0.338 Dippy (1939)	[445,3.865,C ,A]
	0.343 Fischer <i>et al</i> (1961)	[3551,3.862,C ,A]
	0.340 Matsui <i>et al</i> (1974)	[- ,3.865,- , -]
	0.340 Hoefnagel <i>et al</i> (1989)	[- , - ,EG,A]

Mean = 0.340

σ_p =	0.062 Dippy (1939)	[446,4.141,C ,A]
	0.052 Fischer <i>et al</i> (1961)	[3552,4.153,C ,R]
	0.05 Hoefnagel <i>et al</i> (1989)	[- , - ,EG,A]

Mean = 0.054

<u>Note 6: Cl</u>	$\sigma_m =$	0.379	Saxton <i>et al</i> (1934)	[448,3.822,C ,R]
		0.373	Dippy (1939)	[448,3.830,C ,A]
		0.365	Bolton <i>et al</i> (1972)	[3540,3.839,SE,R]
		0.371	Matsui <i>et al</i> (1974)	[- ,3.834,- ,-]

Mean = 0.372

$\sigma_p =$	0.218	Saxton <i>et al</i> (1934)	[449,3.983,C ,A]
	0.226	Dippy (1939)	[449,3.977,C ,A]
	0.227	Briegleb <i>et al</i> (1951)	[449,3.986,EH,R]
	0.216	Bolton <i>et al</i> (1972)	[3541,3.988,SE,R]
	0.219	Matsui <i>et al</i> (1974)	[- ,3.986,- ,-]

Mean = 0.221

<u>Note 7: Br</u>	$\sigma_m =$	0.391	Dippy (1939)	[451,3.812,C ,A]
		0.404	Briegleb <i>et al</i> (1951)	[451,3.809,EH,R]
		0.391	Bolton <i>et al</i> (1972)	[3544,3.813,SE,R]
		0.394	Matsui <i>et al</i> (1974)	[- ,3.811,- ,-]

Mean = 0.396

$\sigma_p =$	0.232	Dippy (1939)	[452,3.971,C ,A]
	0.211	Briegleb <i>et al</i> (1951)	[452,4.002,EH,R]
	0.241	Bolton <i>et al</i> (1972)	[3545,3.963,SE,R]
	0.224	Matsui <i>et al</i> (1974)	[- ,3.981,- ,-]

Mean = 0.227

Appendix to Notes 2 to 7

The values for σ_m and σ_p given above are based entirely on behaviour in purely aqueous solutions, with one minor exception (see Note 2). Most of the mean values for σ_m and σ_p , however, agree closely with values which may be calculated from the pK_a values of benzoic acid and the substituted benzoic acids in 10% v/v EtOH-H₂O (Hoefnagel *et al* (1989)) or 10% v/v acetone-water (Hoefnagel *et al* (1990)) and the corresponding p value for the ionization of substituted benzoic acids in the solvent concerned.

10% EtOH-H ₂ O	σ_m	σ_p	10% acetone-water	σ_m	σ_p
2. Me	-0.06	-0.16		-0.06	-0.15
3. NO ₂	0.72	0.76		0.73	0.77
4. OMe	0.11	-0.27		0.12	-0.28
5. F	0.33	0.08		0.34	0.10
6. Cl	0.37	0.22		0.37	0.24
7. Br	0.38	-		0.40	-

There is a discrepancy for p -F; cf. 0.054 above. There is thus some evidence that a value for σ_p of around 0.05 to 0.06 may be a slightly low estimate.

Notes 8, 9, 10: Et, Prⁱ, and Buⁱ. These σ_m values for *m*-Et, *m*-Prⁱ, and *m*-Buⁱ were calculated by Hoefnagel *et al* (1989) from the pK_a values of benzoic acid and the substituted benzoic acids in 10% v/v EtOH-H₂O, and the ρ value for the ionization of substituted benzoic acids in that solvent. (The pK_a value of the *m*-Buⁱ acid was measured by S; the others by EG.) For the *m*-Buⁱ acid Wilson *et al* (1970) give a pK_a value in water of 4.204 by the S method, which is assessed by Serjeant and Dempsey (1979) as R (their entry 5363). This leads, however, to $\sigma_m \approx 0.00$, which seems unlikely to be correct. Wepster (personal communications, 1991) agrees with this view and claims that a value of about -0.08 for *m*-Buⁱ is consistent with appropriate treatment of results obtained in eight aqueous organic solvents. (This work will be considered in greater detail in another part of this project.)

8. Et	$\sigma_p =$	-0.150 Dippy (1939)	[416,4.353,C ,A]
9. Pr ⁱ	$\sigma_p =$	-0.151 Dippy (1939)	[418,4.354,C ,A]
10. Bu ⁱ	$\sigma_p =$	-0.197 Dippy (1939)	[421,4.400,C ,A]
		-0.180 Wilson <i>et al</i> (1970)	[5364,4.382,S ,R]
		-0.15 Ludwig <i>et al</i> (1986)	[- ,4.36 ,EG,A]
		-0.11 Hoefnagel <i>et al</i> (1989)	[- , - ,S ,A]

Mean = -0.163

The value from Hoefnagel *et al* (1989) was calculated from measurements in 10% v/v EtOH-H₂O, as for the *meta* acid above. The situation for the *p*-Buⁱ acid is clearly unsatisfactory, and at first sight it is the low value obtained by Hoefnagel *et al* (1989) that is the main problem. If this value is discarded, the mean is -0.177. Further support for a value around -0.18 to -0.19 can be found in the work of Shoesmith and Mackie (1936). These authors (whose work is mentioned in passing by Kortüm *et al*), by conductivity measurements at one concentration, found $pK_a = 4.377$ for the *p*-Buⁱ acid, compared with 4.187 for benzoic acid in water, giving a value for σ_p of -0.190. If we classify this work as A and include this value with the other values based on direct measurement in water, the mean is -0.179. Thus we might take -0.18 as a recommended value. However, Wepster (personal communications, 1991) claims that the measurements in 10% EtOH-H₂O were carried out very carefully and that a σ_p value of about -0.10 for Buⁱ in water is consistent with appropriate treatment of results obtained in nine aqueous organic solvents. (This work will be considered in greater detail in another part of this project.) Wepster also states that reproducible results have been obtained with different samples of acid through the years. He also considers that *para*-*t*-butylbenzoic acid presents 'solubility problems' in water and that the work of Dippy (1939) and of Shoesmith and Mackie (1936) may have been affected by these. See note, p. 984 of Hoefnagel *et al* (1989).

<u>Note 11: CH:CH₂</u>	$\sigma_m =$	0.08 Ellam <i>et al</i> (1971)	[- , 4.13,S , -]
	$\sigma_p =$	-0.08 Ellam <i>et al</i> (1971)	[- , 4.28,S , -]

The pK_a values are probably not strictly thermodynamic. The appropriate value for benzoic acid was assumed by the authors to be 4.21. Uncertainty of 0.05 was estimated by Exner, but this seems a little pessimistic, because the work appears to have been carefully done; 0.03 might be fairer.

<u>Note 12:cyclopropyl</u>	$\sigma_m =$	-0.07 Šmejkal <i>et al</i> (1964)	[- , 4.28,EG,A]
	$\sigma_p =$	-0.21 Šmejkal <i>et al</i> (1964)	[- , 4.42,EG,A]

The authors appear to have made their own measurement of the pK_a value of benzoic acid as 4.21. Uncertainty of 0.02 is as given by the authors.

Serjeant and Dempsey (1979) (their entry 4978) quote a pK_a value for the *para* acid of 4.44 from Levina *et al* (1964). This was determined by EG and is assessed as a 'mixed constant' and A.

communication, 1991) the method used was that of Biggs and Robinson (1961), a combined spectrophotometric and electrometric procedure.

Note 18: CO₂H

The determination of accurate pK_a values for the first ionization of isophthalic and of terephthalic acid is very difficult, because the second ionization 'overlaps' with the first. Elaborate treatment of results is required.

Probably the most reliable value for the first ionization constant of isophthalic acid is in Ang (1958) [3966,3.70,SE,A]. When the pK_a value of 3.70 is combined with a value of 4.205 for benzoic acid and a statistical correction of 0.301 is applied for the presence of two ionizable groups, the value of 0.204 for σ_m is obtained. It is generally believed among physical organic chemists that CO₂H should differ but little from CO₂Me in electron-attracting ability and therefore the above σ_m value is anomalously low by at least 0.1 unit (cf. entry 19). The explanation of this is not clear. There does not appear to be any information available for the first ionization of terephthalic acid of reliability comparable with that for isophthalic acid.

However, Exner (personal communication, 1991) has directed attention to the work of Thamer and Voigt (1952, 1955), which is mentioned by Kortüm *et al* (1961), their entries 434 and 435, but classified by them as "unsicher". This work involved SE measurements for both isophthalic and terephthalic acids and a treatment of the results which was claimed to separate K_1 and K_2 . Exner has re-examined the work and suggests that it yields values for K_1 of $2.78 (\pm 0.25) \times 10^{-4}$ and $3.4 (\pm 1.0) \times 10^{-4}$ mol dm⁻³ for isophthalic and terephthalic acids respectively. When the corresponding pK_a values of 3.556 and 3.469 are combined with a value of 4.205 for benzoic acid and the statistical correction of 0.301 is applied, the values of 0.348 and 0.435 are obtained for σ_m and σ_p respectively. These seem reasonable values by comparison with the corresponding values for CO₂Me (see Note 19). Nevertheless it would be unwise to tabulate 'recommended' values for CO₂H.

Note 19: CO₂Me $\sigma_m =$ 0.33 Hoefnagel *et al* (1989) [- , - ,EG,A]

This value was determined by the procedure indicated in Note 14.

$\sigma_p =$ 0.46 See below
0.43 Hoefnagel *et al* (1990) [- , - ,EG,A]

Mean = 0.445

The value 0.46 is cited by Hoefnagel and Wepster (1973) as being from unpublished measurements by A.G.N. Boers and A.J. Hoefnagel on benzoic acids in water at 25°C (see Note 17). The value from Hoefnagel *et al* (1990) was determined by the procedure indicated in Note 16.

Note 20: CN $\sigma_m =$ 0.615 Briegleb *et al* (1951) [456,3.598,EH,R]
0.64 Hoefnagel *et al* (1989) [- , - ,EG,A]

Mean = 0.623

The value from Hoefnagel *et al* (1989) is by extrapolation from measurements in 10, 4, and 2% EtOH-H₂O mixtures.

$\sigma_p =$ 0.662 Briegleb *et al* (1951) [457,3.551,EH,R]
0.68 Hoefnagel *et al* (1989) [- , - ,EG,A]

Mean = 0.668

The value from Hoefnagel *et al* (1989) was determined directly by measurements in water.

<u>Note 21: SiMe₃</u>	$\sigma_m =$	-0.035 Benkeser <i>et al</i> (1953)	[5214, 4.24,S ,A]
		0.113 Wilson <i>et al</i> (1970)	[5214,4.089,S ,R]
	$\sigma_p =$	-0.065 Benkeser <i>et al</i> (1953)	[5215, 4.27,S ,A]
		0.004 Wilson <i>et al</i> (1970)	[5215,4.198,S ,R]

At present it does not seem possible to resolve the discrepancies in these values and the tabulation of recommended values would be unwise.

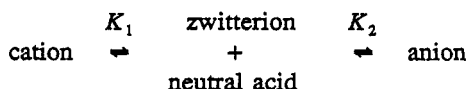
Wepster (personal communications, 1991) considers results obtained in aqueous organic solvents (Hoefnagel *et al* (1989)) and infers that a small negative value, perhaps -0.05, may be appropriate for *m*-SiMe₃ in water, and a small positive value, perhaps 0.04, may be appropriate for *p*-SiMe₃ in water. However, the experiments involved solvents in which the amount of organic component was » 10%. (This work will be considered in another part of this project.)

Note 22: NH₂

The determination of values of σ_m and σ_p for the amino group by studying the ionization of the substituted benzoic acids in water is complicated by the existence of a proportion of the acid in the zwitterionic form:



Values of σ derived by procedures that do not properly consider this are of very doubtful reliability. The observed macroscopic constants K_1 and K_2 relate to equilibria as follows:



The analysis of $\text{p}K_1$ and $\text{p}K_2$ to yield a $\text{p}K_a$ value corresponding to:



is quite complicated: a simplifying assumption is required and the results depend on the particular assumption made. The matter has been considered by certain authors and the original papers should be consulted for details. We give a brief outline here.

Serjeant (1969) used values of 3.08 and 4.77 respectively for the macroscopic $\text{p}K_1$ and $\text{p}K_2$ values of *meta*-aminobenzoic acid in water at 25°C and derived a $\text{p}K_a$ value for the neutral acid of 4.20. He concluded that the value of σ_m for NH₂ is effectively 0.00. Serjeant also considered *para*-aminobenzoic acid and derived a value of σ_p for NH₂ of -0.57.

However, the situation for the latter acid was reconsidered in detail by van de Graaf *et al* (1981). They obtained values of $\text{p}K_1$ and $\text{p}K_2$ (water, 25°C) of 2.419 and 4.877 respectively by spectrophotometric measurements and calculated a value of $\text{p}K_a$ of 4.83 for the ionization of the neutral acid. (The ratio of zwitterion to neutral acid present is 10.5: 89.5.) From this $\text{p}K_a$ value and 4.21 for the $\text{p}K_a$ value of benzoic acid, σ_p of NH₂ is -0.62. We regard this as the preferred value. An uncertainty of 0.02 was estimated by Wepster (personal communication, 1991).

Note 23: NMe₂

The need to consider the effect of zwitterion formation discussed for NH₂ in Note 22 applies also here.

There appear to be no data relevant to obtaining a value of σ_m , but van de Graaf *et al* (1981) have

examined *para*-dimethylaminobenzoic acid. They obtained values of pK_1 and pK_2 (water, 25°C) of 2.568 and 4.996, respectively, by spectrophotometric measurements and calculated a value of pK_a of 4.90 for the ionization of the neutral acid. (The ratio of zwitterion to neutral acid present is 19.4: 80.6.) From this pK_a value and 4.21 for the pK_a value of benzoic acid, σ_p for NMe₂ is -0.69. An uncertainty of 0.02 was estimated by Wepster (personal communication, 1991).

<u>Note 24: NHAc</u>	$\sigma_m =$ 0.175	Bryson (1960)	[4708, 4.03,EG,A]
	0.15	Ludwig <i>et al</i> (1986)	[- , 4.06,EG,A]
	0.17	Hoefnagel <i>et al</i> (1989)	[- , - ,EG,A]

Mean = 0.165

The value from Hoefnagel *et al* (1989) was determined by the procedure indicated in Note 14.

$\sigma_p =$ -0.09	Ludwig <i>et al</i> (1986)	[- , 4.30,EG,A]
-0.03	Hoefnagel <i>et al</i> (1990)	[- , - ,EG,A]

Mean = -0.06

The value from Hoefnagel *et al* (1990) was determined by the procedure indicated in Note 14. Classical constants (based on conductivity measurements) of Ostwald (1889) provide support here (Exner, personal communication, 1990), as yielding $\sigma_m = 0.15$ and $\sigma_p = -0.07$.

<u>Note 25: PO(OMe)₂</u>	$\sigma_m =$ 0.42	Tsvetkov <i>et al</i> (1969)	[- ,3.74 ,EG,A]
	$\sigma_p =$ 0.55	Tsvetkov <i>et al</i> (1969)	[- ,3.61 ,EG,A]

These σ values are based on the authors' own determination of pK_a for benzoic acid as 4.16, cf. the general value of ca. 4.21. It seems likely that the pK_a values measured in this work are 'apparent' rather than thermodynamic. The account of the experimental method in Tsvetkov *et al* (1966) seems to confirm this. The uncertainty of 0.03 is as estimated by Exner (1978).

<u>Note 26: OH</u>	$\sigma_m =$ 0.123	Bray, Dippy, Hughes, and Laxton (1957)	[3398, 4.08,C ,A]
	0.128	Matsui <i>et al</i> (1974)	[- ,4.077, -,]
	0.07	Hoefnagel <i>et al</i> (1989)	[- , - ,EG,A]
	0.06	Hoefnagel <i>et al</i> (1990)	[- , - ,EG,A]

Mean = 0.095

The value from Hoefnagel *et al* (1989) was determined directly by measurements in water. That from Hoefnagel *et al* (1990) was determined by the procedure indicated in Note 16. The situation for the σ_m of OH seems at present not to be entirely satisfactory.

$\sigma_p =$ -0.369	Briegleb <i>et al</i> (1951)	[460,4.582,EH,R]
-0.327	Bray, Dippy, Hughes, and Laxton (1957)	[3399, 4.53,C ,A]
-0.465	Pal'chevskii <i>et al</i> (1960)	[3399, 4.67,ES,A]
-0.377	Matsui <i>et al</i> (1974)	[- ,4.582,- ,]
-0.36	Hoefnagel <i>et al</i> (1989)	[- , - ,EG,A]
-0.34	Hoefnagel <i>et al</i> (1990)	[- , - ,EG,A]

Mean = -0.372

The two determinations from Hoefnagel *et al* (1990) employed the procedures indicated in Notes 14 and 16 respectively. The value determined by Pal'chevskii *et al* (1960) seems to be somewhat eccentric. If this is discarded, the mean value becomes -0.357, so the recommended value of σ_p for OH is tabulated as -0.36.

Note 27: OEt $\sigma_m = 0.10$ Hoefnagel *et al* (1989) [- , - ,EG,A]

The value from Hoefnagel *et al* (1989) was determined by the procedure indicated in Note 14.

Note 28: OPh $\sigma_m = 0.252$ Dippy (1939) [494,3.951,C ,A]
 0.26 Ludwig *et al* (1986) [- ,3.95 ,EG,A]

Mean = 0.256

$\sigma_p = -0.320$ Dippy (1939) [495,4.523,C ,A]

The compilation of Exner (1978) shows great doubt about the validity of this value of σ_p for OPh. *p*-OPh would not be expected to be more electron-releasing than *p*-OMe. See also Hoefnagel *et al* (1990), p.132. It seems best not to tabulate this value.

Note 29: SH $\sigma_m = 0.25$ Ludwig *et al* (1986) [- ,3.96 ,EG,A]

Note 30: SMe $\sigma_p = 0.01$ Ludwig *et al* (1986) [- ,4.20 ,EG,A]

Note 31: SOMe $\sigma_p = 0.53$ Hojo *et al* (1971) [- , 3.66,C ,A]

The authors determined their own value for pK_a of benzoic acid as 4.19.

Note 32: SO₂Me $\sigma_m = 0.68$ Ludwig *et al* (1986) [- ,3.53 ,EG,A]
 0.67 Hoefnagel *et al* (1989) [- , - ,EG,A]

Mean = 0.675

The value from Hoefnagel *et al* (1989) is by extrapolation from measurements in 10, 4, and 2% EtOH-H₂O mixtures.

$\sigma_p = 0.73$ Ludwig *et al* (1986) [- ,3.48 ,EG,A]
 0.69 Hoefnagel *et al* (1990) [- , - ,EG,A]
 0.73 See below

Mean = 0.717

The value from Hoefnagel *et al* (1990) was determined by the procedure indicated in Note 14. The value $\sigma_p = 0.73$ is cited by Hoefnagel and Wepster (1973) as being from unpublished measurements of A.G.N. Boers and A.J. Hoefnagel on benzoic acids in water at 25°C (see Note 17).

Note 33: SO₂NH₂ $\sigma_m = 0.53$ Ludwig *et al* (1986) [- ,3.68 ,EG,A]
 $\sigma_p = 0.58$ Ludwig *et al* (1986) [- ,3.63 ,EG,A]

Note 34: I $\sigma_m = 0.352$ Dippy (1939) [454,3.851,C ,A]
 0.349 Matsui *et al* (1974) [- ,3.856,- , -]
 0.36 Hoefnagel *et al* (1990) [- , - ,EG,A]

Mean = 0.354

The value from Hoefnagel *et al* (1990) was determined by the procedure indicated in Note 16.

$\sigma_p = 0.275$ Robinson *et al* (1959) [3550,3.93 , S,A]
 0.207 Bolton *et al* (1972) [3550,3.997,SE,R]
 0.209 Matsui *et al* (1974) [- ,3.996,- , -]

Mean = 0.225

Wepster (personal communication, 1991) considers that a value of ca. 0.29 for σ_p is supported by experiments with aqueous organic solvents, with the amount of the organic component $\gg 10\%$. On the other hand, Exner (personal communication, 1991) believes the measurement of Robinson *et al* (1959) to be at fault, largely on the grounds that Vandenberg *et al* (1954) have also found a pK_a value of the *p*-iodo acid approaching 4, i.e. 3.98, by a spectrophotometric method. The situation for the σ_p value of I seems at present to be not at all satisfactory.

SUMMARIES OF THE MORE IMPORTANT SOURCE PAPERS

Dippy and co-workers

Extensive conductimetric measurements of ionization constant were made by Dippy and co-workers in the 1930s. The Chemical Reviews article by Dippy (1939), entitled "The dissociation constants of monocarboxylic acids; their measurement and their significance in theoretical organic chemistry", includes references to all this work and summarizes the results, as well as surveying other people's work. Benzoic acid and many substituted benzoic acids were included. As noted in the Introduction above, Dippy's results were the basis of many of the original Hammett σ values. Dippy's work was done with great care and much attention was paid to details which were believed necessary in the determination of the thermodynamic dissociation constants. However, the work was assessed by Kortüm *et al* (1961) as Approximate rather than Reliable. The work was resumed after World War II, e.g. Bray, Dippy, Hughes, and Laxton (1957); Bray, Dippy, and Hughes (1957). This seems to be more highly regarded by Serjeant and Dempsey (1979), who assess some of it as Reliable.

Fischer, Mann, and Vaughan (1961)

Title: "Influence of pressure on the Hammett reaction constant; dissociation of benzoic acids and phenylacetic acid." The thermodynamic pK_a values in water at 25°C were measured for the parent acids and six *meta*- or *para*-substituted acids of each type over the pressure range 1 to 3000 bar. The dissociation constants were measured by a conductance method, with proper attention to the various procedures, corrections, etc. necessary to obtain thermodynamic pK_a values. Serjeant and Dempsey (1979) variously assess the results at 1 bar for the benzoic acids as Reliable or Approximate.

Wilson et al (1967, 1970)

The two parts of this work are published under the general title: "Acid-base equilibria of substituted benzoic acids." Part I contains the spectrophotometric determination of the dissociation constants of benzoic acid and its methyl derivatives at various temperatures to enable the thermodynamic quantities ΔG° , ΔH° , and ΔS° to be calculated at various reference temperatures. Part II was similarly concerned with *t*-butyl and trimethylsilyl substituted acids. This work was variously assessed by Serjeant and Dempsey (1979) as Reliable or Approximate. The papers also contain the thermodynamic quantities for the ionization of halogeno, nitro, cyano, and hydroxy derivatives computed from literature data by the same procedure as the authors applied to their own results. Corresponding pK_a values at 25°C do not amount to entirely independent redeterminations and it does not seem appropriate to consider them in making our compilations.

Bolton, Fleming, and Hall (1972)

Title: "A linear free energy enthalpy-entropy relationship for the ionization of benzoic acids." The enthalpies and entropies of ionization in water of benzoic acid and 11 *meta*- or *para*-substituted benzoic acids were determined. The main experimental method is described as an EMF-spectrophotometric technique "which has been shown to give reliable results for the heats and entropies of proton ionization of phenols and anilinium ions and for which good agreement has been observed between the results obtained and calorimetrically determined data." The *m*- and *p*-nitrobenzoic acids were studied by an indicator spectrophotometric technique. ΔG_{25}° , ΔH_{25}° , ΔS_{25}° values are tabulated. In Serjeant and Dempsey (1979) pK_a values at 25°C are calculated from the thermodynamic data and are uniformly assessed as Reliable.

Matsui, Ko. and Hepler (1974)

Title: "Thermodynamics of ionization of benzoic acid and substituted benzoic acids in relation to the Hammett equation." This work was a combination of new calorimetric experimental measurements by the authors and a critical assessment of work by other authors, with the intention of arriving at 'best' ΔG° , ΔH° , and ΔS° values for the ionization of aqueous benzoic acids at 25°C. From the 'best' ΔG° values, corresponding 'best' σ values were calculated. The work by other authors which was considered included the contributions of some of the authors mentioned above and therefore cannot be regarded in the present context as giving altogether independent values of ΔG° and hence of pK_a for the substituted benzoic acids with which it deals. The paper obviously deserves to be taken into account, however. We have therefore included pK_a values calculated from ΔG° values in this paper and have given the corresponding σ values a weight of unity in the calculation of mean values.

Ludwig, Baron, Kalfus, Pytela, and Večeřa (1986)

Title: "Dissociation constants of substituted benzoic acids in water and organic solvents." Potentiometric titration was used to measure dissociation constants of 38 monosubstituted benzoic acids in water and in six organic solvents. This constituted the experimental material for an investigation of the effect of solvent on the Hammett ρ constant and on the σ values of certain substituents in the immediately following paper: Pytela, Ludwig, and Večeřa (1986). For our present purpose the paper provides some information about aqueous pK_a values of acids for which such values have not previously been available and also provides supporting evidence for other acids. The glass electrode titrations appear to have been done carefully, but it appears from the earlier description of the experimental method in Pytela, Ludwig, and Večeřa (1984) that the pK_a values derived should be regarded as essentially 'apparent' values and the results assessed as Approximate. We have not used these results for substituents in the First Division, but they are useful for the Second Division.

Hoefnagel and Wepster (1989)

Title: "Substituent effects. Part 11. Anomalous dissociation constants of benzoic acids in water-organic solvent mixtures. An extended Hammett equation comprising the hydrophobic constant as an additional parameter." The bulk of this paper is concerned with the peculiar behaviour of benzoic acids in EtOH-H₂O mixtures or *t*-BuOH-H₂O mixtures, and it is relevant to the extension of the benzoic acid based scale of σ values through pK_a measurements in alcohol-water systems. It does, however, contain some new measurements directly on water systems and also on solvents containing only a small percentage ($\leq 10\%$ v/v) of ethanol. The latter measurements permit results for purely aqueous solutions to be calculated by extrapolation. This takes several different forms and these are detailed at appropriate points in the Notes. The authors' Table I expresses the experimental results as $100(pK_a^\circ - pK_a)$ and thus for solutions in water the tabulated figures amount to 100σ . (pK_a° for benzoic acid was taken as 4.21.) In our tabulation of results from these authors we do not back-calculate the values of pK_a . The experimental results were obtained by potentiometric titrations with a glass electrode (except in a small number of cases in which spectrometry was used) and all necessary procedures, corrections, etc. were applied to obtain thermodynamic pK_a values. The authors claims a precision of ± 0.02 and it is fair to assess their results as Approximate, as in the case of other work depending on careful use of the glass electrode.

Hoefnagel and Wepster (1990)

Title: "Substituent effects. Part 12. Further studies on the extended Hammett equation comprising the hydrophobic constant: reactivity data for benzoic acids, arylacetic acids, β -arylpropionic acids, *trans*- and *cis*-cinnamic acids, methyl benzoates; dissociation constants, DDM reaction, and alkaline hydrolysis in various water-organic solvent mixtures." The main feature of interest in the paper for the present part of this project is the results of measurements for further substituted benzoic acids in 10% v/v EtOH-H₂O and also the results of measurements for a range of substituted benzoic acids in 10% v/v acetone-water.

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The camera-ready copy of this report has been prepared under the supervision of Prof. J.-L.M. Abboud.

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