

[CONTRIBUTION FROM THE VENABLE CHEMICAL LABORATORIES, DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF NORTH CAROLINA, CHAPEL HILL, N. C.]

Chronopotentiometric Studies of Ferrocene Derivatives. I. Determination of Substituent Constants with Substituted Phenylferrocenes¹

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Chronopotentiometric quarter-wave potentials were measured for a series of 49 *o*-, *m*-, and *p*-substituted phenylferrocenes. With the twelve *m*- and *p*-derivatives whose primary substituent² constants were known, the regression line was established: $\Delta E_{1/4} = 0.128\sigma + 0.024$ v., and from this line secondary σ -constants were obtained for fifteen groups. Similarly, $\Delta E_{1/4}$ for nine *o*-substituted phenylferrocenes was correlated with Taft's σ -substituent constants and several new secondary σ -constants were determined from the line of regression: $\Delta E_{1/4} = 0.126\sigma_o^* + 0.031$ v. From the potentials of nine *p*-ferrocenylazobenzenes the transmission of electronic effects through the phenylazo system was studied and the ratio, $\rho_{XC_6H_4N_2}/\rho_{X-}$, was determined to be 0.13, which is in good agreement with previously obtained values.

Introduction

It has been amply demonstrated that the oxidation,^{3,4} chronopotentiometric,⁵⁻⁷ and polarographic⁸ potentials of substituted ferrocenes depend on the electronic effects of the substituent groups. Formal oxidation potentials of phenylferrocene and five *p*-substituted phenylferrocenes in ethanol were obtained by Mason and Rosenblum³ and were correlated with Hammett *para* σ -constants. Similarly, a quite precise correlation of these same *p*-substituted phenylferrocenes was obtained by chronopotentiometry in acetonitrile by Hoh, *et al.*⁶

The purpose of the present investigation was to examine the reaction in Fig. 1 by chronopotentiometry, with *o*-, *m*-, and *p*-substituents, as a method for obtaining substituent constants.

Hammett Constants.—McDaniel and Brown² have recommended a return to the use of thermodynamic ionization constants of benzoic acids for evaluating *primary* σ -constants, *i.e.*, constants to be used for established ρ -values for reactions, reserving *secondary* σ -constants, derived from apparent acid constants or from other reactions such as the present reaction, for use only in describing the electronic properties of substituent groups or for demonstrating the correlation of rate and equilibrium constants of substrates with structure. We agree with this proposal and have separated our data into Table III, which contains the data on substrates whose primary σ -constants are known and from which our ρ -value was obtained, and Table IV, which contains the data on other substrates.

There were several advantages anticipated in this approach to σ -constants. First, good general methods have been developed for arylation of ferrocene with substituted benzenediazonium salts⁹; substituents,

once present in arylferrocenes, can be readily elaborated. Thus groups can be obtained *meta* or *para* to ferrocene in such phenylferrocenes that otherwise might be difficult to obtain *meta* or *para* to a carboxyl group for pK_a measurements. Secondly, groups such as the amino group have caused difficulty in σ -constant determinations by pK_a measurements, because of zwitterion formation.¹⁰ Secondary ionization of substituent groups, such as the carboxyl and hydroxyl groups, is not a problem by this method. Solvent influences on the value of substituent constants have been observed,¹¹ but these effects should be minimized with a solvent like acetonitrile, which should not solvate functional groups significantly since it is known to solvate anions very slightly.¹² Substituent constants obtained in this solvent should very nearly represent the effect of the group itself, rather than that of the group solvated by more polar solvents. Finally, chronopotentiometric measurements are rapid, requiring only a few minutes for each measurement.

Taft's σ -Constants.—Taft¹³ has developed a series of substituent constants, σ_o^* , for *o*-substituents on a benzene ring, adjusted to the same scale as Hammett σ -constants. The correlation of rate or equilibrium constants with structure requires the use of either eq. 1 or 2.

$$\log k/k_0 = \rho\sigma_o^* + E_s \quad (1)$$

$$\log k/k_0 = \rho\sigma_o^* \quad (2)$$

Equation 1 contains a steric parameter, E_s , and is useful for correlating data for reactions in which the steric effects of an *o*-substituent affect the value of the rate or equilibrium constant. Equation 2 is useful for those reactions in which $E_s = 0$, *i.e.*, where the *o*-substituent exerts only polar effects on the rate or equilibrium.

Anticipating a good correlation of quarter-wave potentials of *o*-substituted phenylferrocenes with eq. 2, this reaction was investigated as a possible means of

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(4) S. B. Gubin and E. G. Perevalova, *Doklady Akad. Nauk S.S.S.R.*, **143**, 1351 (1962).

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TABLE I
KNOWN PHENYLFERROCENES USED IN THIS STUDY

Substituent	M.p., °C.	Lit. value, °C.	Reference
H	110–111	110–111	9d
<i>p</i> -CH ₃	140–142	139–140	15
<i>o</i> -CH ₃	50–52	51–52	9c
<i>p</i> -NH ₂	159–160	159–160.5	14
<i>m</i> -NH ₂	207–209	207–208	15
<i>p</i> -Br	122–123	125	3
<i>m</i> -Br	85–86	85–86	16
<i>p</i> -OH	165–166	165	9d
<i>o</i> -NO ₂	109–111	112–114	19
<i>m</i> -NO ₂	86–87	84–85	14
<i>p</i> -NO ₂	170–172.5	169–170	9c
<i>p</i> -CO ₂ H	255 dec.	253–257 dec.	15
<i>o</i> -CO ₂ H	128–130	128–129	17
<i>m</i> -NHCOC ₆ H ₅	211–213	207.5–208	15
<i>p</i> -NHCOC ₆ H ₅	217	222–223	15
<i>p</i> -C ₆ H ₅	165.5–166.5	164–165	18
<i>o</i> -C ₆ H ₅	132.5–132	133–134	18
<i>p</i> -COOC ₂ H ₅	92–93	88–90	15

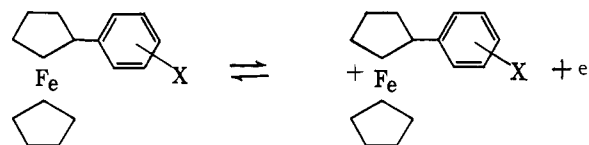


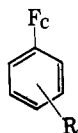
Figure 1.

and acidic hydrolytic conditions, constants cannot be obtained for hydrolyzable substituents such as carboalkoxyl groups or for acidic or basic functions such as the carboxyl, hydroxy, and amino groups. These types of substituents can be studied by this chronopotentiometric method. Secondly, *o*-substituted phenylferrocenes are convenient to prepare, and, finally, the reaction employed is one that can be used for secondary Hammett constants, and thus one reaction can be used to unify these types of substituent constants.

Experimental

Preparation of Materials.—Table I lists the known compounds used in this study, other than the ferrocenylazobenzenes, which

TABLE II
SUBSTITUTED PHENYLFERROCENES



R	M.p., °C.	Formula	Analyses, %			
			Calcd.		Found	
			C	H	C	H
<i>o</i> -F	105.5–107	C ₁₆ H ₁₃ FeF	68.60	4.68	69.01	4.75
<i>o</i> -Cl	55–56	C ₁₆ H ₁₃ FeCl	64.79	4.42	65.04	4.42
<i>o</i> -Br	79–80	C ₁₆ H ₁₃ FeBr	56.35	3.84	56.35, 56.36	3.76, 3.87
<i>o</i> -I	59–60	C ₁₆ H ₁₃ FeI	49.52	3.38	49.49	3.54
<i>o</i> -OCH ₃	44–45	C ₁₇ H ₁₆ FeO	69.89	5.52	70.00	5.64
<i>o</i> -OC ₂ H ₅	72–73	C ₁₈ H ₁₈ FeO	70.61	5.93	70.56	5.48
<i>o</i> -COOCH ₃	74–75	C ₁₈ H ₁₆ FeO ₂	67.52	5.04	67.52	4.97
<i>p</i> -COOCH ₃	70–71	C ₁₈ H ₁₆ FeO ₂	67.52	5.04	67.69	5.21
<i>m</i> -COOCH ₃	124–125	C ₁₈ H ₁₆ FeO ₂	67.52	5.04	67.17	4.94
<i>m</i> -COOC ₂ H ₅	82–83	C ₁₉ H ₁₈ FeO ₂	62.28	5.43	68.07	5.61
<i>m</i> -COOCH(C ₆ H ₅) ₂	150.5–151.5	C ₃₀ H ₂₄ FeO ₂	76.28	5.12	76.43	5.19
<i>p</i> -COOCH(C ₆ H ₅) ₂	132.5–133	C ₃₀ H ₂₄ FeO ₂	76.28	5.12	76.55	5.32
<i>o</i> -CH ₂ OH	65–66	C ₁₇ H ₁₆ FeO	69.89	5.52	70.04	5.63
<i>m</i> -COOH	166–169	C ₁₇ H ₁₄ FeO ₂	66.69	4.61	66.57	4.66
<i>m</i> -CF ₃	97.5–98	C ₁₇ H ₁₃ FeF ₃	61.85	3.97	61.85, 61.74	3.97, 3.98
<i>p</i> -CN	145–146	C ₁₇ H ₁₃ FeN	71.11	4.56	71.40	4.75
2-CH ₃ , 6-NO ₂	129–131	C ₁₇ H ₁₅ FeNO ₂	63.58	4.71	63.49, 63.37	4.73, 4.65
2-CH ₃ , 5-NO ₂	101–102	C ₁₇ H ₁₅ FeNO ₂	63.58	4.71	63.83	4.70
2-CH ₃ , 4-NO ₂	127–129	C ₁₇ H ₁₅ FeNO ₂	63.58	4.71	63.65	4.75
2,6-diCH ₃ , 4-NO ₂	160–161	C ₁₈ H ₁₇ FeNO ₂	64.50	5.11	64.47	5.10
2,4-diCH ₃ , 6-NO ₂	68–69.5	C ₁₈ H ₁₇ FeNO ₂	64.50	5.11	64.45, 64.41	5.09

obtaining secondary *o*-substituent constants. Several advantages of this approach were expected in addition to those listed for Hammett constant determinations. First, this method would offer the advantage of a single reaction series for the determination of these constants; Taft's defining method for *o*-constants requires rate data on two reaction series for each substituent, namely, both alkaline and acid hydrolysis of benzoate esters. More important, however, is the fact that since Taft's defining reactions are carried out under both alkaline

were prepared as described by Little and Clark.¹⁹ Table II lists the new compounds prepared and their melting points and analyses.

Arylation Reactions.—Substituted phenylferrocenes were prepared by the following general arylation procedure:

The appropriately substituted aniline was diazotized at 0° with excess solid NaNO₂ in a sulfuric acid medium (usually 20% H₂SO₄, except for those nitroanilines which required more concentrated H₂SO₄ for solubility). After diazotization was complete, the excess nitrous acid was destroyed with sulfamic acid, and the solution was added to a mixture of an equivalent of ferrocene in methylene chloride and an aqueous solution of sodium acetate in excess of the amount of sulfuric acid used. The addition was made at room temperature. The phenylation reaction required from 2 to 12 hr., depending on the diazonium salt used. After the evolution of nitrogen was complete, the methylene chloride layer was removed and evaporated to a residue. The residue

(14) A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya, and L. S. Shilovtseva, *Doklady Akad. Nauk S.S.S.R.*, **102**, 535 (1955).

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(16) W. F. Little, A. K. Clark, G. Benner, and C. Noe, *J. Org. Chem.*, **29**, 713 (1964).

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was chromatographed on alumina with heptane, and unreacted ferrocene was removed by elution with heptane. The arylated product was eluted with 1:1 benzene-heptane, except in those cases where a nitro group was present in the product; these derivatives required benzene for elution. The arylated products were recrystallized from pentane or heptane. Reduction of the original aqueous layer yielded recovered ferrocene.

Chromatographic fractions containing higher phenylated products were not worked up for those products. In the case of substrates under these conditions, small amounts of ferrocene monoaldehyde were obtained from a side reaction with the solvent.²⁰ Experimental details of this side reaction will be included in a future communication.

The compounds prepared by this procedure, with their yields and recrystallization solvents, were: *o*-bromophenylferrocene (pentane), 22%; *o*-chlorophenylferrocene (pentane), 22%; *o*-methoxyphenylferrocene (pentane), 13%; *o*-ethoxyphenylferrocene (heptane), 4%; *o*-carbomethoxyphenylferrocene (heptane), 23%; *m*-carbomethoxyphenylferrocene (pentane), 15%; *o*-fluorophenylferrocene (heptane), 32%; *o*-iodophenylferrocene (heptane), 33%; *o*-biphenylferrocene (heptane), 28%; 2-methyl-5-nitrophenylferrocene (heptane), 42%; 2-methyl-6-nitrophenylferrocene (heptane), 11%; 2-methyl-4-nitrophenylferrocene (heptane), >90%; 2,6-dimethyl-4-nitrophenylferrocene²¹ (heptane), 39%; *p*-cyanophenylferrocene (ethanol), 10%; *m*-carboethoxyphenylferrocene (pentane), 20%; *m*-trifluoromethylphenylferrocene (heptane).

o-Methylphenylferrocene was prepared in about 40% yield by the addition of the dry diazonium fluoroborate derived from *o*-toluidine to a methylene chloride solution of an equivalent of ferrocene and was recrystallized from ethanol.

o-Carboxyphenylferrocene was prepared in 76% yield from alkaline hydrolysis of the methyl ester (1.0 g.) in 80% ethanol (60 ml.) containing 1.0 g. of KOH. The acid was recrystallized from heptane.

o-Hydroxymethylphenylferrocene was prepared from carbomethoxyphenylferrocene by reduction with LiAlH₄-AlCl₃, essentially by the general procedure for this type of reduction described by Nystrom and Berger.²² The yield of product, recrystallized from heptane, was 73%.

m-Ferrocenylbenzoic acid was prepared by saponification of 0.268 g. of *m*-carbomethoxyphenylferrocene in 10 ml. of 95% ethanol containing 300 mg. of KOH. After 3 hr. at reflux, the ethanol was removed, the residue taken up in 10 ml. of water, and the product was liberated with concentrated HCl. Recrystallization from heptane yielded 0.150 g. (60%) of *m*-ferrocenylbenzoic acid, m.p. 166-169°.

m-Carbobenzhydroxyphenylferrocene (benzhydryl *m*-ferrocenylbenzoate) was obtained by transesterification of *m*-carbomethoxyphenylferrocene in quantitative yield. The methyl ester (330 mg.) was heated under nitrogen at 130-140° in 2 g. of benzhydryl with a few mg. of sodium for 8 hr. Chromatography with benzene on alumina yielded the benzhydryl ester, m.p. 150.5-151.5°.

p-Carbobenzhydroxyphenylferrocene (benzhydryl *p*-ferrocenylbenzoate), m.p. 132.5-133°, was prepared in quantitative yield from ethyl *p*-ferrocenoate and benzhydryl as described for the *m*-isomer above.

p-Carbomethoxyphenylferrocene was prepared by esterification of 1.0 g. of *p*-ferrocenylbenzoic acid in 30 ml. of methanol containing 1 ml. of H₂SO₄. The mixture was heated at reflux for 3 hr. and the alcohol was evaporated. The residue was taken up in ether, washed with aqueous sodium bicarbonate, and recovered by evaporation of the ether. Recrystallization from heptane yielded a product melting at 124-125°.

Measurements.—The chronopotentiometric apparatus was essentially the same as that described by Kuwana, *et al.*³ The measurements were made at 25° on solutions about 10⁻³ *M* in the phenylferrocene, prepared in acetonitrile containing 0.2 *M* lithium perchlorate as the supporting electrolyte. The acetonitrile was previously distilled from P₂O₅ under nitrogen. Generally, measurements were made at three different current densities, ranging from 20 to 55 μ a. per cm.². For a 100% increase in current density, the quarter-wave potential value did not vary more than

± 3 mv. Current reversal was applied in each case with $E_{0.22}$ values, so obtained, agreeing well with the forward $E_{1/4}$ value, indicating reversibility. All chronopotentiograms were well defined, but the τ_B/t_i ratio was often less than the ideal value of $1/3$, for the reverse transition time to the forward time. The solutions of the phenylferrocenes were stable for several hours with the exception of *m*- and *p*-aminophenylferrocene. In these two cases, if measurements were made within 0.5 hr. of the time that the solutions were prepared, normal curves were obtained; however, if the solutions were allowed to stand for long periods before the measurements were taken, poorly defined curves were obtained and values from 80 to 150 mv. higher than those reported were obtained. On standing, these solutions turned dark red.

Discussion

Determination of Hammett σ -Constants.—Tables III and IV list the quarter-wave potentials of the *m*- and *p*-substituted phenylferrocenes. Since absolute

TABLE III
CHRONOPOTENTIOMETRIC QUARTER-WAVE POTENTIALS FOR SUBSTITUTED PHENYLFERROCENES IN ACETONITRILE *vs.* S.C.E.

Substituent	$E_{1/4}$	$\Delta E_{1/4}^a$	$\Delta E_{1/4}^b$	$\overline{\Delta E_{1/4}}$	σ^c
<i>p</i> -OH	0.293	-0.022	...	-0.022	-0.37
<i>p</i> -OCH ₃	-0.018	-0.018	-0.268
<i>p</i> -CH ₃	0.325	0.010010	-.17
H	.346	.031	0.025	.028	.000
<i>p</i> -C ₆ H ₅	.346	.031031	-.01
<i>p</i> -Cl	0.046	.046	.227
<i>p</i> -Br	0.377	0.052	.055	.053	.232
<i>p</i> -COCH ₃085	.085	.502
<i>m</i> -Br	0.390	0.075075	.391
<i>m</i> -NO ₂	.423	.108108	.710
<i>p</i> -CN	.430	.115115	.660
<i>p</i> -NO ₂	.447	.132	0.123	.128	.778

^a Data taken from the present measurements, relative to $E_{1/4}$ for ferrocene = 0.315 v. ^b Taken from data of Hoh, *et al.*,⁶ relative to $E_{1/4}$ for ferrocene = 0.341 v. ^c Values from ref. 2.

TABLE IV
CHRONOPOTENTIOMETRIC QUARTER-WAVE POTENTIALS FOR SUBSTITUTED PHENYLFERROCENES IN ACETONITRILE AT 25° *vs.* S.C.E.

Substituent	$E_{1/4}$	$\Delta E_{1/4}^a$	σ^b	σ^c
<i>p</i> -NH ₂	0.243	-0.072	-0.75	-0.66
<i>m</i> -NH ₂	.328	.013	-.09	-.17
<i>m</i> -CO ₂ H	.381	.066	.33	.37
<i>m</i> -CO ₂ CH ₃	.385	.070	.36	..
<i>m</i> -CO ₂ C ₂ H ₅	.390	.075	.40	0.37
<i>m</i> -CH ₃	.392	.077	.41	.43
<i>p</i> -CO ₂ H	.397	.082	.45	.45
<i>p</i> -CO ₂ CH ₃	.396	.081	.45	..
<i>p</i> -CO ₂ C ₂ H ₅	.402	.087	.49	0.45
<i>m</i> -CO ₂ CH(C ₆ H ₅) ₂	.385	.070	.36	..
<i>p</i> -CO ₂ CH(C ₆ H ₅) ₂	.409	.094	.55	..
<i>m</i> -NH ⁺ COC ₆ H ₅	.356	.041	.12	..
<i>p</i> -NHCOC ₆ H ₅	.330	.015	-.07	..
<i>m</i> -N ₂ C ₆ H ₅	.380	.065	.32	..
<i>p</i> -N ₂ C ₆ H ₅	.389	.074	.39	..

^a Relative to the $E_{1/4}$ of ferrocene = 0.315. ^b Secondary σ -constants calculated from the regression line. ^c Secondary σ -constants from ionization constants.²

values of these potentials may vary, owing to variations in junction potentials or due to traces of moisture in the solvent,²³ $\Delta E_{1/4}$, the difference between the $E_{1/4}$ of the phenylferrocene and ferrocene itself, was used in the correlations. This approach enabled us to utilize the data of Hoh, *et al.*,⁶ where needed. For those compounds for which $E_{1/4}$ values were available

(20) W. F. Little, K. N. Lynn, and R. Williams, *J. Am. Chem. Soc.*, **85**, 3055 (1963).

(21) The starting amine was kindly supplied to us by Prof. B. C. French, Salem College, Winston-Salem, N. C.

(22) R. F. Nystrom and C. R. A. Berger, *J. Am. Chem. Soc.*, **80**, 2896 (1958).

(23) T. Kuwana, personal communication.

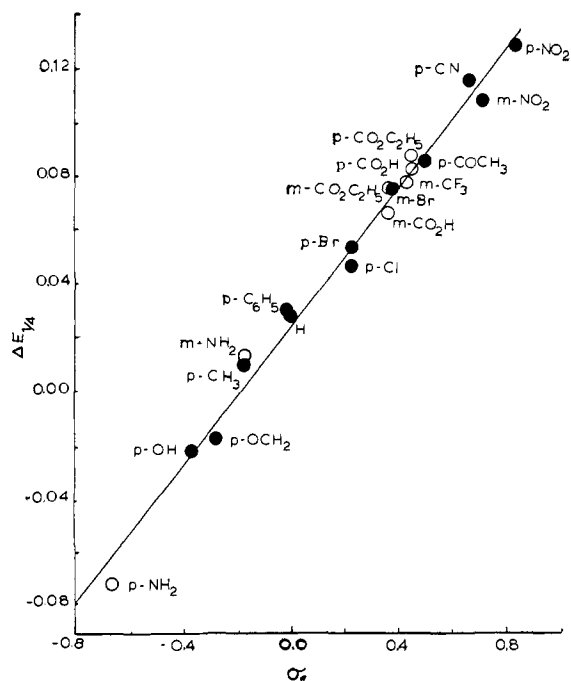


Fig. 2.—Relationship between $\Delta E_{1/4}$ and Hammett σ -constants for substituted phenylferrocenes. Solid circles are for groups with established primary σ -constants; open circles are for groups with secondary σ -constants.

from both our measurements and those of Hoh, *et al.*, average values were used. In some instances, only the values of Hoh, *et al.*, were available.

The data from Table III were used to establish the regression line in Fig. 2, since primary σ -constants were available for these substituent groups.² The regression line, established by a least-squares fit, was found to be

$$\Delta E_{1/4} = 0.128\sigma + 0.024 \text{ v.} \quad (3)$$

with a correlation coefficient of 0.995 and a standard deviation of $\Delta E_{1/4}$ of 0.004 v. from the regression line. In Fig. 2 these points are represented as solid circles.

Table IV gives the data for phenylferrocenes for which primary σ -constants are not available. For some of these groups, secondary σ -constants are available from ionization constant data, and these σ -constants were used to test further the fit of the quarter-wave potentials in Fig. 2 (open circles).

Good agreement was obtained between our secondary σ -constants calculated from eq. 3 and those taken from ionization constant data (Table IV). The greatest deviations between the two sets of values are found in the values for the amino group. McDaniel and Brown refer to the uncertainty of their listed values for this group, allowing for a range of -0.07 to -0.20 for the *m*-amino group. Our value comes well within this range. They further suggest that their listed value for the *p*-amino group is probably 0.1 unit too high, owing to zwitterion formation in *p*-aminobenzoic acid. Our lowest value bears out this suggestion.

The values for the *m*- and *p*-carboxyl group suggested by McDaniel and Brown are taken to be the same as those for the carboethoxy group, since available pK_a data for the corresponding dicarboxylic acids are ambiguous. Our determinations bear out the closeness of this estimate without the element of speculation involved in their assignment.

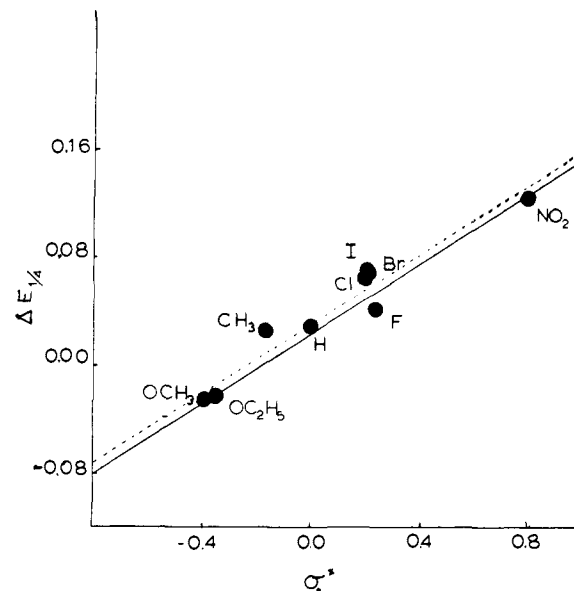


Fig. 3.—Relationship between $\Delta E_{1/4}$ of *o*-substituted phenylferrocenes and Taft's σ^* -constants. Regression line established by these data is the broken line; the solid line was established from $\Delta E_{1/4}$ of *m*- and *p*-substituted phenylferrocenes and Hammett σ -constants.

The values for the carbomethoxy substituent are of interest. While McDaniel and Brown do not list values for this group, constants for this substituent should be close to the values for the carboxyl group and other carboalkoxy groups. Bekkum, Verkade, and Wepster²⁴ have in their compilation recommended values of 0.385 and 0.321 for *p*- and *m*- CO_2CH_3 , respectively. However, in their treatment, heavy weighting was placed on determinations by Bordwell and Boutan²⁵ that were in fact measurements of the substituent effects of the acetate group, rather than the carbomethoxy group. Unfortunately, this error has been carried over into other listings.²⁶ Our values are more in line with the values of other carboxyl functions.

In Table IV the values for the carbobenzhydroxy group are the only listings in the literature for this group.

The benzoylamino group and the phenylazo group have been occasionally studied, and greatly varying values for these groups have been reported,^{24, 27, 28} none of which are based on ionization constant data from the correspondingly substituted benzoic acids.

In summary, chronopotentiometric measurements on substituted phenylferrocenes do seem to offer a sound means of determining substituent constants, but it does suffer from a small spread of potential values, as reflected in the small ρ -constant, 0.128 (2.16, if the scale is converted from units of $\Delta E_{1/4}$ to units of $\log K$, by division of 0.0591). Constants obtained this way can be expressed to no more than two figures.

Taft σ^* -Constants.—Taft has determined substituent constants for nine *o*-groups; the substrates containing these substituents are listed first in Table V and were used in Fig. 3 for establishing the regression line (broken line in Fig. 3). The equation for the regression line was

(24) H. van Bekkum, P. E. Verkade, and B. M. Wepster, *Rec. trav. chim.*, **78**, 815 (1959).

(25) F. G. Bordwell and P. J. Boutan, *J. Am. Chem. Soc.*, **78**, 854 (1956).

(26) J. Hine, "Physical Organic Chemistry," 2nd Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 87.

(27) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

(28) J. F. Bunnett, H. Moe, and D. Knutson, *J. Am. Chem. Soc.*, **76**, 3936 (1954).

TABLE V
 QUARTER-WAVE POTENTIALS FOR *o*-SUBSTITUTED PHENYLFERROCENES AND DERIVED σ -CONSTANTS

R	$E_{1/4}$	$E_{0.22}$	$\Delta E_{1/4}$	σ_0^* (derived, eq. 4)	σ_0^* (derived, eq. 3)	σ_0^* (from ref. 13)	σ_0^* (from ref. 31)
<i>o</i> -OCH ₃	0.292 ± 0.003	0.290	-0.025	-0.44	-0.39	-0.39 ± 0.03	...
<i>o</i> -OC ₂ H ₅	.295 ± .002	.294	-.023	-.43	-.38	-.35 ±
<i>o</i> -CH ₃	.340 ± .001	.341	.021	-.08	-.03	-.17 ± 0.09	+0.003; -0.16
H	.343		.028	.00 ^a	.00 ^a	.00 ^a + ..	0.000 ^a
<i>o</i> -F	.359 ± 0.003	0.359	.041	.07	.12	.24 ± 0.05	.29
<i>o</i> -Cl	.386 ± .002	.384	.064	.26	.31	.20 ± .05	.22
<i>o</i> -Br	.388 ± .002	.386	.068	.29	.34	.21 ± .07	.29
<i>o</i> -I	.389 ± .002	.389	.070	.31	.36	.21 ± .07	.34
<i>o</i> -NO ₂	.444 ± .004	.445	.123	.74	.79	.80 ± .05	...
<i>o</i> -CO ₂ H	.373 ± .002	.371	.054	.18	.23
<i>o</i> -CO ₂ CH ₃	.380 ± .001	.379	.061	.24	.29
<i>o</i> -CH ₂ OH	.352 ± .001	.350	.033	.04	.09
<i>o</i> -C ₆ H ₅	.340 ± .001	.339	.021	-.08	-.03
2-CH ₃ , 6-NO ₂	.436 ± .001117				
2-CH ₃ , 4-NO ₂	.434 ± .001	0.433	.113				
2-CH ₃ , 5-NO ₂	.424 ± .003	0.421	.105				
2,6-diCH ₃ , 4-NO ₂	.415 ± .001096				

^a Assigned value. ^b Reverse wave too short to measure.

determined by a least-squares fit with a correlation coefficient of 0.97 and a standard deviation of $\Delta E_{1/4}$ of 0.011 v. from the regression line (eq. 4).

$$\Delta E_{1/4} = 0.126\sigma_0^* + 0.031 \text{ v.} \quad (4)$$

The value of 0.031 in eq. 4 is not a steric parameter, but simply fixes the origin of the plot.

This correlation without the use of a steric parameter demonstrates the absence of steric effects of the *o*-substituents on the potentials. This is further demonstrated by the closeness of the established regression line to that established from *m*- and *p*-substituted phenylferrocenes with Hammett constants, shown as the solid line in Fig. 3. The slopes are quite close, 0.126 and 0.128. This is not always the case for the correlation of the same reaction with Taft and Hammett constants.¹³

Table V lists derived *ortho* σ -constants, as obtained from eq. 4, for comparison to Taft's constants. It can be seen that, generally, our derived values are close to those of Taft and only in one case, namely, that for *o*-F, is our value significantly outside the range of median deviation of the corresponding Taft constant. Relative to the other halogens, Taft's constant for fluorine is more positive, while our value indicates considerably less electron withdrawal, just as the Hammett value for *p*-fluorine is considerably smaller than those of the other halogens. Leffler and Grunwald²⁹ have attributed the high value for fluorine to hydrogen bonding, but it is not certain that the *o*-constant should parallel the *p*-constant for this substituent, for electrophilic substitution studies indicate that the position *para* to fluorine on a benzene ring is considerably more electron rich than the positions *ortho* to the fluorine.³⁰

Our value for the methyl group, on the other hand, seems somewhat high, compared to Taft's value, but the range of uncertainty in Taft's value for this group is quite large, so that it would be difficult to draw conclusions from this.

(29) J. E. Leffler and E. Grunwald, "Rates and Equilibria in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1963, Chapter VII.

(30) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter VII.

Except for the value of the *o*-fluoro group, our values are in substantially better agreement with those of Chapman, *et al.*³¹ (Table V), who have criticized the method of determining *o*-constants from alkaline and acid hydrolysis in terms of differing degrees of solvation of transition states in the two reaction series; our approach does not suffer from this difficulty. Wells³² has suggested that the values of *o*-constants listed by Taft are too small; our values in Table II lend some support to this. Also listed in Table V are *o*-constants derived from eq. 3 in the interest of common scaling of Hammett and *o*-constants. These values, with the notable exception of that for *o*-fluoro, look especially good when compared to the values of Chapman, *et al.*

In Table V are derived values of *o*-constants for the carboxyl, carbomethoxy, phenyl, and hydroxymethyl groups. The carboxyl and carbomethoxy groups are positive, as would be expected, but there is more difference between these two values than might be expected in view of the similarity of their *p*- and *m*-Hammett constants.² The phenyl group has a value not far different from its *p*-constant, and the hydroxymethyl group is not far different from the value of hydrogen.

Since rates and equilibria of multisubstituted benzene derivatives can be correlated by the summation of Hammett constants^{27,29} for the substituent groups, several polysubstituted phenylferrocenes were studied. Figure 4 shows portions of the regression lines from Fig. 3 and the quarter-wave potentials of four polysubstituted phenylferrocenes plotted *vs.* the appropriate summations of Taft and Hammett constants. The open circles represent the summation of Hammett constants and Taft constants; the closed circles represent summations of Hammett constants and the derived *o*-constants from Table V for comparison. While the use of the derived constants seems to fit the established lines slightly better, no real conclusions can be drawn. Figure 4 simply illustrates the correlation of the quarter-wave potentials in multisubstituted phenylferrocenes with a summation of Hammett and Taft

(31) N. B. Chapman, *J. Chem. Soc.*, 1291 (1963).

(32) P. R. Wells, *Chem. Rev.*, **63**, 171 (1963).

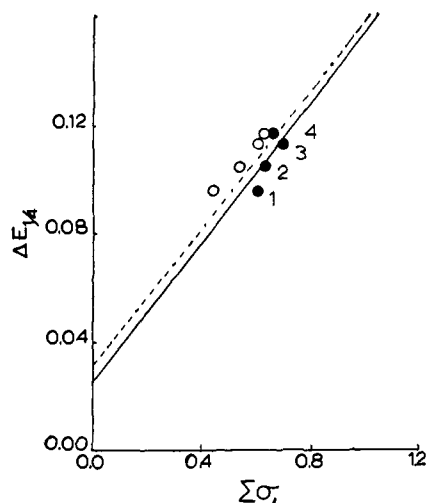


Fig. 4.—Relationship between $\Delta E_{1/4}$ of multisubstituted phenylferrocenes and a summation of Hammett and Taft substituent constants. Open circles are from Taft's original σ -constants; closed circles are from derived σ -constants. Broken line was established with *o*-substituted phenylferrocenes; solid line was established with *m*- and *p*-substituted phenylferrocenes. Identity of points: 1, 2,6-dimethyl-4-nitrophenylferrocene; 2, 2-methyl-5-nitrophenylferrocene; 3, 2-methyl-4-nitrophenylferrocene; 4, 2-methyl-6-nitrophenylferrocene.

constants. This is possible because of the near identity of ρ -values for the *o*-, *m*-, and *p*-substituted series. The fit is established with *either* line.

This approach to obtaining secondary σ -constants seems to give reasonable values, with the advantages listed earlier, but a complete evaluation cannot be made until a more complete set of σ -constants become available for comparison from the defining reactions.

Transmission of Electronic Effects through the Phenylazo System.—Table VI lists quarter-wave potentials for nine *p*-ferrocenylazobenzenes. The variations of $E_{1/4}$ with changes in the substituent is slight, but a least-squares fit (correlation coefficient 0.81; standard deviation of $\Delta E_{1/4}$ from the regression line, 0.003 v.) gives a ρ -value of 0.016 (0.027 if divided by 0.0591 to convert $\Delta E_{1/4}$ units to $\log K/K_0$), and the transmission of electronic effects through the phenylazo system, as measured by the ratio of the ρ -value to that of *p*-substituted phenylferrocenes is 0.13. This value is in good agreement with the determination of 0.16, reported by Jaffé from ionization constants of *p*-aryl-

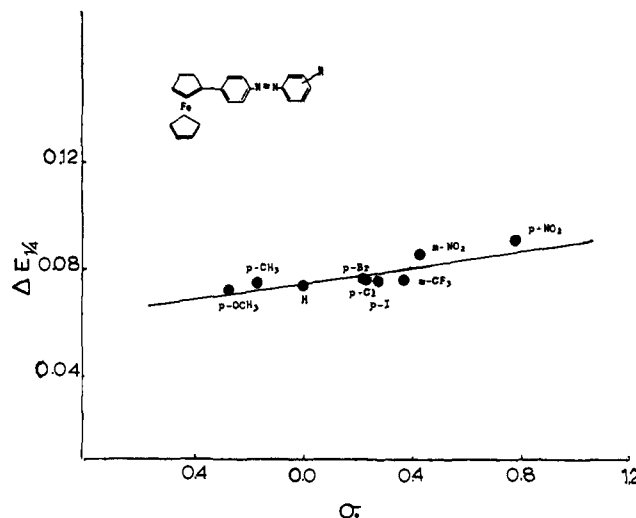
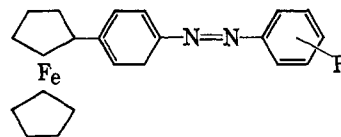


Fig. 5.—Relationship between $\Delta E_{1/4}$ of *p*-ferrocenylazobenzenes and Hammett σ -constants.

azophenols,³³ and 0.13 from the pK_a 's of *p*-arylaazo-*N,N*-dimethylanilinium ions.³⁴ From molecular orbital calculations, the value of 0.14 has been estimated.³⁴

TABLE VI

CHRONOPOTENTIOMETRIC QUARTER-WAVE POTENTIALS FOR SUBSTITUTED *p*-FERROCENYLAZOBENZENES IN ACETONITRILE vs. S.C.E.



Substituent	$E_{1/4}$	$\Delta E_{1/4}^a$	Substituent	$E_{1/4}$	$\Delta E_{1/4}^a$
24 H	0.389	0.074	29 <i>p</i> -Cl	0.392	0.077
25 <i>p</i> -CH ₃ O	.388	.073	30 <i>m</i> -Cl	.391	.076
26 <i>p</i> -CH ₃	.390	.075	31 <i>m</i> -CF ₃	.401	.086
27 <i>p</i> -I	.390	.075	32 <i>p</i> -NO ₂	.406	.091
28 <i>p</i> -Br	.392	.077			

^a Relative to $E_{1/4}$ for ferrocene = 0.315 v.

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(33) S.-J. Yeh and H. H. Jaffé, *J. Am. Chem. Soc.*, **81**, 3287 (1959).

(34) H. H. Jaffé, *J. Chem. Phys.*, **23**, 415 (1953).