

ether extract of the material yielded 0.005 g, mp 188–210°. The insoluble material then melted at 225–228°. Limited solubility of the latter forced use of such a high spectral amplitude that only a qualitative nmr could be obtained (benzene). Neither chloroform, DMSO, nitromethane, nor DMF would dissolve enough of the material for a spectrum. There appeared to be the following absorptions: a doublet at τ 8.96 and 8.87; sharp peak at 6.30 (unsubstituted ferrocene ring); and two poorly resolved triplets at 6.13 and 5.73 (substituted ferrocene ring). Aromatic proton absorption could not be distinguished from that of the solvent. *Anal.* Calcd for $C_{36}H_{34}Fe_2$: C, 74.76; H, 5.93; Fe, 19.31; mol wt, 576. Found: C, 74.47; H, 5.89; Fe, 19.73; mol wt, 549. This represents a 17% yield of dimer, based upon amount of starting chloride.

Elution mixtures containing 5–10% benzene eluted 0.010 g of solid of mp 258–261°. *Anal.* Found: C, 69.58; H, 6.52; mol wt, 3092.

Increasing amounts of benzene eluted additional amounts of solids, which had very wide melting ranges and variable but limited solubility. These could not be recrystallized, and infrared spectra indicated little because of insolubility. Mulls were also unsatisfactory. It was assumed that these fractions were polymers of a polystyrene type.

Preparation and Solvolysis of *p*-Chloromethylbenzyl Ethyl Sulfide (IV). A solution of 13 ml (0.17 mole) of ethanethiol in 100 ml of absolute alcohol containing 0.40 g (0.16 g-atom) of sodium as sodium ethoxide was added to 61 g (0.34 mole) of α, α' -*p*-xylylene dichloride in 700 ml of *t*-butyl alcohol (precipitate). The mixture was maintained at 70–75° during the addition which required about 15 min. After an additional hour stirring at this temperature the mixture was cooled to 0° for a few hours to precipitate the excess dichloride and filtered and the solvent evaporated. The product was distilled through a short Vigreux column at reduced pressure. Four fractions were obtained at 0.4 mm. The first two cuts, bp 103–104.5°, solidified and were shown by their infrared spectra to contain starting dichloride. The third cut, 3 g, bp 104.5–106.4°, $n_D^{21.5}$ 1.5686, showed none of the dichloride absorption at 14.4 μ in the infrared. The fourth cut, bp 106.5–115°, $n_D^{21.5}$ 1.5691, also showed no dichloride. Thin layer chromatography of cuts 3 and 4 using silica gel and cyclohexane–benzene also demonstrated the

absence of dichloride, but cut 4 contained appreciable amounts and cut 3 a small amount of a second, slower moving component, presumably the disulfide. Fraction 3, which was used in kinetic runs, gave the following. *Anal.* Calcd for $C_{10}H_{13}S$: C, 59.98; H, 6.54; S, 17.70; S, 15.90. Found: C, 60.00; H, 6.73; Cl, 15.58; S, 18.10.

Nmr. Whereas α, α' -dichloro-*p*-xylylene showed singlets at τ 5.56 and 2.77, fractions 3 and 4 had the spectra shown in Table IX. Solvolyses of benzyl chloride, α, α' -dichloro-*p*-xylylene, and IV in 50 vol. % aqueous dioxane, followed as described above, gave the first-order rate constants shown in Table X.

Table IX

	Areas under nmr peaks				
	CH ₃ —CH ₂	—S—CH ₂	—C ₆ H ₄	—CH ₂	—Cl
Position, τ	8.9	7.7	6.42	2.82	5.58
Areas, fraction 3	2.9	1.9	1.8	3.9	2.2
Areas, fraction 4	3.6	2.2	2.0	3.6	1.7

Table X

	Rate constants, $k \times 10^5$, sec ⁻¹		
	60°	80°	90°
Benzyl chloride		5.73, 6.10	
α, α' -Dichloro- <i>p</i> -xylylene		5.08, 5.27	
IV	1.57, 1.45	8.53, 8.81,	21.6, 21.0
		8.74	

$\Delta H^\ddagger_{IV} = 20.4$ kcal, $\Delta S^\ddagger = -19$ eu

Acknowledgment. We are grateful to the Air Force Office of Scientific Research for financial support (AF-AFOSR-514-64).

Substituent Effects in the Chronopotentiometric Oxidation of Ferrocene Derivatives. Internal Solvation of Certain Substituted Ferricenium Ions¹

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Contribution from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology,³ Pasadena, California, and the Marathon Oil Company, Denver Research Center, Littleton, Colorado. Received August 12, 1966

Abstract: Chronopotentiometric quarter-wave potentials of a number of substituted ferrocenes were measured in acetonitrile solution. These new data, together with previously published data, indicate that substituent effects in this reaction are best correlated by a blending of Hammett σ_m and σ_p constants, rather than by the Hammett σ_p constants alone as was previously suggested. The quarter-wave potentials of acetamido- and urethano-substituted ferrocenes are anomalously low compared with those of the other compounds studied. This unusual behavior is explained in terms of direct interaction of the acetamido and urethano substituents with the positive iron atom in the oxidized species.

The degree of correlation of chronopotentiometric quarter-wave potentials of substituted ferrocenes with substituent constants such as Taft's polar con-

stants,⁴ Brown's σ^+ constants,⁵ and Hammett's σ_m

(1) (a) Presented in part at the 34th Annual Meeting of the Colorado-Wyoming Academy of Science, Colorado State University, Fort Collins, Colo., May 1963. The experimental portion of this paper is taken from: (b) the Ph.D. Thesis of D. W. Hall, California Institute of Technology, Pasadena, Calif., 1963; (c) the Ph.D. Thesis of C. D. Russell, California Institute of Technology, Pasadena, Calif., 1963.

(2) To whom correspondence should be addressed at the Chemistry Department, University of British Columbia, Vancouver 8, Canada.

(3) Contribution No. 3462.

(4) R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 13.

(5) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958).

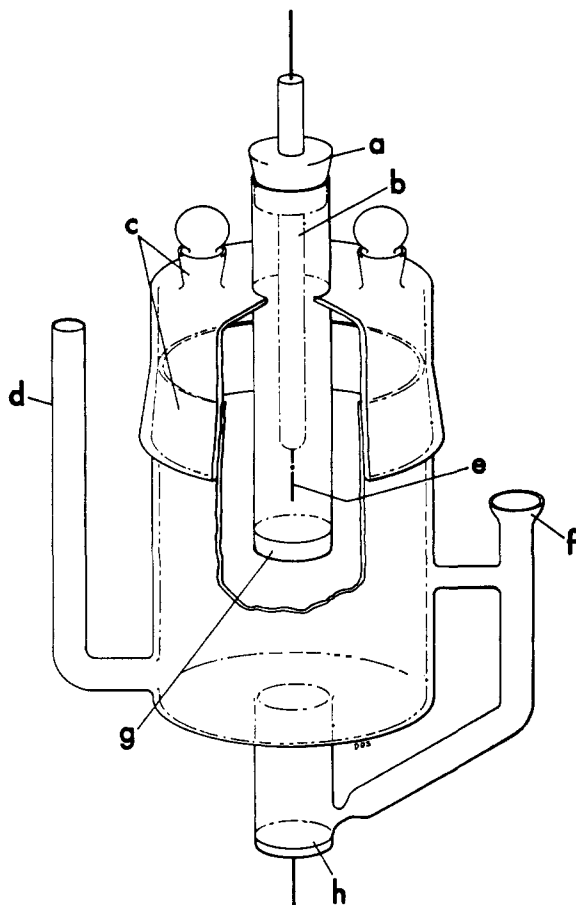


Figure 1. Electrolysis cell: a, cork; b, glass tube; c, ground glass joint; d, N_2 inlet for deaeration; e, platinum wire auxiliary electrode; f, ball joint socket; g, fine porosity fritted glass; and h, platinum disk working electrode.

and σ_p constants⁶ has been the subject of several investigations to date.⁷⁻⁹

It was concluded that these quarter-wave potentials are best correlated with the Hammett σ_p constants, and that the resulting Hammett plot can then be used to obtain secondary σ_p constants¹⁰ for substituents for which such data are not tabulated. It was further shown that the same regression line can be used to correlate monosubstituted ferrocenes and disubstituted ferrocenes.⁹

In addition to the chronopotentiometric measurements in acetonitrile solution, the reduction potentials of ferrocene derivatives have been measured in ethanol-water solutions¹¹ and in acetic acid solution.^{12,13}

It is the purpose of the present paper to point out that the accepted view of substituent effects in the oxidation of ferrocene derivatives and, indeed, in several other reactions of ferrocene compounds warrants re-examination.

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

(7) T. Kuwana, D. Bubltz, and G. Hoh, *J. Am. Chem. Soc.*, **82**, 5811 (1960).

(8) G. Hoi, W. McEwen, and J. Kleinberg, *ibid.*, **83**, 3949 (1961).

(9) W. F. Little, C. N. Reilley, J. D. Johnson, and A. P. Sanders, *ibid.*, **86**, 1382 (1964).

(10) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

(11) J. Komenda and J. Tirouffet, *Compt. Rend.*, **254**, 3093 (1962).

(12) J. G. Mason and M. Rosenblum, *J. Am. Chem. Soc.*, **82**, 4206 (1960).

(13) S. P. Gubin and E. G. Perevalova, *Dokl. Akad. Nauk SSSR*, **143**, 1351 (1962).

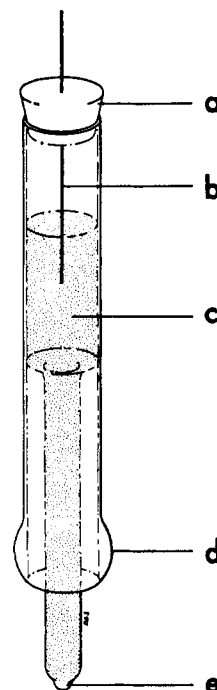


Figure 2. Silver-silver perchlorate reference electrode: a, cork; b, silver wire; c, 0.01 *M* silver nitrate, 0.2 *M* tetraethylammonium perchlorate, and acetonitrile; d, ball joint; e, soft glass bead in Pyrex stem.

Experimental Section

Measurements. Solutions of approximately 2 *mM* concentration in the ferrocene compound and 0.20 *M* in reagent grade, anhydrous $NaClO_4$ (G. F. Smith Chemical Co.) were prepared using spectral grade acetonitrile (Matheson Coleman and Bell Co.). The electrolysis cell is illustrated in Figure 1 and the reference electrode in Figure 2. The current source was a Wenking potentiostat (Elektronische Werkstätten, Göttingen, Germany) which controlled the voltage across a standard resistor in series with the cell and hence the current through the cell. Chronopotentiograms were recorded on a Moseley X-Y time recorder connected to the anode and to the reference electrode through two follower amplifiers of the DeFord type¹⁴ constructed with George A. Philbrick Co. plug-in amplifiers. The ohmic drop between anode and reference electrode was measured using a method described by Anson¹⁵ and found to be only a few millivolts; due correction was made to the measured potentials. All measurements were performed at 25.0°. The chronopotentiometric quarter-wave potentials determined in the present work are reproducible to within at least 10 mv.

The chronopotentiometric quarter-wave potential was interpreted as the formal oxidation potential for the given solution composition, after verifying reversibility of the electrode reaction by current-reversal chronopotentiometry.^{7,16} Reversibility was verified in the case of all but two compounds studied. Neither 3-acetyl-1,1'-di(ethoxycarbonylamino)ferrocene nor 3-acetyl-1,1'-trimethyleneferrocene gave any distinct chronopotentiometric wave upon current reversal. This probably indicates rapid decomposition of the oxidation product. Data for these compounds are excluded from the subsequent discussion.¹⁷

Preparation of Compounds. Most of the compounds listed in Table IA have been described in a previous publication.¹⁸

(14) D. D. DeFord, Symposium on Electroanalytical Techniques, 133rd National Meeting of the American Chemical Society, San Francisco, Calif., April 1958.

(15) F. C. Anson, *Anal. Chem.*, **33**, 939 (1961).

(16) P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, Inc., New York, N. Y., 1964.

(17) More information is available in ref 1a and b concerning chronopotentiometric studies on the two compounds mentioned above, as well as on reversibly oxidized ferrocene compounds not deemed pertinent to the present paper.

(18) D. W. Hall and J. H. Richards, *J. Org. Chem.*, **28**, 1549 (1963).

Samples used in the present study were of known analytical purity except for the compounds discussed below. These compounds were prepared according to published procedures and carefully purified. A check on sample purity was made by comparing melting points with the corresponding literature values when these were available, and by inspection of the infrared spectra.

1,1'-Di(methoxycarbonylamino)ferrocene¹⁹ was prepared in a manner analogous to Rosenblum's²⁰ preparation of 1,1'-di(ethoxycarbonylamino)ferrocene. The compound was purified by chromatography on alumina followed by recrystallization from petroleum ether (melting point, sealed tube, 152–153°; no melting point cited in ref 19). The infrared spectrum of this material compared favorably with the spectrum of a sample of analytically pure 1,1'-di(ethoxycarbonylamino)ferrocene.

Methoxyferrocene was prepared according to the procedure of Nesmeyanov²¹ and purified by vacuum sublimation. The resulting yellow needles possessed a fairly wide melting range (35–40°; sealed tube), but the upper end of the range was comparable to the reported melting point (39.5–40.5°). The infrared spectrum was in accord with the structure. The chronopotentiometric curves for this material displayed no evidence for the presence of other than a single oxidizable component.

3-Acetyl-1,1'-dimethylferrocene was donated by Hill.²² The purity of the sample was rechecked since it had stood on the shelf for some time. The melting point was unchanged from the value reported originally. The infrared spectrum was in accord with the structure.

1,1'-Dibromoferrocene was prepared according to the procedure of Nesmeyanov²¹ and purified by chromatography on alumina. Recrystallization from petroleum ether gave finely divided yellow crystals (mp 50–52°, sealed tube; lit.²¹ mp 50–51°).

Results

Chronopotentiometric quarter-wave potentials *vs.* the silver–silver perchlorate electrode for reversibly oxidized ferrocene derivatives determined in the present study are listed in Table I, part A. We have followed the precedent set by Little, *et al.*,⁹ and reported the data as $\Delta E^{1/4}$ values relative to the quarter-wave potential of ferrocene. The quarter-wave potential of ferrocene *vs.* the silver–silver perchlorate electrode was found to be 0.063 volts.

Quarter-wave potentials previously reported by other workers are listed in Table I, part B. These are $\Delta E^{1/4}$ values relative to the quarter-wave potential of ferrocene *vs.* the standard calomel electrode. These $\Delta E^{1/4}$ data were taken directly from ref 9, and represent in some instances, as outlined in that reference, averages of $\Delta E^{1/4}$ data determined by several research groups. It has been established⁹ that even though the quarter-wave potential of ferrocene *vs.* the standard calomel electrode varies considerably in the studies reported in ref 7–9, it appears to have been held reproducible for a given set of determinations by each individual research group. Thus, $\Delta E^{1/4}$ data for the same ferrocene derivatives are closely comparable throughout the several sets of studies. We chose the silver–silver perchlorate electrode only after experiencing difficulty in obtaining stable potential measurements with the aqueous calomel electrode.

We measured quarter-wave potentials for several ferrocene derivatives which had already been studied by other workers. We found a close correspondence between our $\Delta E^{1/4}$ data and the previously published data. Complete details of these repetitive studies are to be found elsewhere.^{1b,c} A comparison of our measurement of $\Delta E^{1/4}$ for 1,1'-diacetylferrocene (0.488 v)

(19) G. R. Knox, *Proc. Chem. Soc.* (London), 56 (1959).

(20) M. Rosenblum, Ph.D. Thesis, Harvard University, 1953.

(21) A. N. Nesmeyanov, V. A. Sazonova, and V. N. Drozd, *Chem. Ber.*, **93**, 2717 (1960).

(22) E. A. Hill and J. H. Richards, *J. Am. Chem. Soc.*, **83**, 4216 (1961).

Table I. Chronopotentiometric Quarter-Wave Potentials for Reversibly Oxidized Ferrocene Derivatives in Acetonitrile at 25°, Relative to the Quarter-Wave Potential for Ferrocene

No. code	Substituents	$\Delta E^{1/4}$	$\Sigma\sigma_m$	$\Sigma\sigma_p$
A. $\Delta E^{1/4}$ (silver–silver perchlorate electrode ^a)				
1	1,1'-Di(ethoxycarbonylamino)	−0.139	0.204	−0.172
2	1,1'-Di(methoxycarbonylamino)	−0.137	0.204	−0.172
3	Methoxycarbonylamino	−0.070	0.102	−0.086
4	Acetamido	−0.068	0.102	−0.086
5	Methoxy	−0.058	0.115	−0.268
6	3-Acetyl-1,1'-dimethyl	0.148	0.238	0.162
7	1'-Acetyl-1-methoxycarbonylamino	0.157	0.478	0.416
8	1'-Acetyl-1-acetamido	0.171	0.478	0.416
9	2-Acetyl-1-acetamido	0.250	0.478	0.416
10	1,1'-Dibromo	0.317	0.782	0.464
11	Cyano	0.375	0.560	0.660
12	1'-Acetyl-1-bromo	0.406	0.767	0.734
13	1'-Acetyl-1-chloro	0.427	0.749	0.729
14	1,1'-Diacetyl	0.488	0.752	1.004
15	1'-Acetyl-1-cyano	0.598	0.936	1.162
B. $\Delta E^{1/4}$ (standard calomel electrode ^b)				
16	1,1'-Diethyl	−0.115	−0.140	−0.302
17	1,1'-Dimethyl	−0.100	−0.138	−0.340
18	Ethyl	−0.061	−0.070	−0.151
19	Methyl	−0.060	−0.069	−0.170
20	Hydrogen	0.000	0.000	0.000
21	Trimethylsilyl	0.005	−0.040	−0.070
22	1,1'-Di(trimethylsilyl)	0.005	−0.080	−0.140
23	Phenyl	0.028	0.060	−0.010
24	1,1'-Diphenyl	0.055	0.120	−0.020
25	Iodo	0.142	0.352	0.180
26	1'-Ethyl-1-carboxy	0.182	0.300	0.300
27	Carboxy	0.240	0.370	0.450
28	Carbethoxy	0.241	0.370	0.450
29	Benzoyl	0.260	0.343	0.429
30	Acetyl	0.255	0.376	0.502
31	1,1'-Dicarboxy	0.453	0.740	0.900
32	1'-Acetyl-1-carboxy	0.466	0.750	0.950

^a $E^{1/4}$ for ferrocene was determined to be 0.063 v. ^b The $\Delta E^{1/4}$ data cited are taken directly from the appropriate tables in ref 9. In some instances, these data are averages of values reported in ref 7 and 8, as well as in ref 9.

with similar measurements by other workers (0.489 v;⁷ 0.484 v⁹) shows the sort of agreement which is typically observed in these studies.

The substituent constants employed are those tabulated by McDaniel and Brown,¹⁰ unless otherwise indicated. The σ values for the acetamido and benzoyl groups are those reported by White, Schlitt, and Gwynn.²³ The σ constants for the acetamido group differ substantially from those tabulated by McDaniel and Brown, but the discussion to follow does not depend qualitatively on which set is used. The σ constants for the urethano groups were arbitrarily assigned to be the same as those for the acetamido group. Again, the conclusions are qualitatively the same if the derived σ values reported by Kaplan²⁴ for the urethano group are used instead.

Hammett plots of the $\Delta E^{1/4}$ data given in Table I *vs.* $\Sigma\sigma_m$ and *vs.* $\Sigma\sigma_p$ are depicted by Figures 3 and 4, respectively. Figure 5 is a plot of the $\Delta E^{1/4}$ data *vs.*

(23) W. N. White, R. Schlitt, and D. Gwynn, *J. Org. Chem.*, **26**, 3613 (1961).

(24) M. Kaplan, *J. Chem. Eng. Data*, **6**, 272 (1961).

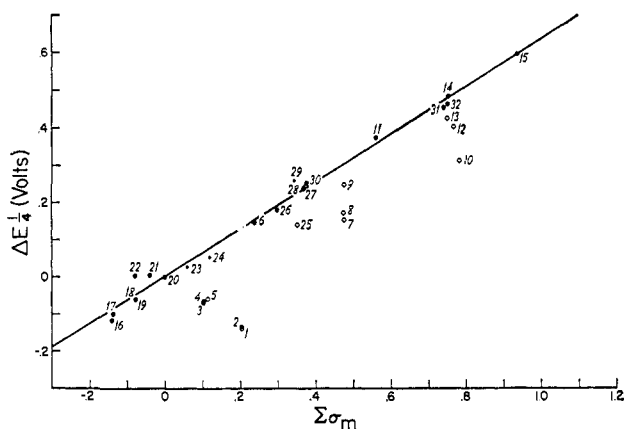


Figure 3. Relationship between $\Delta E^{1/4}$ of ferrocene derivatives and the Hammett σ_m constants. Data represented by closed circles were used to determine the regression line. See Table I for list of data.

an arbitrary blending of the σ_m and σ_p constants. The resulting constant, $\Sigma(\sigma_m + 2\sigma_p)/3$, is intended to represent substituent effects intermediate in the relative degrees of inductive and resonance effects associated with Hammett σ_m and σ_p constants. Hill²⁵ has shown that substituent effects in the solvolysis of heteroannularly substituted methylferrocenylcarbinyl acetates^{1b} are better correlated by the calculated constant discussed above than by either σ_m or σ_p . Since it is believed that the iron atom stabilizes the α -ferrocenylcarbonium ion generated during solvolysis²² and thereby acquires a certain degree of positive character, it is perhaps not unexpected that substituent effects in the solvolysis reaction parallel substituent effects in the chronopotentiometric oxidation studies discussed here. In fact, it has been shown that there is an excellent linear correlation between the solvolysis rate constant data and the quarter-wave potentials of the appropriately substituted ferrocenes.^{1b} This work will be discussed in detail in a future publication.²⁶

Table II lists the results of statistical analyses of the data graphically represented in Figures 3–5.²⁷ These analyses are merely unweighted least-squares treatments of the data. The Hammett equation was used in the form discussed by Jaffé;⁶ therefore, the significance of the statistical parameters is the same as discussed in detail by Jaffé. We have, perhaps, taken some liberties from the standpoint of the statistician in that we have selectively deleted data for substituents falling in a given chemical classification. This was done in order to pinpoint sources of substituent effect variation. We believe these liberties will not lead to errors in the conclusions to be presented. But, they do make it possible inadvertently to omit discussion of statistically significant deviations not falling into our subjectively picked classes of substituent effects. However, we can safely say that the orders of magnitude of any such deviations are far less than is the case with certain data to be discussed.

Although it would be desirable to include in Table II the complete data for the standard deviations of the

(25) E. A. Hill, III, private communication.

(26) E. A. Hill, D. W. Hall, and J. H. Richards, manuscript in preparation.

(27) We are indebted to D. E. Stephens for writing the programs and doing the least-squares computations on the Marathon Oil Co.'s B-5000 computer.

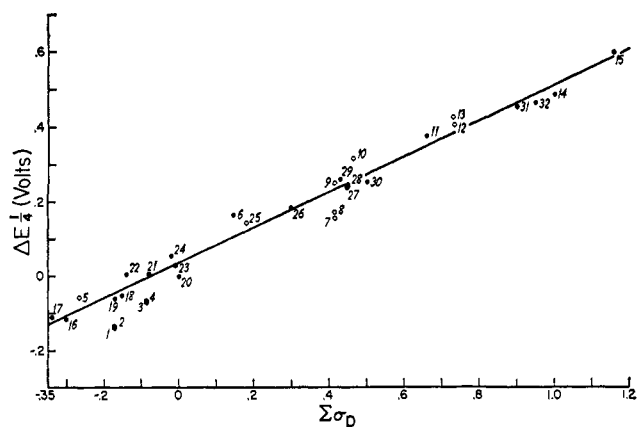


Figure 4. Relationship between $\Delta E^{1/4}$ of ferrocene derivatives and the Hammett σ_p constants. Data represented by closed circles were used to determine the regression line. See Table I for list of data.

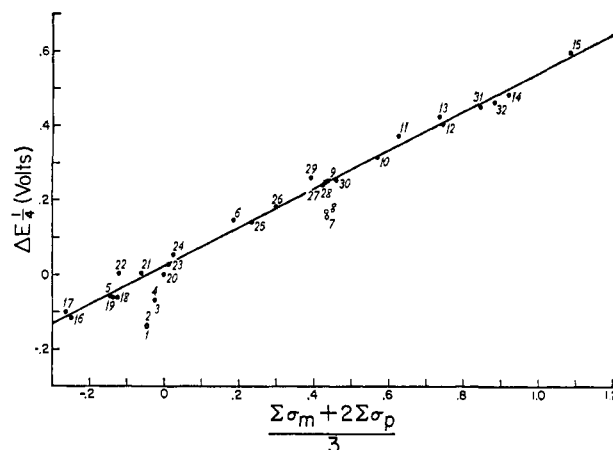


Figure 5. Relationship between $\Delta E^{1/4}$ of ferrocene derivatives and $\Sigma(\sigma_m + 2\sigma_p)/3$. Data represented by closed circles were used to determine the regression line. See Table I for list of data.

quarter-wave potentials, this is not warranted because of limitations on space.²⁸ When it becomes necessary to support a conclusion which cannot be adequately supported by the data presented in Table II, reference will be made to Figures 3–5. Quantitative data for deviations referred to in the Hammett plots will be cited from our files.

Discussion

Comparison of Figures 3 and 4 demonstrates that, as previous researchers have stated, the quarter-wave potentials are better correlated with Hammett's σ_p constants than with the σ_m constants. Discussion of those data which deviate even from the $\Delta E^{1/4}$ vs $\Sigma\sigma_p$ plot will be deferred for the moment.

It is of interest to examine the data given in Figures 3 and 4 in more detail.

Combination of all the previously published data, with but the exception of that for iodoferrocene, and a judicious selection of our data (exclude substituents which can stabilize a positive site by strong conjugation effects) lead to a large set of data which can be correlated very well by the standards listed by Jaffé⁶ with either $\Sigma\sigma_m$ or $\Sigma\sigma_p$. Compare computation numbers 2 and 5 in Table II. For a set of 20 ferrocene deriva-

(28) These data are available upon request.

Table II. Statistical Evaluation of the Correlation between $\Delta E^{1/4}$ and Substituent Constants

Computation no.	Subst const	Compds listed in Table I which were omitted	Slope of regression line	Correln coeff, r^a	Std dev	
					s^a	$\Delta E^{1/4}$, v ^b
1	$\Sigma\sigma_m$	None	0.620	0.920	0.084	0.081
2	$\Sigma\sigma_m$	1-5,7-10,12,13,25	0.639	0.995	0.022	0.021
3	$\Sigma\sigma_p$	None	0.493	0.983	0.040	0.039
4	$\Sigma\sigma_p$	1-4,7,8	0.472	0.993	0.025	0.024
5	$\Sigma\sigma_p$	1-5,7-10,12,13,25	0.468	0.995	0.022	0.021
6	$\Sigma(\sigma_m + 2\sigma_p)/3$	1-4,7,8	0.517	0.997	0.018	0.017

^a See discussion of statistical treatment of Hammett equation in ref 6. ^b Refers to the standard deviation of the quarter-wave potentials from the regression line.

tives, covering a magnitude of 1.5 σ units in the $\Sigma\sigma_p$ plot and 1.1 units in the $\Sigma\sigma_m$ plot, there is no difference in the degree of correlation with $\Sigma\sigma_m$ or $\Sigma\sigma_p$. In fact, both correlations are excellent according to standards suggested by Jaffé. The correlation parameters are identical for both computations ($r = 0.995$; $s = 0.022$; and the standard deviation of $\Delta E^{1/4}$ from the regression line is 0.021 v). Of course, in one sense the comparison here also reflects inherent weaknesses of the statistical parameters r and s as a test of goodness of fit. For this reason, visual inspection of the Hammett plots, even with all the known weaknesses of subjective influences of judgment, can sometimes be more rewarding. The same goal is achieved by utilizing the statistical data on standard deviation of quarter-wave potentials from the regression line. Arbitrarily selecting twice the standard deviation as a criterion for rejection, we find only the data point for 1,1'-di(trimethylsilyl)ferrocene anomalous in the $\Sigma\sigma_m$ plot described by computation 2 (0.055 v compared with 0.042-v limit). Since the same $\Delta E^{1/4}$ is reported for 1,1'-di(trimethylsilyl)ferrocene as for trimethylsilylferrocene, this anomalous point may be due to an error in the determination (or tabulation) of the quarter-wave potential. None of the 20 data points was anomalous in the $\Sigma\sigma_p$ plot described by computation 5 according to our arbitrary criterion. Thus, unless one wishes to weigh very heavily rejection of a dubious data point in computation 2, one must conclude that the correlations with either $\Sigma\sigma_m$ or $\Sigma\sigma_p$ discussed above are equally good. When the data point for iodoferrrocene⁹ (halogen substituents are among those "key" substituents one should select for an investigation of the type discussed here) is included in the comparison, then one indeed finds a better correlation with σ_p than with σ_m by visual inspection of the Hammett plots or by consideration of the standard deviations of quarter-wave potentials from the regression line. The deviation from the regression line is graphically estimated to be 0.084 v. However, if one considers only the r and s parameters of Jaffé's statistical treatment, one finds the deviation by iodoferrrocene in the $\Sigma\sigma_m$ plot is masked, and the correlations still appear to be about equally good. Thus, one would be forced to choose the $\Sigma\sigma_p$ correlation over the $\Sigma\sigma_m$ correlation on the basis of a single previously reported data point.

The problem of comparable correlations of data from a variety of reactions of ferrocene derivatives with either σ_m or σ_p has been a persistent one in our investigations.^{1b}

For example, we found the ionization constants of heteroannularly substituted ferrocenoic acids (litera-

ture values were used) were only slightly better correlated with σ_p than with σ_m . Both correlations were at least "good" by Jaffé's standards.⁶ However, these studies suffered from the fact that too few data were available (4 or 5 data points), key substituents were not included, and the ρ for the reaction was very small, thus making a choice between σ_m and σ_p more difficult for reasons cited by Jaffé.⁶ We found that Nesmeyanov's²⁹ pK_a data for the ferrocenoic acids could be correlated just as well with the quarter-wave potentials of the appropriately substituted ferrocenes as with the Hammett constants.^{1b} What this means is that a sufficiently extensive test of substituent effects has not yet been made for this particular reaction.

The rates of esterification of substituted ferrocenoic acids with diphenyldiazomethane³⁰ have been claimed⁹ to be better correlated with σ_p than with σ_m . However, comparisons were made on the basis of only four data points. In our treatment of the published data, we found no justification for selecting the σ_p correlation over the σ_m correlation. A more extensive study needs to be made before this problem can be resolved. We found the published esterification rate data could be correlated equally well with the appropriate quarter-wave potentials.^{1b} We attach no significance to that observation at the present time.

We believe the problem of equally good correlations of reaction data for ferrocene derivatives with σ_m or σ_p can best be avoided by including larger numbers of compounds in the studies than have generally been used in the past. Substituents should also be more diverse, rather than including only alkyl or carbonyl functions closely related in electronic effects. A study which includes, for example, three or four alkyl derivatives and acetyl, ester, and carboxylic acid derivatives in reality amounts to a study employing only two carefully determined data points.

Returning to the comparison of Figures 3 and 4, we find that $\Sigma\sigma_p$ does correlate more data points than does $\Sigma\sigma_m$ when data for substituents which are electron donating *via* a resonance interaction are considered. Thus, of the 12 compounds not used in computing the regression lines for Figures 3 and 4, six may be included in the $\Sigma\sigma_p$ plot (computation 4 in Table II) without appreciably decreasing the excellent correlation found in the case of the 20 compounds selected for computing the regression line for Figure 4. At least

(29) (a) A. N. Nesmeyanov and O. A. Reutov, *Dokl. Akad. Nauk SSSR*, **115**, 518 (1957); (b) A. N. Nesmeyanov and O. A. Reutov, *Izv. Akad. Nauk SSSR*, 926 (1959).

(30) W. F. Little and R. Eisenthal, *J. Am. Chem. Soc.*, **83**, 4936 (1961). Table II of this reference inadvertently cites Nesmeyanov's value for the pK_a of ferrocenecarboxylic acid (6.11).

five of these six compounds deviate badly in the $\Sigma\sigma_m$ correlation, while in the $\Sigma\sigma_p$ correlation only one of the six data points (that for 1,1'-dibromoferrrocene) deviates by more than two times the standard deviation for the entire group. If one draws the new regression line derived from computation 4 in Table II, thereby adding to the original 20 data points those for methoxyferrocene, 2-acetyl-1-acetamidoferrrocene, and the halogen-substituted ferrrocenes, a decisive trend in the data is noted.³¹ Data points for those substituents which can donate electrons by a resonance interaction tend to fall consistently on one side of the regression line (except for the alkyl substituents) whereas points for substituents which cannot stabilize a positively charged site in this manner fall on the other side of the line. Thus, the data points for both methoxyferrocene and 1,1'-dibromoferrrocene fall off the line in the same direction and, as pointed out above, the data point for 1,1'-dibromoferrrocene is rejected from the correlation according to our arbitrary limit.

We believe this trend indicates that σ_p overestimates the importance of resonance effects in the chronopotentiometric oxidation of ferrrocene derivatives. Therefore, we have plotted the data *vs.* the constant intermediate between σ_m and σ_p which Hill found to give the best correlation for rate data obtained for the solvolysis of methylferrrocenylcarbiny acetates.²⁵ Computation 6 in Table II shows that the correlation for the 26 data points in question is somewhat improved as compared with the $\Sigma\sigma_p$ correlation. Figure 5 graphically displays the treatment, in which $\Delta E^{1/4}$ is plotted against $\Sigma(\sigma_m + 2\sigma_p)/3$.

The only compound among the 26 used in computation 6 which deviates from the regression line shown in Figure 5 by more than two times the standard deviation is, again, 1,1'-di(trimethylsilyl)ferrrocene (0.040 v compared with the arbitrary limit of 0.034 v). It certainly seems that $\Delta E^{1/4}$ for this compound should be re-determined. The data point for 1,1'-dibromoferrrocene now falls almost precisely on the regression line.

We include the correlation of $\Delta E^{1/4}$ with $\Sigma(\sigma_m + 2\sigma_p)/3$ only to point out more strongly that σ_p somewhat overestimates resonance effects in the oxidation of ferrrocene derivatives. Since there is already an abundance of σ constants of various types mentioned in the literature, we are not recommending that our calculated constant be added to the list.

Nesmeyanov has stated that formal oxidation potentials of ferrrocene derivatives are correlated better with Taft's σ_p^0 constants than with Hammett's σ_p constants.³² The σ_p^0 constants place less weight on direct resonance interactions between the substituents and the reaction center.³³ Therefore, a correlation with these constants implies a decreased resonance effect just as does correlation with our calculated constant, $\Sigma(\sigma_m + 2\sigma_p)/3$.³⁴

(31) We chose not to draw this regression line on Figure 4 since the figure would become overly detailed. One may visualize this second line as remaining about the same as the line drawn in Figure 4 in the vicinity of points 16 and 17, but at the other end being shifted upward toward points 12 and 13.

(32) A. N. Nesmeyanov and E. G. Perevalova, *Ann. N. Y. Acad. Sci.*, **125**, 67 (1965).

(33) R. W. Taft, Jr., *J. Phys. Chem.*, **64**, 1805 (1960).

(34) We are indebted to a referee for pointing out ref 32. Although we have not done a statistical treatment on the correlation of $\Delta E^{1/4}$ with σ_p^0 , graphical examination shows the correlation to be at least as good as is obtained using σ_p .

The most important discovery in the present work is that quarter-wave potentials for several of the compounds listed in Table I deviate uniformly and markedly from the regression lines shown in either Figures 4 or 5. Thus, 1,1'-di(ethoxycarbonylamino)ferrrocene, 1,1'-di(methoxycarbonylamino)ferrrocene, methoxycarbonylamino-ferrrocene, acetamidoferrrocene, 1'-acetyl-1-methoxycarbonylamino-ferrrocene, and 1'-acetyl-1-acetamidoferrrocene all are much more readily oxidized than would have been expected on the basis of the σ_p constants for the acetamido and urethano groups, approximate as these may be.

Even if there were no linear correlation of quarter-wave potentials with $\Sigma(\sigma_m + 2\sigma_p)/3$, the fact that acetamido and urethano groups behave as more powerful electron donors than the methoxy group in the oxidation reaction would be quite unexpected. There is ample evidence based on reactions of benzene derivatives to indicate that the methoxy group should be the most potent of the three in stabilizing an electron-deficient reaction center.³⁵

Brown³⁶ and Stock³⁷ have shown that in mercuration and bromination reactions of substituted benzenes the methoxy group is about ten times more potent an electron donor than is the acetamido group.

We believe the anomalous behavior observed for the acetamido- and urethano-substituted ferrrocenes is due to a direct interaction of the carbonyl oxygen atoms of these substituents with the positively charged iron atom in the oxidized species. This interaction may be viewed as an "internal solvation" effect.

Gubin and Perevalova, in their determination of normal oxidation potentials of monosubstituted ferrrocenes in acetic acid-perchloric acid solution, postulated a direct field effect by phenyl, carbomethoxy, carboxyl, and halogen substituents.¹⁸ They stated that the methoxy, acetoxy, and alkyl groups showed no such effect.

Little, *et al.*,⁹ found no evidence in their work to support the direct field effect postulated by Gubin and Perevalova. In fact, they questioned that the field effect could be the magnitude suggested by the Russian workers for substituents such as the halogens, carboxyl, and carboalkoxy groups and yet be minor in the case of the methoxy and acetoxy groups. Little and co-workers concluded that the correlations observed in their work indicated that a direct field effect was either small or else proportional to the Hammett σ_p constants for the series of substituents studied.

It should be pointed out that 2-acetamido-1-acetyl-ferrrocene (compound 9 in Table I) deviates from the regression line only in the σ_m correlation. It appears to behave normally in the two correlations shown in Figures 4 and 5. We have previously shown that the amide hydrogen in this compound is strongly hydrogen bonded to the carbonyl oxygen of the acetyl group.¹⁸ It may be that this hydrogen bond is sufficiently strong so as to restrain the amide group from rotating to a favorable position for interacting with the positive iron atom in the oxidized species. Or, it may be that the energy required to break the hydrogen

(35) Ref 1b, pp 165-170, reviews the pertinent literature available at the time.

(36) H. C. Brown and G. Goldman, *J. Am. Chem. Soc.*, **84**, 1650 (1962).

(37) L. M. Stock and F. W. Baker, *ibid.*, **84**, 1661 (1962).

bond closely approximates that gained through rotation of the amide group and subsequent coordination with the iron atom.

Little, *et al.*, found that both acetoxyferrocene and phenoxyferrocene were not only oxidized more readily than expected, but also were irreversibly oxidized. We suggest that coordination of the acetoxy and phenoxy substituents with the positive iron atom in the oxidized species may have provided a pathway for decomposition. It would seem that more research is indicated to determine why methoxyferrocene is stable and acetoxy- and phenoxyferrocenes unstable under oxidation conditions. Apparently, the urethano- and acetamidoferrocenes do not have a similar pathway for facile decomposition when oxidized.

In conflict with the present study wherein acetamido- and urethanoferrocenes are oxidized at anomalously low quarter-wave potentials, Tirouflet and Komenda observed no unusual behavior for acetamidoferrocene in a polarographic study.¹¹ The data point for this compound fell very nearly on the correlation line in their plot of the oxidation potentials of 17 ferrocene derivatives *vs.* σ_p . Unless the ethanol-water solvent

used in the study of Tirouflet and Komenda minimized the effect of internal solvation by the acetamido group as compared with the effect in acetonitrile, we are at a loss to explain the conflicting results. It is our feeling that a polar hydroxylic solvent system should not completely mask an internal solvation phenomenon. This problem should be investigated further.

Tirouflet and Komenda also reported that their data did not correlate nearly as well with σ_m or Taft's polar constants. It is interesting to note that in their σ_p plot the point for aminoferrocene fell off the correlation line in the same direction that the point for methoxyferrocene did in our own study. Here again it seems that the electron-donating effect of substituents is overestimated by σ_p .

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Rates and Isotope Effects in the Proton Transfers from 2-Nitropropane to Pyridine Bases¹

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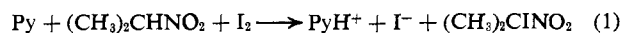
Abstract: The reaction between pyridine bases and 2-nitropropane in the presence of iodine is uncomplicated in *t*-butyl alcohol-water mixtures. In the absence of excess iodide ion and with only a small fraction of the pyridine converted to its conjugate acid, the reversibility can be neglected, and the reaction is apparently free from solvent and lyate ion catalysis. Steric retardation from 2- and 6-alkyl groups in the pyridine is significant, and comparable in magnitude to the acceleration resulting from the increase in base strength. Isotope effects measured when using 2-nitropropane-2-*d* are large and variable, increasing not only with base strength but also with steric hindrance from a value of $k_H/k_D = 9.8$ at 24.88° for pyridine catalysis to $k_H/k_D = 24.2$ for 2,4,6-trimethylpyridine catalysis at the same temperature. Reasons for the unusually large isotope effects are considered; both tunneling and extensive loss of zero-point energy are invoked.

The proton transfer reaction is one of the most important reactions of chemistry, because of the prevalence of hydrogen and also because of the widespread use of hydroxylic solvents, which serve as both proton donors and acceptors. Aliphatic nitro compounds are experimentally desirable as proton donors to bases because the slow reaction is not susceptible to acid catalysis, so that the interpretation of measured rates is simplified. In previous work³ aqueous ethanol was used as a solvent, and complications resulting from the side reactions with iodine were significant. In the present work *t*-butyl alcohol-water was used as a solvent to avoid this difficulty, and the extent of the reverse

reaction, the existence of which has been established,^{3,4} was reduced by minimizing the concentrations of inorganic products, acid, and iodide ion.

Results

The rates of reaction 1 were followed by disappearance of iodine measured spectrophotometrically in a



system containing *ca.* 0.1 *M* pyridine base, *ca.* 0.1 *M* 2-nitropropane, and *ca.* 10⁻⁴ *M* iodine in a solvent consisting of six volumes of *t*-butyl alcohol made up to ten with water. The small amount of perchloric acid used in previous studies^{3,5} is not necessary, but was usually

(4) R. P. Bell and E. Gelles, *Proc. Roy. Soc. (London)*, **A210**, 310 (1952).

(5) R. G. Pearson and F. V. Williams, *J. Am. Chem. Soc.*, **75**, 3073 (1953).

(1) A portion of this work has been published before in preliminary form: L. Funderburk and E. S. Lewis, *J. Am. Chem. Soc.*, **86**, 2531 (1964). From the Ph.D. Thesis of L. H. Funderburk, 1964.

(2) Robert A. Welch Foundation Predoctoral Fellow, 1962-1964. We thank this Foundation for this and other support of this work.

(3) E. S. Lewis and J. D. Allen, *J. Am. Chem. Soc.*, **86**, 2022 (1964).