Determination of micro boiling points. For determination of micro boiling points a common method[22] was used, with an atmosphere of nitrogen above the sample. The method involved placing the sample in a glass tube 20-cm. long, degassing the tube and an inserted capillary, and introducing nitrogen, prior to heating the tube (now open to the air) in a hot air bath. In instances in which ferrocene sublimed from the sample area, identification was made by infrared comparison.

Thermal decomposition of ferrocenoic acid (X). *Ferrous ferrocenoate* (XI). A bulb was blown in the end of a 20-cm. length of 7 mm. tubing and 0.50 g. of analytically pure X was introduced. The tubing was evacuated, nitrogen introduced, and this process repeated twice. With the end open to the air, the bulb was quickly placed in a Wood's-metal bath at 360°. After the sample melted, there was vigorous evolution of gas, yellow solid sublimed from the bulb, and a tan powder remained. After two min. near 340°, the bulb was cooled, separated from the tubing, and the residue placed under vacuum to remove any condensed cyclopentadiene. The residue, ferrous ferrocenoate (XI), was insoluble in common solvents and did not melt below 300°.

Anal. Calcd. for $C_{22}H_{18}Fe_3O_4$: C, 51.41; H, 3.53; Fe, 32.60. Found: C, 51.42, 51.34; H, 3.56, 3.44; Fe, 32.1, 32.3.

In an initial experiment the yield of XI was 0.28 g. (75%). The infrared spectrum showed a strong band at 1550 cm.$^{-1}$ (carboxylate) and a weak band at 1650 cm.$^{-1}$ (trace of carboxyl). The intensity of the weak band was only slightly reduced by extraction of the sample with boiling toluene to remove X.

When 0.10 g. of XI was shaken for 30 min. with 4 ml. of 5% sodium hydroxide solution, filtered, and the filtrated acidified, 0.08 g. (90%) of X was obtained and identified by infrared comparison.

Decomposition of X also occurred to some degree at 250°, inasmuch as the infrared spectrum of the residue from a sample which had boiled near 250° showed a new medium band at 1550 cm.$^{-1}$ in addition to the expected strong band at 1650 cm.$^{-1}$

Thermal decomposition of 2-hydroxybenzoylferrocene (III). Treatment of 0.50 g. of III as described above for X yielded 0.41 g. of residue. Extraction with benzene left 0.36 g. of brittle glass, the infrared spectrum of which was complex; a strong new band was present at 1500 cm.$^{-1}$ A small amount of ferrocene and III distilled from the sample area during the test and were identified by infrared comparison.

Diferrocenylmethanol (XIII). A mixture of 9.3 g. (0.05 mole) of ferrocene and 29.6 g. (0.2 mole) of ethyl orthoformate in 65 ml. of ethylene chloride at 50° under nitrogen was treated with 13.3 g. (0.10 mole) of aluminum chloride in one portion and a cold bath was applied to control the immediate exothermic reaction. The mixture was refluxed 1 hr., cooled, and added to a cold solution of 37.5 g. of sodium hydroxide in 750 ml. of water in an ice bath; the temperature rose to 15°. After the mixture was stirred 10 min., the aqueous layer was extracted with chloroform, and the organic solutions were combined, dried, and evaporated *in vacuo.* Chromatography of the residue on alumina by elution with petroleum ether–benzene (1:1) yielded 5.43 g. (58%) of recovered ferrocene (infrared comparison). Subsequent elution with chloroform and recrystallization of the eluted solid from toluene furnished 2.02 g. (10%) of diferrocenylmethanol (XIII), m.p. 170–175° (dec.); after two recrystallizations, it melted at 175–180° (dec.) (lit., m.p. 166–167°[14]). The infrared spectrum showed a medium band at 3500 cm.$^{-1}$ (hydroxyl) and strong bands at 1100 and 1000 cm.$^{-1}$ (monosubstituted ferrocene).

Anal. Calcd. for $C_{21}H_{20}Fe_2O$: C, 63.04; H, 5.04; Fe, 27.92. Found: C, 63.11; H, 5.01; Fe, 27.3.

Acknowledgment. The author is grateful to Mr. J. M. Vandenbelt of Parke Davis Laboratories for determination of the absorption spectra in the 200 to 500-mμ range, and to Mr. J. T. Hayes for the preparation of quantities of diethyl ferrocenedicarboxylate and ferrocenoic acid.

WYANDOTTE, MICH.

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[CONTRIBUTION NO. 1089 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

Quantitative Estimates of the Strong Electron Donor Properties of Metallocenyl Nuclei[1,2]

EDWARD McCOLLIN ARNETT AND RONALD D. BUSHICK

Received June 13, 1961

The pK_a's of the conjugate acids of acetylferrocene (−2.80) and diferrocenyl ketone (−2.55) have been determined in aqueous sulfuric acid solutions. These two results demonstrate the extraordinary ability of the ferrocenyl nucleus to stabilize carbonium ions and indicate that the σ^+ substituent parameter for the ferrocenyl group in this reaction is about −1.3 (relative to phenyl as 0.00). Estimates for the σ parameter of −0.20 and −0.42 for the ferrocenyl nucleus are also made from dissociation constants of ferrocene carboxylic acid in the literature. It is concluded that the ferrocenyl nucleus is one of the most powerful electron donating aromatic nuclei known. Data in the literature also suggest that there may be two classes of electrophilic substituent constants for metallocene compounds, one of which is even larger than we report and which is associated with direct participation by the metal in carbonium ion stabilization in the order Os > Ru > Fe. The value of σ^+ we report may be associated with indirect metal stabilization through the rings and is expected to follow the order Fe > Ru > Os. Unsuccessful attempts were made to measure the basicities of ferrocenyl ruthenocenyl ketone and ferrocene itself.

The explosive growth of research and interest in the properties of metallocene systems has been recorded in a plethora of reviews.[3–10]

It is by now clear that as an aromatic system the ferrocenyl nucleus is an unusually powerful electron donor, and that it far outstrips the *p*-methoxyphenyl group in this capacity. Probably the most persuasive quantitative evidence of this fact has

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[1] Stereoelectronic Effects in Organic Bases V. Previous paper in this series, E. M. Arnett, T. Cohen, A. A. Bothner-By, R. D. Bushick, and G. Sowinski, *Chem. & Ind. (London)*, 1961, 473.

been provided by Richards and Hill[11] who have shown that ferrocenyl carbinyl acetate undergoes solvolysis through an intermediate carbonium ion in 80% acetone-water at nearly the same rate as does trityl acetate. The results of Trifan and Bacskai[12] provide interesting developments in this area.

Several equilibrium studies described by Nesmeyanov[8] also attest to the electron releasing ability of the ferrocene nucleus in situations where carbonium ions are not involved. Thus ferrocenylamine is twenty times more basic than aniline under the same conditions and p-ferrocenyl phenol is half as strong an acid as p-phenylphenol.

Results[8,13-15] on the strengths of carboxylic acids in which the ferrocene nucleus may be compared with a phenyl nucleus show that here again the former is inhibiting the loss of protons through electron release. In addition, a number of more qualitative results for electrophilic substitution,[16-19] migration aptitude[20] and spectral shifts[21] support the picture of metallocene nuclei being electron releasing and having unusual ability to delocalize positive charge.

It is generally accepted that the best way of comparing the electrical effects of substituents on the reactivity of aromatic systems is through linear free energy relationships.[22-27]

The purpose of the present paper is to describe the results of a quantitative study of the ferrocenyl nucleus in a strongly electron-demanding reaction, the protonation of an adjacent carbonyl group, and to use our results to estimate an electrophilic σ^+ substituent parameter for the ferrocenyl nucleus. We shall also attempt to derive a σ substituent parameter for the same group from several of the publications listed above.

We chose to study the basicities of acetylferrocene and diferrocenyl ketone in aqueous sulfuric acid at 25° because recent work by Stewart and Yates[28,29] provides a good quantity of data from the protonation of acetophenones and benzophenones for the calculation of electrophilic substituent parameters. They have shown that the reaction calls forth large resonance effects when they are available so that the rho values based on Brown's and Okamoto's σ^+ scale[26,27] are -2.17 and -1.66 for acetophenones and benzophenones, respectively. Furthermore, an early observation of Rosenblum's[15] that acetyl ferrocene is somewhat soluble in dilute acid and exhibits a large bathochromic shift for the carbonyl group relative to acetophenone was encouraging.

In order to make such comparisons of ferrocenyl compounds with substituted benzene derivatives we have regarded substituent parameters σ and σ^+ as functions describing the electrical properties of the entire X—Ar-nucleus relative to H—Ar- instead of as a property peculiar to group X. We therefore refer to the substituent parameters of the ferrocenyl nucleus in acetyl ferrocene as being compared with the p-methoxyphenyl group in p-methoxyacetophenone.

RESULTS

By means of the Hammett indicator-method[28,30-32] we have determined the pK_a of the conjugate acid of acetylferrocene in aqueous sulfuric acid at 25° as -2.80. This means that it is by far

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[2] This work was supported by a grant (NSF-G5904) from the National Science Foundation for which we are most appreciative. We also wish to acknowledge the financial aid of the National Science Foundation and the National Institutes of Health, respectively, for the purchase of the Perkin-Elmer 21 and Cary-14 spectrophotometers used in this investigation.

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the most basic aromatic ketone yet studied. Acetophenone (pK_a −6.15) is 2200 times less basic and *p*-hydroxyacetophenone (pK_a −4.73), the most basic of the series studied by Stewart, is less basic by a factor of eighty-five.[33] Using Stewart's value of $\rho = -2.17$ and the pK_a of acetophenone this leads to a σ^+ value for the ferrocenyl group of −1.54 which (by this criterion) places it second only to *p*-dimethyl aminophenyl ($\sigma^+ = -1.7$)[27] in its ability to promote electrophilic reactions. Since the latter group is converted to a strongly electron-attracting function by complexing with Lewis acids, we see at once that *the ferrocenyl group outstrips all substituted phenyl nuclei in promoting electrophilic reactions in acid media.*

To provide a check on this interesting result we have also obtained an estimate of the pK_a of diferrocenyl ketone. Stewart and co-workers[29] have recently studied the protonation of benzophenones; a ρ value for this reaction of −1.66 may be derived. We obtain a pK_a for diferrocenyl ketone of −2.55 which when combined with this ρ value and the pK_a for benzophenone (−6.16) gives $\Sigma\,\sigma^+ = -2.18$ for two ferrocenyl groups or σ^+ for ferrocenyl $= -1.09$.[34]

Ferrocene carboxylic acid. In attempting to calculate substituent parameters from other sources in the literature we were hampered by the fact that available rate or equilibrium constants for ferrocene derivatives have not in general been measured under conditions where Hammett reaction parameters are known. Nevertheless, by suitable interpolation of existing data σ parameters for ferrocenyl may be estimated from data at hand although of necessity, selection of the data to be employed is somewhat arbitrary and the interpolation procedures are tenuous.

Rausch, Fischer, and Grubert[13] determined the pK_a of ferrocene carboxylic acid to be 5.72 in 38% (volume) aqueous ethanol at 20°. In order to derive a σ value for ferrocenyl from this it would be necessary to have ρ for the dissociation of benzoic acids and the pK_a of benzoic acid itself under these conditions. The data that are most comparable are found[23] for 25° in 40% aqueous ethanol. The data compiled in Jaffe's review article[23] indicate that neither ρ for this reaction nor the pK_a of benzoic acid will change appreciably over a 5° temperature range. To correct for difference in medium, plots were constructed from Jaffe's tables[23] for the variation of both ρ and the pK_a of benzoic acid *vs.* alcohol content of aqueous ethanol solutions. Both sets of data generated good straight lines for six solutions from 50–100% ethanol studied by Bright and Briscoe.[35] From these lines a ρ value of 1.535 and pK_a of 5.07 for benzoic acid were estimated and hence σ for ferrocenyl is calculated to be −0.42. For ruthenocene carboxylic acid[13] a σ value for the ruthenocenyl group may be estimated to be −0.24.

The data of Rinehart, Motz, and Moon[14] for the pK_a of ferrocene carboxylic acid were obtained in water where the pK_a of benzoic acid and ρ are very well established at 25°. However, they list no temperature for their measurement and did not use an ionic strength correction since they were working at low concentration. If we assume that their determination of pK_a (4.4) was obtained at 25° a σ for ferrocenyl may be derived as −0.20.

DISCUSSION

The above results lead to a rather well supported average $\sigma^+ = -1.31$ for ferrocenyl and σ values of −0.20 and −0.42. This σ^+ value falls between σ^+ for *p*-hydroxyphenyl and *p*-dimethylaminophenyl[27] while the higher σ value also falls between those for these same groups in Jaffe's tabulation.[23] Since there is a general tendency for σ^+ and σ values to parallel each other this pattern serves to support our conclusions. On Wepster's[24] scale of "normal" substituent parameters the higher value for the σ of ferrocenyl places it as the most powerful available electron-releasing aromatic nucleus, while from Wepster's values based on dissociation of anilinium ions only *p*-dimethylaminophenyl is greater. The excellent analysis of Wepster and his group[24] shows clearly that there is no simple duality for substituent parameters but that in varying degrees the parameters for all groups cover ranges in which the "normal" σ and "exalted" electrophilic σ^+ values are extremes, and the ranges are largest for those groups that can enter into strong resonance interactions with the reacting center of the molecule. Knowles, Norman, and Radda have

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(33) *p*-Aminoacetophenones are of course not comparable because protonation of the amino group occurs at a much lower acidity than protonation of the carbonyl function.

(34) The σ^+ *vs.* pK_a plot for the benzophenones does not produce as good a straight line as does that for the acetophenones and so the σ^+ value of −1.54 is probably more reliable than the −1.08 figure. Professor R. Stewart has informed us that if the pK_a's for the two ferrocenyl ketones given here are included on a plot of his values of pK_a's for the aryl methyl ketones *vs.* those for benzophenones a smooth curved line results.

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recently arrived at the same conclusion,[36] and indeed it appears to be such a widely held opinion that it is difficult to establish priority for it. Although substituent parameters do not show the constancy which might be hoped for them, the relative orders of groups does for the most part remain as a measure of electrical involvement and despite the well justified reservations that one may have about the presentation of σ and σ^+ values as though they really were constants they have proved to be so useful for comparison and rough calculations that it seems premature to dispense with them.

So far we have treated the data as though there were in fact only two substituent parameters for the ferrocenyl nucleus, but there are clear indications that even if one allows for a sliding scale of "normal" and "exalted" values this will still be inadequate to deal with the special case of the metallocenes. The σ^+ value presented above seems to be too small to account for the enormous rate enhancements observed by Richards and Hill[11] and Trifan and Bacskai.[12] Richards and Hill[11] found that ferrocenyl carbinyl acetate solvolyses in 80% acetone-water at a rate nearly equal to that of trityl acetate. Unfortunately, there are no comparable data for other aromatic systems under the same conditions, but some perspective can be gained by considering the results of Deno and coworkers for carbinol-carbonium ion equilibria in sulfuric acid. Deno, Groves, Jaruzelski, and Lugasch[37] find the pK_{R^+} of benzyl alcohol to be close to -19. If now, as suggested by Richards' and Hill's results, the pK_{R^+} of ferrocenyl carbinol is close to that of triphenyl carbinol (-6.63),[38] a stability enhancement for the carbonium ion of over twelve pK_{R^+} units results from replacing phenyl with ferrocenyl. If our value for the σ^+ of ferrocenyl can be applied here it leads to an estimate of $\rho = -9.2$ for the benzyl alcohol–carbonium ion equilibrium which is very large indeed[26,27] but by no means out of the question. We think it more likely that our value of σ^+ does not apply to Richards' and Hill's case and that there is an as yet undetermined σ^+ value which does apply.

Richards and Hill[11] also observed that other metallocenyl nuclei were even more effective at enchancing the rate of solvolysis, the order in terms of the central metal being Os > Ru > Fe, and they suggest that this corresponds to the ability of the metal to participate directly in stabilizing the carbonium ion. Trifan and Bacskai[39] have also observed that ruthenium is superior to iron as an intramolecular hydrogen bond acceptor in metallocenyl-substituted alcohols. The exact reverse order of electron-releasing power, however, is observed for ease of electrophilic substitution,[13] acid strength of metallocene carboxylic acids,[13] and for hydrogen bonding to the π-electrons to the rings of the metallocenes.[39] If these results may be accepted at face value, the ability of a metallocene metal atom to participate directly in carbonium ions and hydrogen bonding[40] would seem to be mainly conditioned by its polarizability. Contrary to this, the indirect participation of the metal through the rings presumably observed in electrophilic substitution, ionization of carboxylic acids and hydrogen bonding to the ring follows an order which is the reverse of the electronegativities of the central metals:[41] Fe (1.8), Ru (2.2), Os (2.2).

One may expect from this that for the metallocenes there will be two classes of electrophilic substituent parameters; those in which the metal participates directly in stabilizing the carbonium ion, and those where the metal is only exerting its influence indirectly through the cyclopentadiene rings. The first class will show an order of electron-releasing ability: Os > Ru > Fe while the second may be expected to follow the reverse order. The relatively small effect observed by us relative to that of Richards and Hill suggests that we may be observing the latter type of σ^+ parameter and they the former. On the basis of this reasoning, if the carbonium ion generated by protonation of the ketones does not involve direct metal participation, ruthenocenyl and osmocenyl ketones should be less basic than the ferrocenyl ones. In order to test this prediction an attempt was made to measure the basicity of ferrocenyl ruthenocenyl ketone. This compound was found to be too insoluble[42] in aqueous acid to allow study by the Hammett indicator method and gave uninterpretable results when examined by the solvent extraction method due apparently to decomposition by light. Insofar as the relation between water solubility and basicity suggested by Rosenblum's observations applies here, this supports the idea that ferrocenyl ruthenocenyl ketone is less basic than diferrocenyl ketone.

It is clearly desirable to obtain measurements of the protonation equilibria of other metallocenyl ketones and the carbinol-carbonium ion equilibria as well as more solvolysis rates in order to see if further evidence can be found here for two classes of carbonium ions and the conditions where they appear. Equilibrium measurements have the dis-

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[42] Ferrocene itself also proved to be too insoluble for a basicity measurement in aqueous sulfuric acid containing stannous chloride to prevent oxidation to ferricinium ion.

tinct advantage over rate studies of being free of speculation about mechanisms or transition states.

EXPERIMENTAL

Acetyl ferrocene was taken from a sample originally prepared in the laboratory of Professor R. B. Woodward of Harvard University. The samples of diferrocenyl ketone and ferrocenyl ruthenocenyl ketone were donated by Dr. M. D. Rausch, Monsanto Chemical Company, Dayton, Ohio.[43] Comparison of the melting points and infrared spectra with literature values[13] attested to their purity.

The pK_a of the conjugate acid of monoacetylferrocene was determined by the Hammett indicator method using the procedure of Davis and Geissman[28,29,32,44] for treatment of the data. A stock solution was prepared by dissolving 4.434 × 10^{-4} mole of the ketone in 25.00 ml. of Spectrograde (Fisher) methanol in a volumetric flask. The procedure for preparing samples for measurement with the thermostated Cary-14 spectrophotometer was that described by Arnett and Wu.[32] Experimental data are presented in Table I. The pK_a of the protonated ketone was obtained from the inflection point of the plot of Δ O.D. *vs.* H_0.[28,44]

TABLE I

THE PROTONATION OF ACETYLFERROCENE

Indicator Study by Davis-Geissman Method (Matched 1-Cm. Silica Cells)

$-{}_0H$	O.D. 230 mμ	O.D. 262.5 mμ	Δ O.D.
Water	0.974	0.505	−0.469
1.22	0.841	0.548	−0.293
1.52	0.909	0.612	−0.297
1.81	0.852	0.560	−0.292
2.25	0.819	0.629	−0.190
2.60	0.627	0.623	−0.004
2.84	0.732	0.673	−0.059
3.12	0.620	0.689	+0.069
3.32	0.610	0.730	+0.120
3.65	0.578	0.741	+0.163
4.14	0.522	0.792	+0.270
4.43	0.507	0.823	+0.316
4.58	0.529	0.831	+0.302
5.36	0.498	0.853	+0.355
5.60	0.510	0.864	+0.354
5.85	0.523	0.856	+0.373
6.06	0.500	0.880	+0.380
6.55	0.497	0.852	+0.355
6.94	0.526	0.894	+0.368
7.03	0.515	0.875	+0.360
7.75	0.497	0.884	+0.387
8.88	0.550	0.914	+0.364

An attempt to determine the basicity of diferrocenyl ketone by the Hammett indicator method led to an uninterpretable scatter of points. This was attributed to the high sensitivity of this compound to light and another attempt was made using the solvent extraction method previously described by us[44] analyzing the organic layer spectrophotometrically. Measurements were made at night in a darkened room with black-painted equipment to reduce decomposition. The stock solution was prepared by dissolving 3.749 × 10^{-5} mole of diferrocenyl ketone in exactly 500 ml. of carefully purified cyclohexane in a blackened volumetric flask. The observed distribution ratio D, was obtained as the ratio of the concentration of diferrocenyl ketone in the organic layer (after equilibration of the organic layer with aqueous acid of acidity H_0) to its concentration in the aqueous acid layer after the equilibration. These concentrations are obtainable directly from the extinction coefficients of the diferrocenyl ketone in the organic layer after equilibration and in the original stock solution. The distribution constant for the free base alone in the region of protonation, (K_D = 19.0) was obtained as described in ref. 45 and pK_a was obtained by plotting H_0 *vs.* log $D/(K_D - D)$ and yielded a straight line of slope 0.994 through eight points over five pK_a units. The data are presented in Table II.

TABLE II

SOLVENT EXTRACTION OF DIFERROCENYL KETONE

$-H_0$	O.D. λ = 275 mμ	D	$\log \frac{D}{K_D - D}$
1.19	0.426	18.52	+1.59
2.25	0.404	8.98	−0.06
2.92	0.376	5.15	−0.43
3.12	0.359	3.99	−0.46
3.65	0.272	1.54	−1.05
3.97	0.214	0.911	−1.30
4.37	0.093	0.261	−1.85
5.36	0.042	0.103	−2.27
Stock solution	0.449		

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(43) We wish to express our gratitude to Dr. Rausch for his generosity in providing us with samples of these difficultly prepared materials.

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