methanol there was added dropwise a solution of sodium methoxide (1.75 g., 0.032 mole) with ice cooling. After the addition the solution was stirred at room temperature for 2.5 hr. Approximately 100 ml. of solvent was distilled off *in vacuo* at 20–25°. Fractionation of this distillate afforded six fractions collected in the range of 53.2–63.9°. The infrared examination showed that the product was identical to authentic methanol–methyl acetate azeotrope. The refractive index data showed that the product contained 1.6 g. of methyl acetate (69% of theoret). Twelve ml. of the azeotrope was refluxed with 4 ml. of benzylamine and 1.0 g. of ammonium chloride for 42 hr. Methanol then was distilled off, and the residue neutralized with aqueous HCl. Ether extraction and evaporation gave white crystals which melted at 63–64° after recrystallization from *n*-hexane–ether. No melting point depression was observed with an authentic sample of N-benzylacetamide.

The reaction mixture remaining after the first distillation was treated with methyl iodide (13.6 g., 0.096 mole) and stirred at room temperature for 2.5 hr. The solvent was evaporated *in vacuo*, leaving 60 ml. of a brown solution. Methyl manganese pentacarbonyl (0.48 g.) sublimed out of the reaction mixture during the evaporation. Yellow-brown flakes, presumably bis-cyclohexylamine iodomanganese tricarbonyl, crystallized out of the brown solution after standing overnight. After recrystallization from chloroform the solid melted at 192.0–192.5° with decomposition.

Anal. Calcd. for $C_{15}H_{26}IMnN_2O_3$: C, 38.8; H, 5.65; I, 27.4; Mn, 11.9, N, 6.04. Found: C, 39.3; H, 5.89; I, 27.9; Mn, 11.6; N, 6.03.

Ammonia Acetylmanganese Tetracarbonyl.—A mixture of methylmanganese pentacarbonyl (4.0 g., 0.019 mole) and liquid ammonia (200 ml.) was refluxed with stirring for 2 hr. Excess ammonia was allowed to evaporate slowly. A greenish-yellow solid (4.11 g., 95%) remained in the reaction vessel. Recrystallization from ether gave 3.65 g. of ammonia acetylmanganese tetracarbonyl, light yellow crystals, melting at 95.5–96.0° with decomposition.

Anal. Calcd. for $C_6H_6MnNO_5$: C, 31.8; H, 2.69; Mn, 24.2; N, 6.17. Found: C, 32.4; 2.70; Mn, 24.4; N, 6.16.

N-Methylcyclohexylamine Acetylmanganese Tetracarbonyl.—Methylmanganese pentacarbonyl (5.0 g., 0.024 mole) and N-methylcyclohexylamine (4.0 g., 0.036 mole) were dissolved in 50 ml. of tetrahydrofuran and stirred at room temperature for 2 hr. Excess solvent was evaporated *in vacuo*. The residues were cooled in Dry Ice giving 3.1 g. (40%) of yellow crystals. The product, recrystallized from petroleum ether (b.p. 38–42°), melted at 73–74°.

Anal. Calcd. for $C_{13}H_{18}MnNO_5$: C, 48.3; H, 5.60; Mn, 17.0; N, 4.33. Found: C, 48.3; H, 5.58; Mn, 17.4; N, 4.44.

Aniline Acetylmanganese Tetracarbonyl.—Methylmanganese pentacarbonyl (3.0 g., 0.014 mole) and aniline (2.0 g., 0.022 mole) were dissolved in 50 ml. of tetrahydrofuran and kept under nitrogen at room temperature for 75 hr. Then the solution was poured into 400 ml. of ice water, giving a yellow precipitate, which after washing and drying weighed 1.72 g. (38%). Recrystallization from ether gave yellow crystals, melting at 83–84°.

Anal. Calcd. for $C_{12}H_{10}MnNO_5$: C, 47.6; H, 33.3; Mn, 18.1; N, 4.62. Found: C, 46.6, H, 33.3; Mn, 17.8; N, 4.70.

Cyclohexylamine Benzoylmanganese Tetracarbonyl.—Phenylmanganese pentacarbonyl (2.0 g., 0.0074 mole) and cyclohexylamine (0.80 g., 0.0081 mole) were dissolved in 35 ml. of ether and stirred at room temperature for 1.5 hr. The resulting orange solution was cooled in Dry Ice giving 0.25 g. (12% recovery) of phenylmanganese pentacarbonyl. The mother liquor was concentrated, cooled in Dry Ice and filtered, giving 0.87 g. of an orange, heterogeneous, solid mass. Infrared examination suggested the presence of starting materials; however, no definite products could be isolated. The orange-brown viscous filtrate was dried over potassium hydroxide pellets and paraffin flakes, giving 0.70 g. of a tacky, brown solid. Repeated extraction with petroleum ether, concentration of extracts and cooling gave 0.23 g. (10% yield) of crude cyclohexylamine benzoylmanganese tetracarbonyl. Recrystallization from petroleum ether gave a yellow solid, melting at 75–78°.

Anal. Calcd. for $C_{17}H_{18}MnNO_5$: C, 55.0; H, 4.89; Mn, 14.8. Found: C, 54.8; H, 5.90; Mn, 14.7.

Aniline Benzoylmanganese Tetracarbonyl.—Phenylmanganese pentacarbonyl (2.72 g., 0.010 mole) and aniline (1.02 g., 0.011 mole) were dissolved in 30 ml. of ether and allowed to stand at room temperature under nitrogen for 163 hr. The resulting yellow-brown solution was filtered and cooled in Dry Ice giving 0.83 g. of yellow crystals. Fractional crystallization from petroleum ether gave 0.22 g. of benzoylmanganese pentacarbonyl and 0.61 g. of starting material. The mother liquor was concentrated and cooled giving 0.50 g. of starting material (total recovery of 41%). After further concentration the mother liquor was treated with isoöctane precipitating a dark yellow solid (0.23 g., 10%). The crude product melted at 78–79°.

Anal. Calcd. for: $C_{17}H_{12}MnNO_5$: C, 55.9; H, 3.13; Mn, 15.0. Found: C, 55.9; H, 3.62; Mn, 15.8.

Oxidation Potentials of Arylferrocenes[1]

BY JOHN G. MASON AND MYRON ROSENBLUM

Formal oxidation potentials for several *para* substituted phenylferrocenes have been determined in aqueous acetic acid by potentiometric titration. Differences between the oxidation potential of phenylferrocene and the arylferrocenes exhibit a linear correlation with the Hammett σ constant for the *para* substituent. A value of -2.41 for the reaction constant is calculated from the data.

The reversible oxidation of ferrocene to the singly charged ferricinium cation is the simplest and perhaps the most characteristic reaction exhibited by this unique organometallic substance. This transformation, which may be effected anodically as well as by a variety of chemical oxidants,[2a] is by no means confined to ferrocene and its derivatives but occurs with bis-cyclopentadienyl complexes involving other transition metals as well. Reversible polarographic oxidation potentials have been reported by Wilkinson and co-workers for bis-cyclopentadienyl compounds of cobalt(II),[2a] nickel (II),[2b] vanadium(III)[2c] and titanium(III),[2c] and for bis-indenyl cobalt(II).[2d] In all cases, the

(1) Presented in part before the Division of Inorganic Chemistry, 136th National Meeting, American Chemical Society, Atlantic City, N. J., September, 1959.

(2) (a) J. A. Page and G. Wilkinson, THIS JOURNAL, **74**, 6149 (1952). G. Wilkinson, M. Rosenblum, M. C. Whiting and R. B. Woodward, *ibid.*, **74**, 2125 (1952). (b) G. Wilkinson, P. L. Pauson and F. A. Cotton, *ibid.*, **76**, 1970 (1954). (c) G. Wilkinson and J. M. Birmingham, *ibid.*, **76**, 4281 (1954). (d) P. L. Pauson and G. Wilkinson, *ibid.*, **76**, 2024 (1954).

oxidation involved a one-electron transfer. Reversibility of these systems was demonstrated by comparing anodic polarographic halfwave potentials with cathodic reduction half wave potentials of the species produced by chemical oxidation.

The object of the present research was to determine the formal oxidation potentials for a series of substituted ferrocenes. Qualitative observations had suggested that substitution of electron donating groups on either one or both of the ferrocene rings greatly increased the ease with which oxidation occurred, while substitution by electron withdrawing groups rendered such derivatives more resistant to oxidation than ferrocene itself. Thus, aminoferrocenes[3] and hydroxyferrocenes[4] are rapidly and irreversibly oxidized in air. By contrast, 1,1'-diacetylferrocene is not attacked by ferric chloride,[3a] although ferrocene is efficiently oxidized by this reagent.

The arylferrocenes, and in particular those bearing a substituent in the *para* position of the benzene ring, appeared best suited for a systematic study of the relationship between the electronic character of the substituent and the oxidation potential of the ferrocene derivative. These substances are readily available by treatment of ferrocene with the requisite diazotized aniline derivative,[5] and preliminary studies had indicated that their corresponding ferricinium salts were stable in acid media.

Experimental

Preparation of Materials.—The arylferrocenes were prepared according to the following general procedure. A cold aqueous solution of the diazotized *p*-substituted aniline was prepared in the usual manner and added rapidly to ferrocene in acetic acid. After allowing the reaction mixture to stir overnight at 0°, it was poured into water and treated with an aqueous solution of sodium bisulfite. The aqueous acetic acid solution was extracted several times with ether or chloroform. After drying the combined extracts, solvent was removed, and the crude product was purified by chromatography on alumina.

These several arylferrocenes were prepared: *p*-nitrophenylferrocene, m.p. 167° (lit.[6] 163°), *p*-chlorophenylferrocene, m.p. 122° (lit.[6] 122°), 1,1'-bis-*p*-chlorophenylferrocene, m.p. 196° (lit.[6] 192°), phenylferrocene, m.p. 112° (lit.[5] 112°), 1,1'-bis-phenylferrocene, m.p. 156° (lit.[5] 154°), *p*-methoxyphenylferrocene, m.p. 112° (lit.[5] 112°), *p*-acetylphenylferrocene, m.p. 177°,[13] and *p*-bromophenylferrocene, m.p. 125°.

Anal. Calcd. for $C_{16}H_{13}FeBr$: C, 56.4; H, 3.8; Br, 23.4. Found: C, 56.5; H, 3.5; Br, 23.6.

All ferrocene derivatives were recrystallized several times until they exhibited a melting point range of 1–2°.[7]

Determination of the Formal Potentials.—Initially, polarographic determination of the oxidation potentials was attempted. However, it was found that oxidation of the dropping mercury electrode occurred prior to oxidation of most of the substituted ferrocenes examined. Moreover, the low solubility of certain of these substances in solvents commonly employed in organic polarography rendered accurate measurements difficult. For these reasons we sought instead to determine oxidation potentials by the method of

potentiometric titration. Of the several solvents tested, acetic acid appeared most satisfactory. This solvent has been employed previously as a medium for quantitative oxidations using Ce(IV) and CrO_3,[8] and Cr(VI) oxidations in acetic acid–water mixtures have been shown to be stoichiometric.[9]

Glacial acetic acid as a titration medium proved to be unsatisfactory. The platinum indicating electrodes were found to be sluggish and insensitive in this medium, making precise measurements difficult. In the vicinity of the equivalence point, the potentials of the electrode reached a maximum and then decreased when both Cr(VI) and Ce (IV) were used as oxidants. In the former case, some ion pair formation seemed indicated while in the latter oxidative decomposition of the ferricinium ion occurred. Addition of water improved the sensitivity of the titration and no anomalous behavior was observed when Cr(VI) was used as a titrant.

The solvent mixture finally selected was 75% acetic acid–25% dilute aqueous perchloric acid (by volume). In order to avoid change in composition of the medium during the course of the titration, the titrant solution of Cr(VI) was prepared by dissolving analytical reagent grade potassium dichromate in the above solvent mixture.

The indicating electrode was a conventional platinum wire electrode. Initial potentials and the rate at which equilibrium was attained were found to be dependent upon the pretreatment of the electrode. For this reason, all titrations were performed using two or three platinum wire electrodes which differed in the method of cleaning. When stable potentials were attained, agreement among the electrodes was within 0.5 millivolt. Electrodes stored in distilled water and not subjected to any other cleaning after a titration were found to attain steady values very quickly.

The potential measurements were made with a Leeds and Northrup Model K-2 potentiometer *versus* a saturated calomel reference electrode connected to the solution by a saturated sodium chloride-agar bridge. The potential of the reference was checked daily *versus* the reference electrode in a Beckman *p*H meter Model G. All titrations were performed under an atmosphere of nitrogen at a temperature of 25.0 ± 0.10°.

All chemicals were reagent grade and used without further purification. The Cr(VI) solution was standardized daily *versus* ferrous ammonium sulfate.

For each titration, appropriate quantities (20–40 mg.) of the ferrocene compound were weighed directly into a 100 ml. volumetric flask which had been rinsed with glacial acetic acid. Sufficient glacial acetic acid was added to dissolve the compound, then 25 ml. of aqueous perchloric acid of the proper concentration was added and the flask was filled with glacial acetic acid. After thorough mixing, 50 ml. of the solution was placed in the titration cell and nitrogen was passed through the solution for 15 minutes. Additions of approximately 0.01 N Cr(VI) solutions were made with a micro-buret.

The reversibility of each system was established by titration of the ferrocene with Cr(VI) until close to the equivalence point and then back titration with the original ferrocene solution. All of the compounds for which potentials are recorded were potentiometrically reversible.

For each individual titration, E_f^0 values were calculated from the Nernst equation, $E = E_f^0 - 0.0591 \log V \cdot N/50 \ c - V \cdot N$ where V = volume of Cr(VI) solution, N = normality of Cr(VI) and c = concentration of the ferrocene in moles/liter, for a series of points on both sides of the E_f^0 value. The average deviation among E_f^0 values calculated in this manner was generally no more than ± 1.5 millivolts. The reproducibility of the E_f^0 values from different titrations was ordinarily of the same order of magnitude. Since, for two of the substances examined, the reproducibility was of the order of ± 5 millivolts, this value is taken as being the maximum error in the E_f^0 values.

Results and Discussion

The data obtained from three different series of determinations are summarized in Table I. In spite of the considerable range in both composition

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(7) We are indebted to Messrs. V. Story and W. G. Howells and to Mrs. R. Fajer for the preparation of some of the substances used in this study.
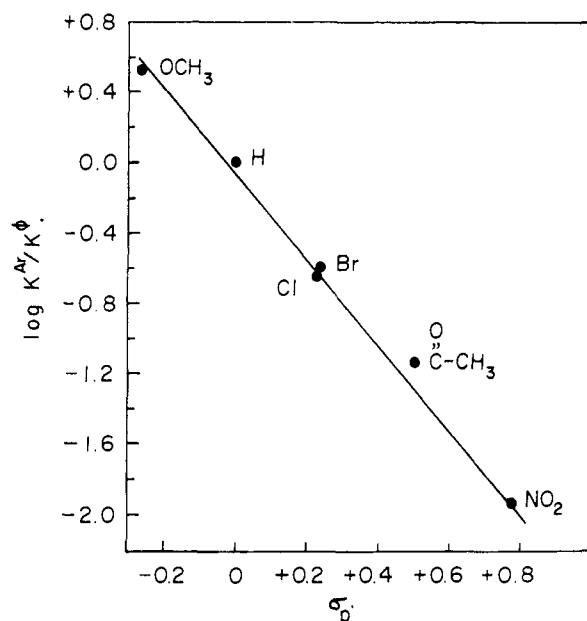
(8) O. N. Hiavark and K. G. Stone, *Anal. Chem.*, 27, 371 (1955); 28, 334 (1956).

(9) For example, K. P. Wibery and T. Mill, THIS JOURNAL, 80, 3022 (1958).

Fig. 1.—Hammett plot for oxidation potentials of p-substituted phenylferrocenes.

and ionic strength of the media, differences between the oxidation potentials of ferrocene and each of the substituted ferrocenes remain reasonably constant.

TABLE I

FORMAL OXIDATION POTENTIALS OF SUBSTITUTED FERROCENES ($vs.$ S.C.E.)[a]

Compound	75% HOAc 0.034 M HClO₄	75% HOAc 0.045 M HClO₄	99% HOAc 0.002 M HClO₄
Ferrocene	−0.225	−0.237	−0.367
p-Methoxyphenyl-	− .230	....	.....
Phenyl-	− .261	− .266	− .399
p-Bromophenyl-	− .296	− .300	.....
p-Chlorophenyl-	− .299	.312	− .432
p-Acetylphenyl	− .328	.....	.....
p-Nitrophenyl	− .375	.....	.....
1,1′-Bis-phenyl-	.....	− .267[b]	.....
1,1′-Bis-p-chlorophenyl	.....	− .321[b]	− .441[b]

[a] Sign convention that of Latimer, "Oxidation Potentials," 2nd Ed., Prentice Hall, New York, N. Y., 1952, for the reaction $(C_5H_5)_2Fe \rightleftarrows (C_5H_5)_2Fe^+ + 1e^-$. [b] Values uncertain due to very low solubility.

The small differences in oxidation potentials obtained for the substances in solutions of similar ionic strength (columns 1 and 2) may be due to either a change in junction potential due to changing the salt bridge or possibly some small difference in water content. The effect of water content on the formal potentials is best exemplified by a comparison of potentials determined in 75% acetic acid with those observed in 99% acetic acid. It is unlikely that ion-pair formation is an important factor in those determinations carried out in 75% acetic acid with a relatively low perchloric acid

background, since Wiberg and Evans[10] have recently reported measurements of ion pair constants for similar solutions and conclude that in solution of greater than 15% water this constant is very small.

Differences between the formal oxidation potentials for phenylferrocene and the various $para$ substituted phenylferrocenes $(E_0^{Ar} - E_0^{\phi})/0.0591 = \log (K^{Ar}/k^{\phi})$ are plotted in Fig. 1 against the Hammett substituent constants.[11]

The data exhibit good linearity and the slope of the plot gives a value of -2.41 for the reaction constant. Similar correlations involving oxidation reduction potentials with Hammett substituent constants have been reported for numerous polarographic reductions.[12]

The data confirm the qualitative observations made previously regarding the effect of various substituents on the ease of oxidation of the metal atom in ferrocene. Of particular interest is the observation that substitution of a phenyl group results in a marked decrease in oxidation potential. This result is consistent with the known polarity of a phenyl substituent and with the effect of this group on the course of electrophilic substitution reactions in phenyl- and 1,1′-diphenylferrocene.[13] Resonance stabilization of the cationic charge on the iron atom by the phenyl group is either not operative or is masked by the inductive effect of the substituent.

Oxidation potentials of certain substituted ferrocenes have been reported recently, based on data obtained by chromopotentiometry.[14] Unfortunately, there is no direct comparison possible between these data and those reported here. However, the qualitative observations are the same, $i.e.$, electron withdrawing substituents make oxidation more difficult, electron donating groups facilitate oxidation.

Determination of the potentials for the heteroannularly substituted diaryl derivatives was rendered difficult due to their low solubility in the aqueous acetic acid medium. Consequently, the accuracy of the potentials for bis-phenylferrocene and bis-p-chlorophenylferrocene is not as great as that of the monoarylferrocenes. However, the limited data suggest that substitution of a second aryl group has a much smaller effect on the oxidation potential of the ferrocene nucleus than does the introduction of the first such group.

(10) K. B. Wiberg and R. J. Evans, THIS JOURNAL, 80, 3019 (1958).
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(13) M. Rosenblum, THIS JOURNAL, 81, 4530 (1959).
(14) D. E. Bublitz, G. Hoh and T. Kuwana, Chem. & Ind. (London), 635, (1959). T. Kuwana, D. E. Bublitz and G. Hoh, Paper 37, Division of Analytical Chemistry, 136th National Meeting, American Chemical Society, Atlantic City, September 1959.