

ORGANIC AND BIOLOGICAL CHEMISTRY

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS, LAWRENCE, KANS.]

Substituent Effects in the Chronopotentiometric Oxidation of Ferrocenes

BY GEORGE L. K. HOH, WILLIAM E. McEWEN AND JACOB KLEINBERG

RECEIVED APRIL 17, 1961

A large number of mono- and disubstituted ferrocenes has been oxidized chronopotentiometrically at a platinum foil electrode in lithium perchlorate-acetonitrile medium. Plots of $E_{1/4}$ values vs. σ^* , σ_m - and σ_p -values, respectively, have been constructed. Only the plot of $E_{1/4}$ vs. σ_p proved satisfactory in all respects. The implications of the results are discussed.

A previous investigation¹ has suggested that chronopotentiometric quarter-wave potentials, $E_{1/4}$, obtained for the oxidation of a limited number of substituted ferrocenes in acetonitrile can be correlated with the appropriate summation of the Taft substituent constants, $\Sigma\sigma^*$. Many additional mono- and disubstituted ferrocenes, covering a wide range of steric, resonance and inductive effects, have now been oxidized at a platinum foil electrode in lithium perchlorate-acetonitrile medium. A plot of $E_{1/4}$ vs. $\Sigma\sigma^*$ for these compounds shows a definite linear relationship. The equation of the regression line is

$$E_{1/4} = 0.0978\Sigma\sigma^* - 0.1374$$

with a correlation coefficient of 0.977. On the basis of this plot, the $E_{1/4}$ values of certain compounds are more anodic than expected. Interaction of the substituents with the $h_a g$ molecular orbital of the ferrocene nucleus is the most likely explanation for this behavior.

An equally good correlation is obtained for a similar plot of $E_{1/4}$ vs. $\Sigma\sigma_p$. The equation of the regression line for this relationship is

$$E_{1/4} = 0.431\Sigma\sigma_p + 0.367$$

with a correlation coefficient of 0.979. Moreover, this relationship takes into account the substituents which are not successfully correlated by the $\Sigma\sigma^*$ substituent constants. Because of this fact, the relationship of $E_{1/4}$ and $\Sigma\sigma_p$ is favored as best describing the effects of substituents in the oxidation of ferrocenes.

$E_{1/4}$ values for *p*-substituted phenylferrocenes show excellent correlation with the Hammett substituent constants, σ_p . This result is in agreement with the work of Mason and Rosenblum,² who correlated formal oxidation potentials of arylferrocenes with σ_p for the same series of compounds. The equation of the regression line for the plot of $E_{1/4}$ vs. σ_p is

$$E_{1/4} = 0.132\sigma_p + 0.361$$

with a correlation coefficient of 0.998.

Experimental³

Preparation of Compounds.—The previously known compounds which were studied are listed in Table I, along with the references from which methods for their preparation were taken.

(1) T. Kuwana, D. E. Bublitz and G. L. K. Hoh, *J. Am. Chem. Soc.*, **82**, 5811 (1960).

(2) J. G. Mason and M. Rosenblum, *ibid.*, **82**, 4206 (1960).

(3) All melting points are corrected, unless otherwise noted. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

A list of newly synthesized compounds, along with their analyses and physical constants, is given in Table II. The methods of preparation of these compounds are given below.

All compounds synthesized were purified by means of chromatography on alumina. Additional purification, if needed, was carried out by sublimation or recrystallization from an appropriate solvent. The alumina used was Alcoa F-20, which was activated in a muffle furnace at 400° and deactivated to a known activity.⁴ It was found that activity III (A_{III}) was most useful.

Development and elution of the chromatograms was carried out with Skelly B solvent, or with mixtures of Skelly B-diethyl ether, depending on the polarity of the adsorbed compound. The Skelly B solvent used for elution purposes was purified by distillation through a column packed with perforated stainless steel saddles (Scientific Development Co., State College, Pa.). The fraction boiling in the range 60–68° was taken, and then passed through a 3 cm. \times 75 cm. column containing A_I alumina. The diethyl ether was dried by distillation from sodium metal or calcium hydride.

Propenylferrocene was prepared by a modification of the method used for the preparation of vinylferrocene.⁵ A solution of 2.0 g. of ethylferrocenylcarbinol (ref. d, Table I) in 40 ml. of Skelly B solvent was poured onto 20 g. of A_I alumina. The solvent was removed under reduced pressure on a rotary evaporator. A Pyrex wool plug served to keep the alumina from entering the rotary evaporator. The flask was flushed with nitrogen and maintained under a nitrogen atmosphere while it was immersed in an oil-bath maintained at 150°. Uniform distribution of heat to the contents of the flask was accomplished by rotation of the flask while in the oil-bath. After 2 minutes, the flask was removed from the oil-bath and cooled by immersion in a water-bath. The mixture was extracted with Skelly B solvent in a Soxhlet apparatus and, on completion of the extraction, the solution was concentrated and chromatographed on A_{III} alumina with Skelly B solvent as the eluent. The first material eluted proved to be propenylferrocene, which was obtained on evaporation of the solvent. Propenylferrocene decomposes rapidly on exposure to air.

Alkyl- and Dialkylferrocenes Substituted with -CH₂R Groups.—Ferrocenes bearing -CH₂R substituents were conveniently prepared by the method of Weliky and Gould.⁶ This method involves the reduction of an acylferrocene or diacylferrocene to the corresponding hydrocarbon by means of zinc and acetic acid containing hydrochloric acid.

In general, approximately 2 g. of the ketone was dissolved in 50 ml. of glacial acetic acid, with warming on the steam-bath, if necessary, to effect solution. To this solution which was stirred with a magnetic stirrer was added 25 g. of zinc dust followed by 20 ml. of 6 N hydrochloric acid. The reaction mixture was allowed to stir for 3 hours, after which time an additional 10 ml. of the 6 N hydrochloric acid was added. The reaction was allowed to proceed for at least 18 hr., stirring being maintained throughout this period. The reaction mixture then was diluted with 100 ml. of water, and this solution decanted from the zinc into a separatory funnel. The zinc dust was rinsed several times with ether until the rinsings were colorless. These rinsings were poured into the separatory funnel and the

(4) G. Hesse, I. Daniel and G. Wohlleben, *Angew. Chem.*, **64**, 103 (1952).

(5) P. J. Graham, R. V. Lindsey, G. W. Parshall, M. L. Peterson and G. M. Whitman, *J. Am. Chem. Soc.*, **79**, 3416 (1957).

(6) N. Weliky and E. S. Gould, *ibid.*, **79**, 2742 (1957).

TABLE I
KNOWN COMPOUNDS

Substituent*	M.p., °C.		<i>n</i> ²⁵ _D obsd.	<i>n</i> _D (<i>t</i> , °C.) lit.	Ref
	Obsd.	Lit.			
Di-C ₂ H ₅	Liquid		1.5762	1.5761(25)	^a
<i>i</i> -C ₃ H ₇	Liquid		1.5868	1.5897(20)	^d
C ₂ H ₅	Liquid		1.5988	1.6010(20)	^d
CH ₃	31-33 ^b	35-36			^e
PhCH ₂	75.0-76.0	73-74			^f
Di-PhCH ₂	103.2-104.2	105-106			^f
H	172-173 ^b	173-174			^g
CH ₃ OCH ₂	Liquid		1.5969	1.5996(20)	^h
PhOCH ₂	130.2-130.6	129-130			ⁱ
CH ₃ CO	84.6-85.6	85-86			ⁱ
Di-CH ₃ CO	125.8-127.0	127.0-127.5			^c
C ₂ H ₅ CO	37-39 ^b	38-39; liq.		^{k, l}
<i>i</i> -C ₃ H ₅	64.5-66.5	74-75			^m
CH ₃ CH(OH)	77.4-77.8	73-75			^e
C ₂ H ₅ CH(OH)	Liquid		1.5994		^d
CH ₂ =CH	51-52 ^b	48-49			^e
PhCH(OH)	80.0-80.8	80.3-80.5			^f
PhCO	110.5-112.0	111.5-112.0			^f
Di-PhCO	105.8-106.4	106.5-106.7			^f

* Ph = phenyl; all disubstituted compounds are 1,1'. ^b Uncorrected. ^c M. Vogel, M. D. Rausch and H. Rosenberg, *J. Org. Chem.*, **22**, 1016 (1957). ^d A. N. Nesmeyanov and N. S. Kochetkova, *Dokl. Akad. Nauk. S.S.S.R.*, **114**, 800 (1957). ^e A. N. Nesmeyanov and E. G. Perevalova, *Uspekhi Khim.*, **27**, 3 (1958). ^f M. D. Rausch, M. Vogel and H. Rosenberg, *J. Org. Chem.*, **22**, 903 (1957). ^g G. Wilkinson, *Org. Syntheses*, **36**, 34 (1956). ^h A. N. Nesmeyanov, E. G. Perevalova, Yu. A. Ustynuk and L. S. Shilovtseva, *Izvest. Akad. Nauk, S.S.S.R., Otdel. Khim. Nauk*, 554 (1960). ⁱ A. N. Nesmeyanov, E. G. Perevalova, L. S. Shilovtseva and Yu. A. Ustynuk, *Dokl. Akad. Nauk, S.S.S.R.*, **124**, 331 (1958). ^j P. J. Graham, R. V. Lindsey, G. W. Parshall, M. L. Peterson and G. M. Whitman, *J. Am. Chem. Soc.*, **79**, 3416 (1957). ^k C. R. Hauser and J. K. Lindsay, *J. Org. Chem.*, **22**, 482 (1957). ^l M. D. Rausch and L. E. Coleman, Jr., *ibid.*, **23**, 107 (1958). ^m K. L. Rinehart, Jr., P. A. Kittle and A. F. Ellis, *J. Am. Chem. Soc.*, **82**, 2082 (1960).

TABLE II
NEWLY SYNTHESIZED COMPOUNDS

Substituent Ph = phenyl ¹	M.p., °C.	<i>n</i> ²⁵ _D	<i>d</i> ₂₀	Formula	Carbon, %		Hydrogen, %		Iron, %	
					Calcd.	Found	Calcd.	Found	Calcd.	Found
CH ₃ CH=CH	Liquid	1.6310	1.24	C ₁₃ H ₁₄ Fe	69.06	69.12	6.24	6.37	24.70	24.60
<i>n</i> -C ₃ H ₇	Liquid	1.5846	1.22							
PhCH(CH ₃)	Liquid	1.6270	1.19	C ₁₈ H ₁₈ Fe	74.50	74.79	6.25	6.58	19.25	19.44
PhCH(C ₂ H ₅)	58.4-59.6			C ₁₉ H ₂₀ Fe	75.01	75.39	6.63	6.58	18.36	18.57
C ₂ H ₅ CH(CH ₃)	Liquid	1.5951	1.20							
PhCH ₂ CH ₂	55.0-57.0			C ₁₈ H ₁₈ Fe	74.50	74.25	6.25	6.18	19.25	19.25
(CH ₃) ₂ CCH(CH ₃)	Liquid	1.5687		C ₁₉ H ₂₀ Fe	71.12	71.31	8.21	8.48	20.67	20.85

aqueous acetic acid solution extracted. The two layers were separated and the aqueous layer extracted with several fresh portions of ether. The ethereal extracts were combined and washed twice with water, then twice with 10% sodium carbonate solution. After the solution had been dried over magnesium sulfate, the ether was removed by means of a rotary evaporator. The residue was taken up in a small quantity of Skelly B solvent or Skelly B-benzene and chromatographed on A₁₁₁ alumina with Skelly B solvent as eluent. If benzene was required to dissolve the residue, the first compound to be eluted was rechromatographed on A₁₁₁ alumina with Skelly B solvent as eluent.

Reduction of the appropriate acylferrocenes by this method gave *n*-propyl- and β -phenylethylferrocene. Both of these compounds proved to be relatively unstable and decomposed rapidly on standing.

Alkylferrocenes Substituted with -CHRR' Groups.—Ferrocenes bearing branched hydrocarbon substituents were synthesized by a two-step method: (1) the appropriate acylferrocene was condensed with a suitable Grignard reagent to give a tertiary alcohol; (2) the alcohol was then reduced to the hydrocarbon by the action of zinc dust in acetic acid containing hydrochloric acid. The compounds prepared by this procedure were: α -phenylethyl-, α -phenyl-*n*-propyl-, *sec*-butyl- and methyl-*t*-butylcarbonylferrocene.

The syntheses were carried out on a 0.02- to 0.05-mole scale. Grignard reagents were made up in anhydrous ether in twofold molar excess over the acylferrocene. In the preparation of *t*-butylmagnesium chloride, the recommendations given by Kharasch and Reinmuth⁷ were followed.

Acetylferrocene was added to the Grignard reagents in ether solution, whereas benzoylferrocene was added to the Grignard mixtures in 1:1 benzene-ether solution. On completion of the addition, reaction mixtures were refluxed for at least 2 hours, then poured with stirring into an ice-water mixture. Hydrochloric acid (3 *N*) was added to the stirred mixture to dissolve the magnesium hydroxide, and the ether layer was separated from the aqueous layer by means of a separatory funnel. After the ethereal solution of the tertiary alcohol had been dried over magnesium sulfate, the ether was removed by the use of a rotary evaporator. The crude tertiary alcohol was dissolved in approximately 50 ml. of glacial acetic acid. To this stirred solution was added 25 g. of zinc dust, followed by 20 ml. of 6 *N* hydrochloric acid. The solution immediately darkened on the addition of the mineral acid. An additional 20 ml. of 6 *N* hydrochloric acid was added after the reaction had proceeded for 2 hours. After the reaction mixture had been stirred for at least 18 hours, it was diluted with 100 ml. of water and decanted from the remaining zinc. The zinc was rinsed with several portions of ether until the rinsings were colorless. The aqueous acid was extracted with the ether rinsings of the zinc, followed by additional extractions with fresh portions of ether until little color was evident in the aqueous layer. All ether extracts were combined, washed with water and 10% sodium carbonate solution, then dried over magnesium sulfate. The ether was re-

(7) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Non-metallic Substances," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1954, p. 19.

moved by means of a rotary evaporator, and the crude product taken up in Skelly B solvent or Skelly B-benzene. This concentrated solution was chromatographed on A₁₁₁ alumina with Skelly B solvent as eluent. If benzene was required to dissolve the crude product, the first compound to be eluted was rechromatographed on another column of A₁₁₁ alumina with Skelly B solvent as eluent. In most cases, side products of the reaction contained in bands following the first one were neglected.

Isopropylferrocene, one of the previously known compounds, was also prepared by this general method. In the chromatographic separation of the compound from side products of the reduction reaction, the second compound eluted from the column was also isolated. The infrared spectrum of this compound indicated the absence of unsaturated substituents. It is thought that this compound is either the reduced coupling-reaction product of the isopropylferrocenyl radical-ion, or else a low molecular weight polymer of isopropylferrocene. The observed melting point (210–212° dec.) is not in agreement with the reported⁸ melting point of 2,3-diferrocenyl-2,3-dimethylbutane (74–75°).

Anal. Calcd. for C₂₆H₃₀Fe₂: C, 68.75; H, 6.66; Fe, 24.59. Found: C, 68.84; H, 6.76; Fe, 24.33.

With the exception of α -phenylpropylferrocene (a solid) and methyl-*t*-butylcarbonylferrocene (a liquid), the liquid alkylferrocenes obtained here decompose readily on standing. It is interesting that the methyl-*t*-butylcarbonylferrocene did not decompose on storage for several months in a glass-stoppered flask; the pure liquid remained clear. On the other hand, the other alkylferrocenes, especially α -phenylethylferrocene, decompose on standing for only a short while.

Chronopotentiometric Oxidation of Ferrocenes.—The chronopotentiometric equipment was conventional, and similar to that described previously.¹ Daily calibration of the entire measuring circuit was accomplished by use of a stepped output from a portable potentiometer. The bright platinum foil working electrode was cleaned prior to obtaining a series of chronopotentiograms by anodization in the 0.2 *M* lithium perchlorate-acetonitrile medium, with subsequent washing by a portion of the solution to be analyzed. Cleaning by this method gave more reproducible results than did cleaning with chromic or nitric acid. With a clean electrode, the background medium was electrochemically inactive up to +2.0 volts vs. the saturated calomel electrode on electrolysis at a current density of 250 microamp. per cm.². Potentials are reported using the European convention, with no corrections being made for any junction potentials which may appear between the aqueous calomel electrode and the acetonitrile medium.

Cathodic transition times, τ_c , were obtained by reversing the current at a potential which corresponded to an anodic transition time, τ_a , of 20 seconds, as determined by a previous anodic scan at the same current density.

At least five scans at different current densities giving τ_a ranging from 5 to 25 seconds were used to obtain the average values of $E_{1/4}$ and the chronopotentiometric current constant, $i\tau^{1/2}/C$, reported for each compound. The chronopotentiograms of the compounds studied were all well defined. The results are given in Tables III and IV.

Discussion of Results

The Taft Relationship: $E_{1/4}$ vs. $\Sigma\sigma^*$.—In Fig. 1 there is shown a plot of the $E_{1/4}$ values vs. known $\Sigma\sigma^*$ values for the substituents of the first twenty compounds listed in Table III. The equation for the line obtained, as calculated by the method of least squares, is

$$E_{1/4} = 0.0978\Sigma\sigma^* - 0.1374 \quad (1)$$

with a correlation coefficient of 0.977.

The fact that the plot of $E_{1/4}$ values vs. $\Sigma\sigma^*$ values is linear for most of the substituted ferrocenes given in Table III would seem to indicate that the effects of the substituents are primarily inductive in nature and that resonance effects

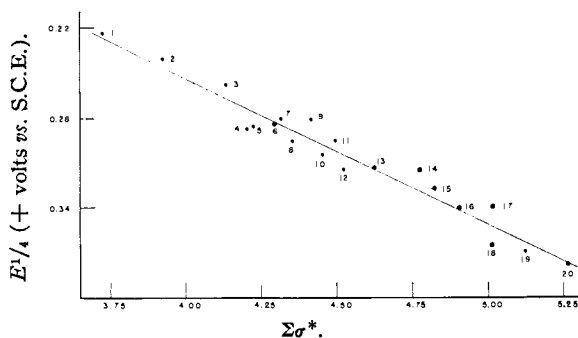


Fig. 1.—Plot of $E_{1/4}$ vs. $\Sigma\sigma^*$

remain constant. Steric hindrance to the removal of an electron from a substituted ferrocene at the platinum electrode in acetonitrile apparently is not of importance, even when the substituent is a bulky one such as the methyl-*t*-butylcarbonyl group. This lack of steric inhibition of oxidation at the electrode has been attributed^{8a} to the ability of the cyclo-

TABLE III
FERROCENES WITH KNOWN σ^* OR σ_p -VALUES FOR THE
SUBSTITUENT

Substituent ^a	$E_{1/4}$ ^b	$E_{0.25}$ ^b	τ_a/τ_c	Concn. ^c	$i\tau^{1/2}/C$ ^d	Dev., %
1 Di-C ₂ H ₅	224 ± 1	221	3.16	8.64	551	0.6
2 Di-CH ₃	241 ± 4	224	3.35	9.46	650	1.3
3 CH ₃ CHC(CH ₃) ₂	258 ± 2	252	3.34	10.74	612	0.8
4 <i>sec</i> -C ₄ H ₉	288 ± 1	287	3.50	8.10	674	1.0
5 <i>i</i> -C ₃ H ₇	286 ± 1	282	3.46	7.45	664	0.9
6 <i>n</i> -C ₃ H ₇	284 ± 1	278	3.41	8.76	648	0.8
7 C ₂ H ₅	281 ± 2	274	3.65	12.42	689	1.4
8 Di-PhCH ₂	296 ± 1	285	3.80	5.62	536	1.5
9 CH ₃	281 ± 2	272	3.80	12.90	665	1.2
10 α -PhC ₂ H ₅	305 ± 2	297	3.21	6.84	582	1.0
11 β -PhC ₂ H ₅	296 ± 1	287	2.68	6.06	536	2.2
12 α -PhC ₂ H ₅	315 ± 2	315	3.38	8.54	550	0.7
13 PhCH ₂	314 ± 1	309	3.57	7.60	622	0.7
14 CH ₃ CH=CH	316 ± 2	307	4.14	8.84	639	1.6
15 PhCH=CH	328 ± 3	314	3.13	6.78	575	1.9
16 H	341 ± 2	335	3.24	9.87	680	0.9
17 CH ₂ OCH ₃	340 ± 3	335	3.46	7.82	606	.6
18 Ph	366 ± 1	360	3.44	7.40	638	.8
19 Di-Ph	370 ± 1	365	3.26	7.21	589	.8
20 PhOCH ₂	378 ± 1	374	3.61	6.36	664	.9
21 CH ₃ CO	587 ± 3	560	9.70	9.38	645	14.4
22 (CH ₃) ₂ Si	346 ± 2	337	3.60	10.46	621	0.7
23 Bis-(CH ₃) ₂ Si	346 ± 1	340	3.36	5.94	585	0.5
24 <i>p</i> -OCH ₃ C ₆ H ₄	323 ± 1	314	3.56	6.91	599	1.3
25 <i>p</i> -ClC ₆ H ₄	387 ± 1	378	4.01	7.55	578	2.2
26 <i>p</i> -BrC ₆ H ₄	396 ± 1	390	3.46	7.75	608	0.6
27 <i>p</i> -CH ₃ COC ₆ H ₄	426 ± 1	412	3.58	7.96	266 ^e	1.7
28 <i>p</i> -NO ₂ C ₆ H ₄	464 ± 1	455	3.82	7.62	583	1.7

^a Ph = phenyl; all disubstituted ferrocenes have 1,1'-orientation of the substituents. ^b Values in millivolts vs. saturated calomel electrode. ^c Concentration in *M* × 10⁴. ^d Values in units of amp. cm. sec.^{1/2} mole⁻¹. ^e The reason for this low value is unknown.

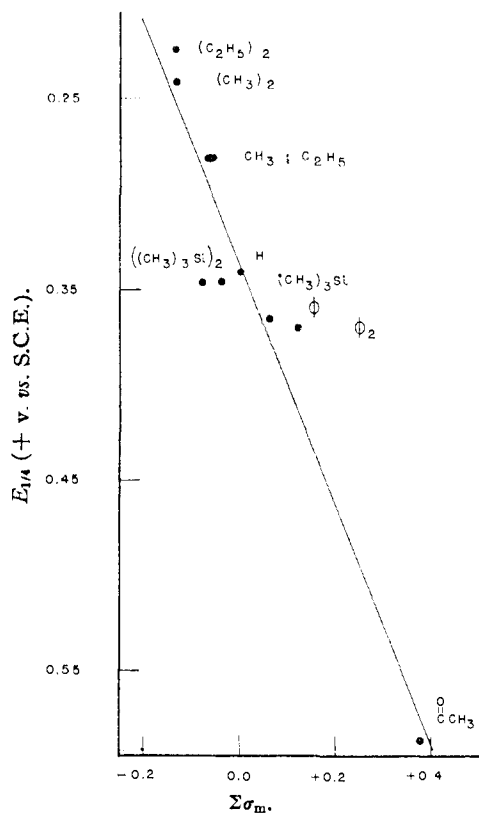
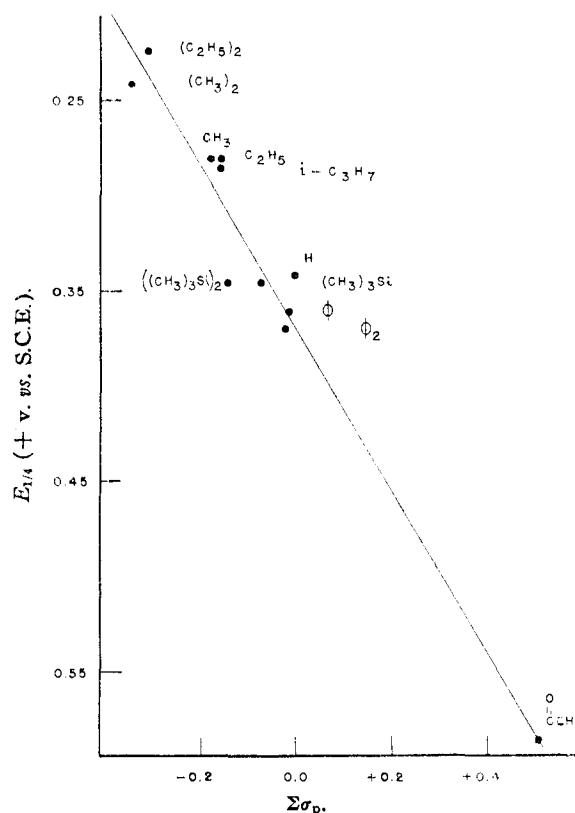
TABLE IV
SUBSTITUTED FERROCENES (σ^* - AND σ_p -VALUES FOR SUBSTITUENTS UNKNOWN)

Substituent	$E_{1/4}$ ^a	$E_{0.25}$ ^a	τ_a/τ_c	Concn. ^b	$i\tau^{1/2}/C$ ^c	Dev., %
1 Dioctyl	228 ± 1	207	4.62	5.41	496	2.8
2 Didecyl	222 ± 1	212	3.54	5.33	463	2.5
3 Cinnamoyl ^d	594 ± 1	578	8.25	8.03	562	2.0
4 Formyl ^d	624 ± 2	598	9.44	4.48

^a Values in millivolts vs. saturated calomel electrode. ^b Concentration in *M* × 10⁴. ^c Values in units of amp. cm. sec.^{1/2} mole⁻¹. ^d Data obtained over limited range of current density.

(8) K. L. Rinehart, Jr., P. A. Kittle and A. F. Ellis, *J. Am. Chem. Soc.*, **82**, 2082 (1960).

(8a) T. Kuwana, Ph.D. Thesis, University of Kansas, 1959.

Fig. 2.—Plot of $E_{1/4}$ vs. $\Sigma\sigma_m$.Fig. 3.—Plot of $E_{1/4}$ vs. $\Sigma\sigma_p$.

pentadienyl rings of the ferrocenes in solution to undergo rotation about the iron atom, thus permitting a close approach of the molecules to the electrode.

It was observed that the $E_{1/4}$ values for certain substituted ferrocenes could not be correlated with $\Sigma\sigma^*$ -values. Specifically, the $E_{1/4}$ values for acetylferrocene (cmpd. 21, Table III), trimethylsilylferrocene (cmpd. 22) and 1,1'-bis-(trimethylsilyl)-ferrocene (cmpd. 23) indicated that these compounds underwent oxidation less readily than predicted on the basis of the Taft relationship. It appears reasonable to attribute this increased stability to oxidation either to the overlap of the h_g molecular orbital⁹ of the ferrocene nucleus or the cyclopentadienyl π -orbitals with the π -orbital of the carbonyl group in the acetyl derivative and with a d -orbital of the silicon atom in the trimethylsilyl derivatives. This overlap in effect decreases the electron density on the iron atom and increases the stability of the molecule as a whole. The significance of such overlap in reactions involving α -metallocenylcarbonium ions has recently been emphasized in a number of publications.^{8,10-13}

Of the monosubstituted ferrocenes investigated, ferrocenecarboxaldehyde (cmpd. 4, Table IV)

(9) W. Moffitt, *J. Am. Chem. Soc.*, **76**, 3386 (1954).

(10) G. R. Buell, W. E. McEwen and J. Kleinberg, *Tetrahedron Letters*, No. 5, 16 (1959).

(11) J. H. Richards and E. A. Hill, *J. Am. Chem. Soc.*, **81**, 3484 (1959).

(12) D. S. Trifan and R. Bacskai, *Tetrahedron Letters*, No. 13, 1 (1960).

(13) A. Berger, W. E. McEwen and J. Kleinberg, *J. Am. Chem. Soc.*, **83**, 2274 (1961).

proved to be the compound most difficult to oxidize. Tirouflet and Boichard¹⁴ have studied the oxidation of a number of ferrocenes at the rotating platinum electrode in aqueous ethanol and have reported that acetylferrocene and ferrocenecarboxaldehyde undergo oxidation at the same potential (0.51 v. vs. S.C.E.). In the present study, the aldehyde was found to be oxidized at a potential 37 mv. more positive (polarographers' convention) than that observed for the ketone. This is consistent with the fact that a formyl group has a greater attraction for electrons than an acetyl group.

The Hammett Relationship: $E_{1/4}$ vs. $\Sigma\sigma_m$ and $\Sigma\sigma_p$.—In Figs. 2 and 3 there are shown plots of $E_{1/4}$ values vs. $\Sigma\sigma_m$ and $\Sigma\sigma_p$ values, respectively, for those compounds in Table III for which σ_m and σ_p values are available. As shown in Fig. 2, the Hammett correlation for $E_{1/4}$ vs. $\Sigma\sigma_m$ is not a particularly good one. The equation of the regression line is

$$E_{1/4} = 0.628\Sigma\sigma_m + 0.337 \quad (2)$$

with a correlation coefficient of 0.957. A plot of $E_{1/4}$ vs. $\Sigma\sigma_p$, however, gives a better correlation. The equation of the line shown in Fig. 3 is

$$E_{1/4} = 0.431\Sigma\sigma_p + 0.367 \quad (3)$$

with a correlation coefficient of 0.979.

It is noteworthy that the use of σ_p -values permits the Hammett correlation to be extended to the substituents acetyl and trimethylsilyl which could not be accommodated by the Taft relationship. Apparently, the σ_p -values take into consideration all of the interactions between these groups and

(14) J. Tirouflet and J. Boichard, *Compt. rend.*, **250**, 1861 (1960).

the ferrocene nucleus. Values for σ_p were originally derived from the ionization constants of benzoic acid and its substitution products, and, in a *p*-substituted benzoic acid, there exists a resonance interaction between substituent and carboxyl group as relayed through the ring. Values of σ_m and σ^* do not include a resonance contribution of this type. Thus, it may be concluded that the resonance interactions between substituents and the ferrocene nucleus parallel those between substituents and the carboxyl group in *p*-substituted benzoic acids.

In Fig. 4 there is shown a plot of $E_{1/4}$ values vs. σ_p -values for a series of *p*-substituted phenylferrocenes. The equation of the line is

$$E_{1/4} = 0.132\sigma_p + 0.361 \quad (4)$$

with a correlation coefficient of 0.998. These results are in substantial agreement with the findings of Mason and Rosenblum,² who have determined formal oxidation potentials for the same compounds¹⁵ by titration with dichromate ion in aqueous acetic acid containing perchloric acid. Calculation of the equation for the regression line from the data of Mason and Rosenblum in the form employed in this study gives

$$E_{0.1}^{Ar} = 0.151\sigma_p + 0.255 \quad (5)$$

From eq. 4 and 5 it is evident that the slope for the line based upon chronopotentiometric data is less than the slope for the line obtained by the titrimetric method. The difference in slopes is probably due in large part to the difference in solvation effects between acetonitrile (the solvent employed in our study) and aqueous acetic acid.

The linearities of the plot of $E_{1/4}$ values vs. $\Sigma\sigma^*$ values (except for the values of acetylferrocene and the trimethylsilylferrocenes) and of the plot of $E_{1/4}$ values vs. $\Sigma\sigma_p$ permit the calculation of substituent constants which are unknown for one system but known for the other. From eq. 1 and

(15) We are indebted to Professor Rosenblum for his gift of samples of these compounds.

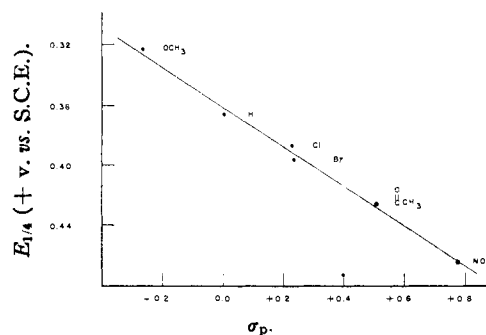


Fig. 4.—Plot of $E_{1/4}$ vs. σ_p for *p*-substituted phenylferrocenes.

3 the following relationships are derived

$$\Sigma\sigma^* = 4.406\Sigma\sigma_p - 5.156 \quad (6)$$

$$\Sigma\sigma_p = 0.227\Sigma\sigma^* + 1.170 \quad (7)$$

It should be emphasized that eq. 6 and 7 are applicable only in those instances in which there cannot be significant overlap between the h_a molecular orbital of the ferrocene nucleus and a suitable p or d orbital of an atom of the substituent group. It must also be remembered that the $\Sigma\sigma^*$ term in eq. 1 includes proper values for the weighting of hydrogen as well as the substituents.

Finally, the values of substituent constants calculated by use of eq. 6 and 7 must be regarded as tentative ones and must be tested in other systems before their validity can be considered to be established.

Acknowledgment.—This research was supported by grants from the Petroleum Research Fund administered by the American Chemical Society, and the Office of Ordnance Research, U. S. Army. Grateful acknowledgment is made to the donors of these funds. We are indebted to Dr. Marvin D. Rausch and to Dr. D. E. Bublitz for their gifts of samples of several ferrocenes, and to Dr. Theodore Kuwana and to Dr. Ralph N. Adams for helpful discussions.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI, CINCINNATI 21, OHIO]

The Kinetics and Mechanism of the Reaction of Borohydrides with Weak Acids¹

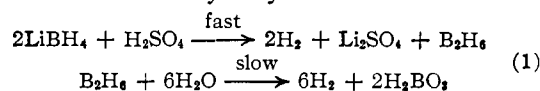
BY RAYMOND E. DESSY AND EDWARD GRANNEN, JR.

RECEIVED DECEMBER 6, 1960

The mechanism of the reaction of NaBH_4 and $\text{C}_6\text{H}_5\text{OH}$ in diglyme to yield hydrogen plus sodium phenoxyborohydride has been investigated, and found to obey the rate law $d(\text{H}_2)/dt = (k(\text{C}_6\text{H}_5\text{OH})^2(\text{NaBH}_4)/(\text{C}_6\text{H}_5\text{ONa}))$. Evidence indicates that $\text{C}_6\text{H}_5\text{OH}_2^+$ is the attacking species; $k_H/k_D(\text{C}_6\text{H}_5\text{OH})$ is 1.7. The reaction of LiBH_4 with CH_2OH is similar in character. $k_H/k_D(\text{LiBH}_4)$ is 0.63. These isotope effects, along with the fact that the rate of reaction of LiBH_4 with HA increases along the series C_6H_6 , $\text{C}_4\text{H}_8\text{N}$, *t*-BuOH, CH_3OH , as HA is varied, while the K_a 's of the acids increase along the series C_6H_6 , *t*-BuOH, CH_3OH , C_6H_6 , suggests a four-center transition state for the reactions.

Although reactions of the alkali borohydrides with acids have been investigated, relatively few systematic surveys have been undertaken. Kilpatrick² measured the rate of reaction of LiBH_4

with H_2SO_4 in water by a manometric method involving a pressure transducer. He suggested that the mechanism of hydrolysis was



(1) The Research reported in this paper was partially supported by the Air Force Office of Scientific Research, Air Research and Development Command, under contract AF 49(638)-824 with the University of Cincinnati. The paper is identified as AFOSR TN-60-1467.

(2) M. Kilpatrick and C. D. McKinney, *J. Am. Chem. Soc.*, **72**, 5474 (1950).