December, 1981] © *1981 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, 54, *3723—3726 (1981)* 3723

Electrochemical Properties of Ferrocenophanes. I. Voltammetric Studies on the Oxidation of Mono-, Di-, and Tri-bridged Ferrocenophanes in Acetonitrile

Tateaki OGATA,* Kazuo OIKAWA, Tadashi FUJISAWA, Shunsuke MOTOYAMA,†
Taeko IZUMI,† Akira KASAHARA,† and Nobuyuki TANAKA††
Department of Environmental Chemistry, Yamagata Technical College, Jonan, Yonezawa 992
†*Department of Applied Chemistry, Faculty of Engineering, Yamagata University, Jonan, Yonezawa 992*
††*Department of Chemistry, Faculty of Science, Tohoku University, Aramaki, Sendai 980*

(Received May 18, 1981)

Electrode reactions of mono-, di- and tri-bridged ferrocenophanes ([3]Fcp, [4]Fcp, [3][3]Fcp, [4][3]Fcp, [4][4]Fcp, [3][3][3]Fcp, [4][4][3]Fcp and [4][4][4]Fcp) in acetonitrile were investigated by direct current polarography, pulse polarography, and cyclic voltammetry. The oxidation of these compounds proceeds reversibly as a one-electron process. The linear relationship between the half-wave potential and the number of methylene groups was obtained for ferrocene and ferrocenophanes other than [3][3]Fcp and [3][3][3]Fcp. The Taft substituent constants of trimethylene and tetramethylene groups were estimated.

Electrochemical properties of ferrocene and substituted ferrocenes have been studied by many authors.[1,2] These studies have revealed that the oxidation of ferrocene and its derivatives proceeds reversibly as a one-electron process in nonaqueous solutions. Their reversible oxidation potentials change in ways dependent on the substituent: the oxidation potential of the derivatives with the electron donating substituents, such as alkyl groups, is lower than that of ferrocene. Such substituent effects have been discussed through the examination of the relation between the oxidation potential and some substituent constant, for example, the Taft substituent constant (σ^*). Thus, Hoh, McEwen, and Kleinberg[3] have reported the following experimental equation:

$$(E_{1/4}\ vs.\ \text{aq SCE})/\text{V} = 0.0978\,\Sigma\sigma^* - 0.1374, \qquad (1)$$

where $E_{1/4}$ is the chronopotentiometric quarter-wave potential in acetonitrile and $\sum\sigma^*$ is the summation of Taft substituent constants. This equation is applicable to ferrocene and nineteen mono- and disubstituted ferrocenes.

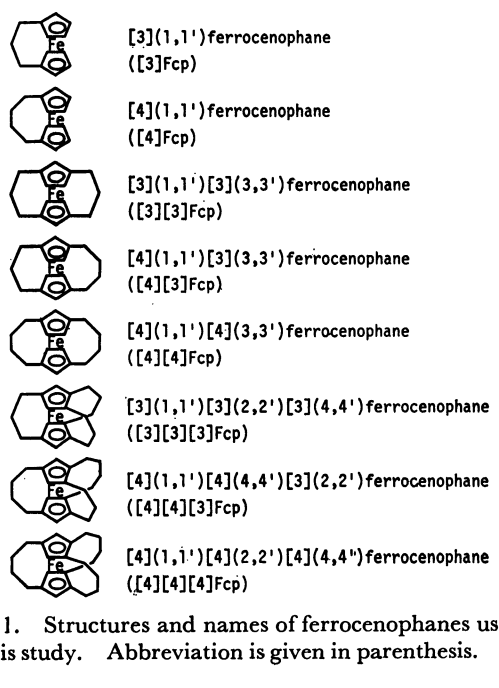

Fig. 1. Structures and names of ferrocenophanes used in this study. Abbreviation is given in parenthesis.

Recently, many ferrocenophanes have become increasingly important in the organometallic chemistry. However, the electrode reactions and the substituent effects, as mentioned above, still remain open to investigation. Therefore, the electrode reactions of the eight ferrocenophanes shown in Fig. 1 have been investigated by direct current polarography, pulse polarography, and cyclic voltammetry in acetonitrile. The results are reported here. Furthermore, the substituent effects on the oxidation potentials of ferrocenophanes are discussed.

Experimental

Acetonitrile (Wako Chemical Co.) was purified by the method proposed by Coetzee.[4] Ferrocenophanes used in this study were prepared according to the methods given in the literature,[5–9] and identified by the elemental analysis and the measurements of NMR and IR spectra. Tetraethylammonium perchlorate (TEAP) was prepared and dried by the usual method.[10] Ferrocene (Eastman Kodak Co.) and other chemicals were of guaranteed reagent grade and used without further purification.

Direct current (d.c.) polarograms, pulse polarograms, and cyclic voltammograms were recorded with a PAR Model 174A polarographic analyzer equipped with a Rikadenki Model RW-11 x-y recorder and a potential scanner made in this laboratory at Yamagata University. All the measurements were carried out at 25 °C under a dry nitrogen atmosphere by use of a three electrode system consisting of a working electrode (dropping mercury electrode for d.c. and pulse polargraphy, and spherical platinum electrode for cyclic voltammetry), a coiled platinum wire counter electrode, and an aqueous saturated calomel electrode (aq SCE) as a reference electrode. The dropping mercury electrode used had a flow rate of 1.02 mg s^{-1} in acetonitrile at open circuit. Drop time for pulse polarography was controlled to 5 s with the drop timer attached to the Model 174A. The pretreatment of the platinum working electrode (approximately 1 mm in diameter) prior to measurements was to apply a cycling potential (between −0.3 V and 1.1 V *vs.* aq SCE) to the electrode in an aqueous solution of 0.1 mol dm^{-3} sulfuric acid. This electrode was washed with distilled water, dried, and then used in the measurements. For electrolytic contact of aq SCE, an agar salt bridge with 1 mol dm^{-3} aqueous sodium chloride solution was inserted into one compartment of the electrolytic cell. The half cells in the electrolytic cell were interconnected through a sintered glass disk. All the test solutions contained 0.2 mol dm^{-3} TEAP as a supporting electrolyte.

Results and Discussion

Electrode Reactions of Ferrocenophanes. Ferrocenophanes used here gave one d.c. polarographic oxidation wave in acetonitrile containing 0.2 mol dm^{-3} TEAP as a supporting electrolyte. The limiting current of the wave was found to be diffusion-controlled. The diffusion coefficients at 25 °C calculated from the Ilkovic equation by assuming $n=1$ are given in Table 1. The diffusion coefficient of ferrocene obtained in this study is also given in Table 1. From the result that the values of diffusion coefficients of ferrocenophanes were nearly equal to that of ferrocene, the electrode reaction of each ferrocenophane at the mercury electrode was concluded to be a one-electron process. Table 1 also gives the experimental results for the d.c. polarographic half-wave potential, $E_{1/2}$, and the d.c. polarographic slope, $\Delta E(=E_{3/4}-E_{1/4})$, as conventional criteria of reversibility. The values of ΔE indicate that the oxidation step of ferrocenophanes is a reversible one-electron process.

Table 1. D. c. and pulse polaorgraphic data in acetonitrile containing 0.2 mol dm^{-3} TEAP at 25 °C

Compound[a]	$E_{1/2}$ *vs.* aq SCE / V	ΔE / mV	D[b] / 10^{-5} cm^2 s^{-1}	$\lvert I_{1c}/I_{1a}\rvert$
Ferrocene	0.365	56	3.8	0.89
[3]Fcp	0.300	57	3.3	0.99
[4]Fcp	0.279	56	3.3	0.98
[3][3]Fcp	0.291	56	2.9	1.03
[4][3]Fcp	0.202	58	2.6	1.03
[4][4]Fcp	0.196	56	2.8	1.02
[3][3][3]Fcp	0.292	57	2.6	1.03
[4][4][3]Fcp	0.119	57	2.5	1.03
[4][4][4]Fcp	0.103	55	2.5	1.01

a) Concentration of each compound is 1 mmol dm^{-3}.
b) Diffusion coefficient.

In order to investigate the reversibility of the electrode reactions of the above compounds more exactly, pulse polarograms were obtained by use of the dropping mercury electrode with a drop time of 5 s. Typical pulse polarograms obtained for [4]Fcp, [4][4]Fcp, and [4][4][4]Fcp are shown in Fig. 2. In the case of a reversible oxidation process, the current-potential curve for anodic potential scan coincides with that for cathodic one, and the magnitude of the limiting current ratio for cathodic to anodic scan, $|I_{1c}/I_{1a}|$, closely approximates unity.[11] The values of $|I_{1c}/I_{1a}|$ in last column of Table 1 indicate that the electrode reactions of ferrocenophanes are reversible.

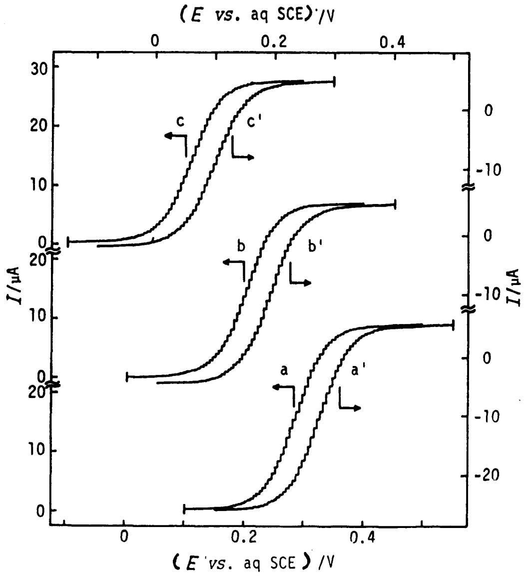

Fig. 2. Pulse polarograms of [4]Fcp (a, a′), [4][4]Fcp (b, b′), and [4][4][4]Fcp (c, c′) in acetonitrile containing 0.2 mol dm^{-3} TEAP at 25 °C. Concentration of each compound is 1 mmol dm^{-3}. Curves a, b, and c are by anodic scan, and a′, b′, and c′, cathodic scan.

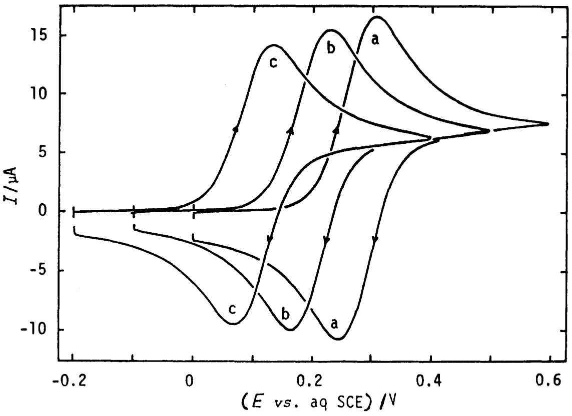

Fig. 3. Cyclic voltammograms of [4]Fcp (a), [4][4]Fcp (b), and [4][4][4]Fcp (c) in acetonitrile containing 0.2 mol dm^{-3} TEAP at 25 °C. Concentration of each compound is 1 mmol dm^{-3}.

Cyclic voltammograms of these compounds were measured by using a spherical platinum electrode at scan rates of 10 to 500 mV s^{-1}. In the region, −0.2 to 1.0 V *vs.* aq SCE, only one anodic and one cathodic current peak were observed. Typical cyclic voltammograms of [4]Fcp, [4][4]Fcp, and [4][4][4]Fcp are shown in Fig. 3. The cyclic voltammetric data at a scan rate of 100 mV s^{-1} for the formal potential, $E_f(=(E_{pa}+E_{pc})/2$, calculated from anodic peak potential, E_{pa}, and cathodic one, E_{pc}), the anodic-cathodic peak separation, $\Delta E_p(=E_{pa}-E_{pc})$, the anodic peak current, I_{pa}, the cathodic peak current, I_{pc}, and the cathodic to anodic peak current ratio, $|I_{pc}/I_{pa}|$, are given in Table 2. The values of I_{pa} of ferrocenophanes almost agree with the value of ferrocene, indicating that the electrode reaction of ferrocenophanes at the platinum electrode is a one-electron oxidation process. In addition, the values of ΔE_p and $|I_{pc}/I_{pa}|$ indicate that the electrode reactions of these compounds are reversible.

From all the results described above, it is concluded

Table 2. Cyclic voltammetric data in acetonitrile containing 0.2 mol dm^{-3} TEAP at 25 °C

Compound$^{a)}$	$\frac{E_f \text{ vs. aq SCE}}{\text{V}}$	$\frac{\Delta E_p}{\text{mV}}$	$\frac{I_{pa}}{\mu\text{A}}$	$\frac{-I_{pc}}{\mu\text{A}}$	$\lvert I_{pc}/I_{pa}\rvert$
Ferrocene	0.363	65	17.1	17.6	1.03
[3]Fcp	0.297	61	16.3	16.4	1.01
[4]Fcp	0.276	65	16.4	16.8	1.02
[3][3]Fcp	0.286	63	15.0	15.6	1.04
[4][3]Fcp	0.206	63	14.8	15.4	1.04
[4][4]Fcp	0.196	61	15.1	15.7	1.04
[3][3][3]Fcp	0.293	60	14.7	15.3	1.04
[4][4][3]Fcp	0.114	62	14.6	14.8	1.01
[4][4][4]Fcp	0.100	64	13.9	14.2	1.02

a) Concentration of each compound is 1 mmol dm^{-3}.

that the electrode reactions of ferrocenophanes used here correspond to a simple reversible one-electron oxidation from the neutral compound to its mono cation in acetonitrile at both mercury and platinum electrodes. As seen in Tables 1 and 2, the values of $E_{1/2}$ and E_f are almost the same. For this reason, the $E_{1/2}$ values are used when the substituent effects on the oxidation potential are discussed below.

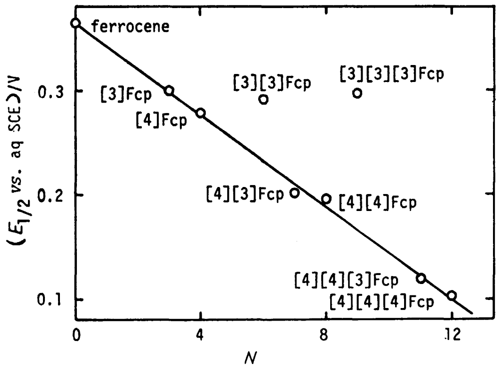

Fig. 4. Half-wave potential, $E_{1/2}$, *vs.* the number of methylene groups, N. Solid line represents Eq. 2.

Substituent Effects on the Oxidation Potential. As seen in Table 1, the $E_{1/2}$ values of ferrocenophanes are lower than the value of ferrocene and generally become more negative with an increase in the number of methylene groups. In Fig. 4, there is shown a plot of the $E_{1/2}$ value *vs.* the number of methylene groups. A linear relationship was observed for ferrocene and ferrocenophanes, except for [3][3]Fcp and [3][3][3]Fcp. The equation of the regression line for this relationship is

$$(E_{1/2} \text{ vs. aq SCE})/\text{V} = -0.0221N + 0.3654 \qquad (2)$$

with a correlation coefficient of -0.9986, where N is the number of methylene groups. This result indicates that the additivity is established between the $E_{1/2}$ value and the number of methylene groups. For example, the $E_{1/2}$ of [4]Fcp is 0.086 V lower than that of ferrocene, and addition of a second tetramethylene group, as in [4][4]Fcp, lowers $E_{1/2}$ by 0.169 V, nearly twice the value found between [4]Fcp and ferrocene. A similar additive effect has been observed in the case of mono- and disubstituted ferrocenes, such as ethylferrocene and 1,1'-diethylferrocene.[12] Therefore, the linear relationship given by Eq. 2 supports the suggestion that the bridge of trimethylene and tetramethylene groups gives rise to few metal-ring distortions in ferrocenophanes, except for [3][3]Fcp and [3][3][3]Fcp. The $E_{1/2}$ values of [3][3]Fcp and [3][3][3]Fcp are more positive than the values expected from Eq. 2. The deviation from this linearity is presumed to be due to steric effects, that is, to metal-ring bond distortions. The distortions in these two compounds can be confirmed by making a molecular model. On the basis of molecular models of [3][3]Fcp and [3][3][3]Fcp, the compression of the metal-ring bond needed to accommodate the bridge was found to be remarkable. Ferrocenophanes except for these two compounds, however, can keep enough distance between ferrocene rings at the normal distance of 332 pm.

The linear relationship between the $E_{1/2}$ and the number of methylene groups suggests that trimethylene and tetramethylene groups have a certain substituent constant. As described above, Eq. 1 is established for many substituted ferrocenes. This equation enables us to estimate the Taft substituent constant, σ^*, of trimethylene and tetramethylene groups. In the case of a reversible electrode reaction, the chronopotentiometric quarter-wave potential, $E_{1/4}$, is equal to the d.c. polarographic half-wave potential, $E_{1/2}$. Furthermore, from the $E_{1/2}$ value of ferrocene obtained in this study, Eq. 1 can be rewritten as follows:

$$(E_{1/2} \text{ vs. aq SCE})/\text{V} = 0.0978\,\Sigma\sigma^* - 0.1142, \qquad (3)$$

where $\sum\sigma^*$ is the total of Taft substituent constants. When the $E_{1/2}$ values of 0.300 V for [3]Fcp and 0.279 V for [4]Fcp are substituted for $E_{1/2}$ in Eq. 3, the $\sum\sigma^*$ values of [3]Fcp and [4]Fcp are calculated to be 4.24 and 4.02, respectively. Then, the σ^* values of trimethylene and tetramethylene groups (σ^*_3 and σ^*_4) are obtained to be 0.32 and 0.10, respectively (σ^*_3 or $\sigma^*_4 = \sum\sigma^* - 8\sigma^*_H$). The $\sum\sigma^*$ values of di- and tri-bridged ferrocenophanes are calculated by using these values of σ^*_3 and σ^*_4: for example, $\sum\sigma^*$ value of [4][3]Fcp is 3.36 by the sum of $6\sigma^*_H$, σ^*_3, and σ^*_4. The results of the calculation are given in Table 3. The plot of $E_{1/2}$ *vs.* $\sum\sigma^*$ is shown in Fig. 5. The solid line in Fig. 5 represents Eq. 3. In the case of [4][3]Fcp, [4][4]Fcp, [4][4][3]Fcp, and [4][4][4]Fcp, which have the linear relationship between the $E_{1/2}$ and the number of methylene groups and have little metal-ring bond

Table 3. Total Taft substituent constant ($\Sigma\sigma^*$) of ferrocene and ferrocenophanes

Compound	$\Sigma\sigma^*$
Ferrocene	4.90 ($10\sigma^*_H$)
[3]Fcp	4.24 ($8\sigma^*_H+\sigma^*_3$)
[4]Fcp	4.02 ($8\sigma^*_H+\sigma^*_4$)
[3][3]Fcp	3.58 ($6\sigma^*_H+2\sigma^*_3$)
[4][3]Fcp	3.36 ($6\sigma^*_H+\sigma^*_4+\sigma^*_3$)
[4][4]Fcp	3.14 ($6\sigma^*_H+2\sigma^*_4$)
[3][3][3]Fcp	2.92 ($4\sigma^*_H+3\sigma^*_3$)
[4][4][3]Fcp	2.48 ($4\sigma^*_H+2\sigma^*_4+\sigma^*_3$)
[4][4][4]Fcp	2.26 ($4\sigma^*_H+3\sigma^*_4$)

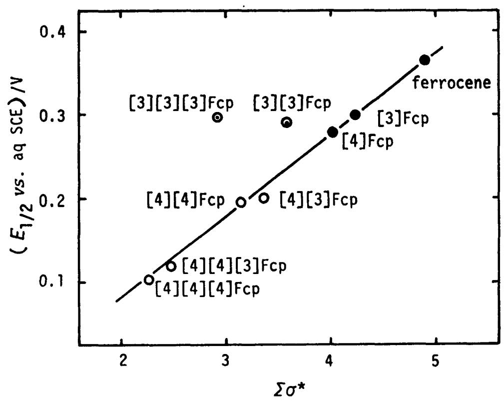

Fig. 5. Half-wave potential, $E_{1/2}$, *vs.* total Taft substituent constant, $\sum\sigma^*$. Solid line represents Eq. 3.

distortions, the points (open circles) are on the solid line. Therefore, the values of σ^*_3 and σ^*_4 obtained by assuming that Eq. 1 or Eq. 3 are valid for [3]Fcp and [4]Fcp seem to be reasonable. If so, the electronic effects of substituents for ferrocenophanes other than [3][3]Fcp and [3][3][3]Fcp are transmitted to the reaction center, *i.e.*, iron atom, through an inductive mechanism.

Since the ferrocenophanes studied here undergo a simple electrode reaction, it is expected that these compounds can be used as a "standard" for electrochemical studies. Application of ferrocenophanes to a reference redox system is now being investigated in many solvents.

References

1) C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Nonaqueous Systems," Marcel Dekker, New York (1970), p. 418.

2) G. J. Janz and R. P. T. Tomkins, "Nonaqueous Electrolytes Handbook," Vol. 2, Academic Press, New York (1978), p. 611.

3) G. L. K. Hoh, W. E. McEwen, and J. Kleinberg, *J. Am. Chem. Soc.*, **83**, 3949 (1961).

4) J. F. Coetzee, *Pure Appl. Chem.*, **25**, 305 (1971).

5) K. L. Rinehart, Jr., R. T. Curby, D. H. Gustafson, K. G. Harrison, R. E. Bozak, and D. E. Bublitz, *J. Am. Chem. Soc.*, **84**, 3263 (1962).

6) M. Rosenblum, A. K. Banerjee, N. Danieli, R. W. Fish, and V. Schlatter, *J. Am. Chem. Soc.*, **85**, 316 (1963).

7) K. L. Rinehart, Jr., D. E. Bublitz, and D. H. Gustafson, *J. Am. Chem. Soc.*, **85**, 970 (1963).

8) M. Hisatome, T. Sakamoto, and K. Yamakawa, *J. Organomet. Chem.*, **107**, 87 (1976).

9) M. Hisatome, N. Watanabe, T. Sakamoto, and K. Yamakawa, *J. Organomet. Chem.*, **125**, 79 (1977).

10) I. M. Kolthoff and J. F. Coetzee, *J. Am. Chem. Soc.*, **70**, 870 (1957).

11) K. B. Oldham and E. P. Parry, *Anal. Chem.*, **42**, 229 (1970).

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