

CYCLIC VOLTAMMETRY OF ARYLFERROCENES AND FERROCENE ANALOGUES OF CHALCONES. SUBSTITUENT EFFECTS ON THE ELECTRON DENSITY DISTRIBUTION IN FERROCENE DERIVATIVES

AGNES G. NAGY*

Chemistry Department, Central Research Institute for Physics, 1121 Budapest (Hungary)

and STEFAN TOMA

Organic Chemistry Department, Comenius University, 84215 Bratislava (Czechoslovakia)

(Received November 10th, 1983)

Summary

Cyclic voltammetry studies of arylferrocenes and two series of ferrocene analogues of chalcone are presented. Good correlations of the oxidation potentials ($E_{1/2}$) with the σ Hammett constants as well as with the ^{13}C chemical shifts for carbon atoms with different positions in the ferrocenyl moiety have been found. The different sensitivities of these series to the substituent effects is discussed. The variation of the electron density distribution at the carbon atoms of the cyclopentadienyl rings is given numerically as a function of the electron-donating or electron-withdrawing strengths of the substituents.

Introduction

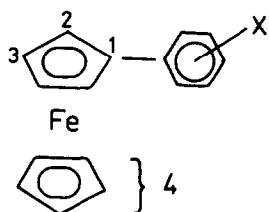
Unlike the benzene derivatives [1–4], the effects of substituents on the electron density distribution of cyclopentadienyl (cp) rings has been investigated for only a few ferrocene derivatives. Investigations have mainly focused on two methods: a chemical method that estimates the relative reactivity of the (2,5) and (3,4) positions of the substituted cp-ring in acylation or alkylation reactions [5–7]; and a spectroscopic method that measures the relative shielding of (2,5) and (3,4) protons or carbon atoms by ^1H or ^{13}C NMR [8–11]. In certain cases the identification of spectrum signals presents a problem for NMR: e.g. the unequivocal assignment of the shift for the (2,5) and (3,4) carbons of cp has only recently been achieved for some ferrocenes by means of deuterated samples [11,12].

The oxidation of ferrocene derivatives depends on the electronic character of the substituents, as revealed in the early years of ferrocene chemistry [13–15]. The

investigations reported, for example, a linear correlation between the Hammett substituent constants and the redox potentials of phenylferrocenes and of the directly substituted ferrocenes [16–18]. Analysis of the results of chronopotentiometric and cyclic voltammetric measurements showed that the oxidation potentials of ferrocene derivatives were sensitive to structural and conformation effects as well; a correlation was found, for example, between the changes of the molecular geometry and the redox potentials in the bridged ferrocenes [19–21].

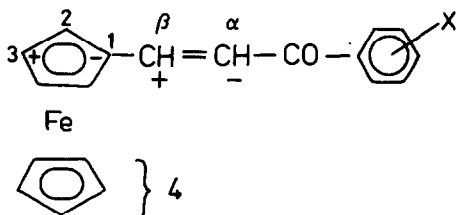
The purpose of this paper is to report the oxidation potentials ($E_{1/2}$) of two series of chalcone analogue ferrocenes and to show the correlation between the $E_{1/2}$ values of these compounds and the Hammett substituent constants as well as to present a numerical correlation between the electron-donating and electron-withdrawing strength of the different substituents and the electron density distribution of cyclopentadienyl rings in chalcone analogue ferrocenes and phenylferrocenes.

Series I



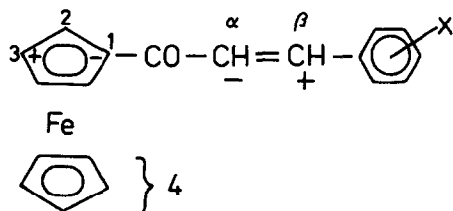
Phenylferrocene ($X = H$)

Series II



1-aryl-3-ferrocenyl-2-propene-1-one ($X = H$)

Series III



3-aryl-1-ferrocenyl-2-propene-1-one ($X = H$)

Fig. 1. Ferrocene derivative schemes (Series I, II, III).

TABLE 1

OXIDATION POTENTIALS AND ^{13}C CHEMICAL SHIFTS AND THE HAMMETT CONSTANTS OF PHENYLFERROCENE

Line number	Substituent	$E_{1/2}$ (mV)	ΔE (mV)	Chemical shift (ppm)				σ^a
				C(1)	C(2)	C(3)	C(4)	
1.	<i>p</i> -H	473 ± 1	0	85.4	66.4	68.8	69.5	—
2.	<i>p</i> -OCH ₃	429 ± 2	-44	85.8	66.0	68.4	69.3	-0.268
3.	<i>p</i> -COCH ₃	525 ± 1	52	83.3	67.0	70.0	70.0	0.502
4.	<i>p</i> -CHO	536 ± 1	63	82.9	67.1	70.2	70.0	0.420
5.	<i>p</i> -NO ₂	565 ± 2	92	81.7	67.4	70.7	70.2	0.778
6.	<i>m</i> -CHO	516 ± 5	43	83.6	66.7	69.5	69.7	0.350
7.	<i>m</i> -COCH ₃	506 ± 4	33	84.3	66.6	69.3	69.6	0.376
8.	<i>m</i> -OCH ₃	473 ± 2	0	85.3	66.7	68.8	69.7	0.115
9.	<i>m</i> -CF ₃	525 ± 2	52	83.9	66.8	69.6	69.8	0.430
10.	<i>p</i> -COOC ₂ H ₅	521 ± 1	48	83.6	67.0	70.1	70.1	0.45
11.	<i>p</i> -C ₂ H ₅	447 ± 1	-26	85.9	66.5	68.7	69.4	-0.151

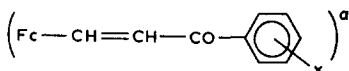
^a Values from refs. 32 and 33.

Experimental

The 1-aryl-3-ferrocenyl-2-propene-1-ones and 3-aryl-1-ferrocenyl-2-propene-1-ones (Fig. 1) were prepared by base-catalysed Claisen-Schmidt condensation with the corresponding substituted acetophenones and ferrocenealdehyde, or acetylferrocene with appropriate benzaldehydes. The purities of all compounds were checked by their melting points, TLC, and in some cases by ^1H NMR [22]. Details on the preparation and physical constants of phenyl ferrocenes were given in a previous paper [23].

The oxidation potential ($E_{1/2}$) of these compounds was measured by cyclic voltammetry in acetonitrile containing 0.1 *M* tetrabutylammonium perchlorate. A

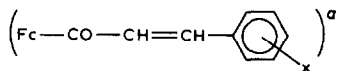
TABLE 2

OXIDATION POTENTIALS AND ^{13}C CHEMICAL SHIFTS OF SERIES II

Line number	Substituent (x)	$E_{1/2}$ (mV)	ΔE (mV)	Chemical shift (ppm)					
				C(1)	C(2)	C(3)	C(4)	C(α)	C(β)
1.	H	563 ± 1	0	79.40	69.02	71.29	69.80	119.40	146.48
2.	<i>p</i> -Br	572 ± 1	9	79.01	69.07	71.54	69.78	118.38	147.55
3.	<i>p</i> -NO ₂	585 ± 2	22	78.57	69.33	72.06	69.98	118.18	149.44
4.	<i>p</i> -OCH ₃	552 ± 1	-11	79.67	68.89	71.09	69.73	119.34	145.44
5.	<i>p</i> -F	569 ± 1	6	79.14	69.00	71.77	69.78	118.51	147.10
6.	<i>p</i> -CN	471 ± 2	-92 ^b	78.55	69.26	71.93	69.91	117.99	149.05
7.	<i>p</i> -CH ₃	559 ± 0.5	-5	79.54	68.97	71.16	69.80	119.60	145.96
8.	<i>m</i> -NO ₂	583 ± 1	19	78.62	69.39	72.06	69.98	117.54	149.31
9.	<i>m</i> -Cl	577 ± 2	13	78.89	69.09	71.59	69.80	118.30	147.85

^a Fc = ferrocenyl. ^b Out of line.

TABLE 3

OXIDATION POTENTIALS AND ^{13}C CHEMICAL SHIFTS OF SERIES III

Line number	Substituent x	$E_{1/2}$ (mV)	ΔE (mV)	Chemical shift (ppm)					
				C(1)	C(2)	C(3)	C(4)	C(α)	C(β)
1.	H	686 ± 1	0	80.58	69.72	72.80	70.11	122.95	140.85
2.	<i>p</i> -OCH ₃	664 ± 2	-22^b	80.76	69.65	72.58	70.04	120.65	140.60
3.	<i>p</i> -Cl	689 ± 1	3	80.44	69.72	72.90	70.11	123.32	139.37
4.	<i>p</i> -CN	698 ± 1	12	80.24	69.85	73.29	70.24	125.98	138.33
5.	<i>p</i> -F	684 ± 1	-2	80.64	70.76	72.66	70.06	122.97	139.47
6.	<i>p</i> -NO ₂	698 ± 1	12	80.18	69.85	73.36	70.24	126.63	137.75
7.	<i>p</i> -Br	689 ± 1	3	80.44	69.78	72.97	70.11	123.45	139.50
8.	<i>p</i> -CH ₃	676 ± 1	-10	80.70	69.65	72.64	70.04	121.95	140.86
9.	<i>m</i> -Cl	690 ± 1	4	80.31	69.72	72.97	70.11	124.10	139.11
10.	<i>m</i> -NO ₂	700 ± 1	15	80.18	69.85	73.29	70.24	125.53	137.94

^a Fc = ferrocenyl. ^b Out of line.

three-electrode cell was used in which the working and auxiliary electrodes were platinum and the reference electrode was Ag/AgCl (sat.). The measurements were carried out in an oxygen-free nitrogen atmosphere using an internal standard. Ferrocene ($E_{1/2}$ 440 mV), ferrocenyl-phenyl-ketone ($E_{1/2}$ 689 mV) or 11', 22'-bis(tetramethylene)-bridged ferrocene ($E_{1/2}$ 270 mV) were used as internal standards. The use of internal standards enabled the usual errors of cyclic voltammetry (± 10 mV) to be greatly reduced (see Tables 1, 2 and 3) [24,25]. The measurements were made at a scan rate of 66 mV/s (a Radelkis OH-105 apparatus was used). Details of ^{13}C NMR measurement are available in refs. 26 and 27. The ^{13}C NMR spectra were obtained (JEOL JNM-FX 60 spectrometer with proton noise decoupling) at 15.03 MHz. The spectra were measured for deuteriochloroform solution at 10%. The temperature of the samples was 25°C. The chemical shifts were determined with an accuracy of $\pm 1\%$. The slope values were calculated by the least squares method.

Results and conclusion

The chemical shift and oxidation potential values of the three ferrocene series (Fig. 1) are shown in Tables 1, 2 and 3. The ΔE values, the differences between the oxidation potentials of the substituted derivatives and the basic compound ($X = \text{H}$), are given in the fourth column of each table. The oxidation potentials refer, of course, to the iron component of the ferrocenyl moiety. The phenyl group itself (Series I) is a slightly electron-withdrawing substituent which increases the oxidation potential of the ferrocene by 33 mV [25]. The transmission coefficient of the phenyl group is about 0.24. This was shown, for example, by the fact that the formyl group (-CHO) substituted directly to ferrocene increases the oxidation potential of the ferrocene by 284 mV [28]; however, the difference between the oxidation potentials of *p*-CHO-phenylferrocene and the phenylferrocene is only 63 mV [25].

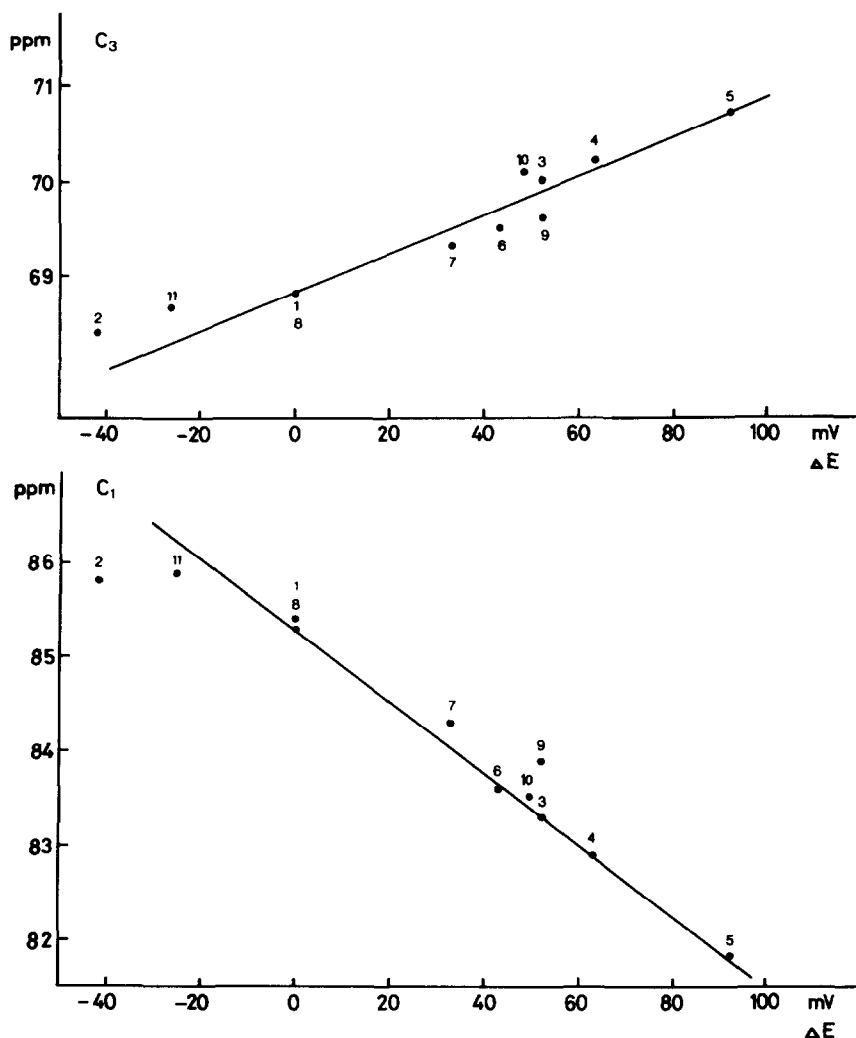
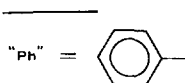


Fig. 2. Chemical shifts of $C(1)$ and $C(3)$ as a function of ΔE value (Series I). The substituents are indicated by arabic numbers (Table 1).

It is known that the carbonyl group is a strong electron-withdrawing substituent; as a direct substituent of ferrocene it increases the oxidation potential of the ferrocene by 280–300 mV [24]. Despite the fact that the carbonyl is directly substituted to the ferrocenyl moiety in Series III, it increases the oxidation potential only by 246 mV (Table 3). This is probably because the withdrawal of carbonyl is decreased by the ethylene and by the phenyl group ($-\text{CH}=\text{CH}-\text{Ph}$)*. In series II, the ethylene radical is between the carbonyl and ferrocenyl; the withdrawal of the carbonyl affects the ferrocenyl through the ethylene, thereby in this Series the



difference between the oxidation potential of the basic compound ($X = H$) and that of the ferrocene is only 125 mV. The transmission coefficients of the ethylene group is 0.50 [29]. The carbonyl group can be considered as the dominant component in the compounds of Series II and III. The X substituent in Series II modifies the effect of carbonyl via the phenyl group, and this modified effect reaches the ferrocenyl moiety through the ethylene group. In Series III, the substituent reaches and modifies the effect of the carbonyl group on ferrocenyl through phenyl and ethylene.

The ΔE values of the compounds of all three Series plotted against the ^{13}C NMR data are shown in Figs. 2 and 3. A linear correlation can be seen between the ΔE values and the chemical shifts of the carbon atoms in different positions of the cp rings. The slopes of the curves differ from each other; furthermore, the slope of curve C(1) has a negative sign for all three series. The slopes of curves C(2), C(3) and C(4) are positive. The opposite sign of the slopes is in agreement with the assumed change in the electron density distribution in the ring [10]. The electron-withdrawing substituent increases the electron density of the C(1) atom, i.e. it draws the electrons to C(1) (down-field); the electron-donating substituents decrease the C(1) electron density, i.e. its chemical shift (up-field). The change of the electron density distribution of the C(2) and C(3) atoms of the cp ring is in the opposite direction. With regard to all three series it should be mentioned that the original distribution of the cp rings in the ferrocene has already been perturbed by the phenyl, the $-\text{CH}=\text{CH}-\text{CO}-\text{Ph}$ and $-\text{CO}-\text{CH}=\text{CH}-\text{Ph}$ "substituents" in the basic compounds. Thus,

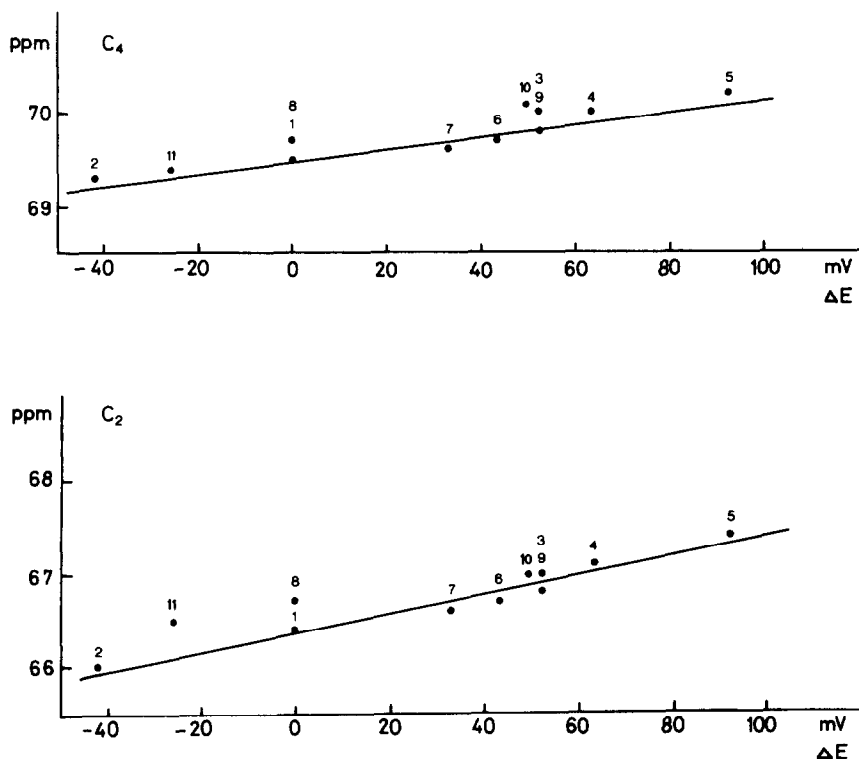


Fig. 3. Chemical shifts of C(2) and C(4) as a function of ΔE (Series I). The substituents are indicated by arabic numbers (Table 1).

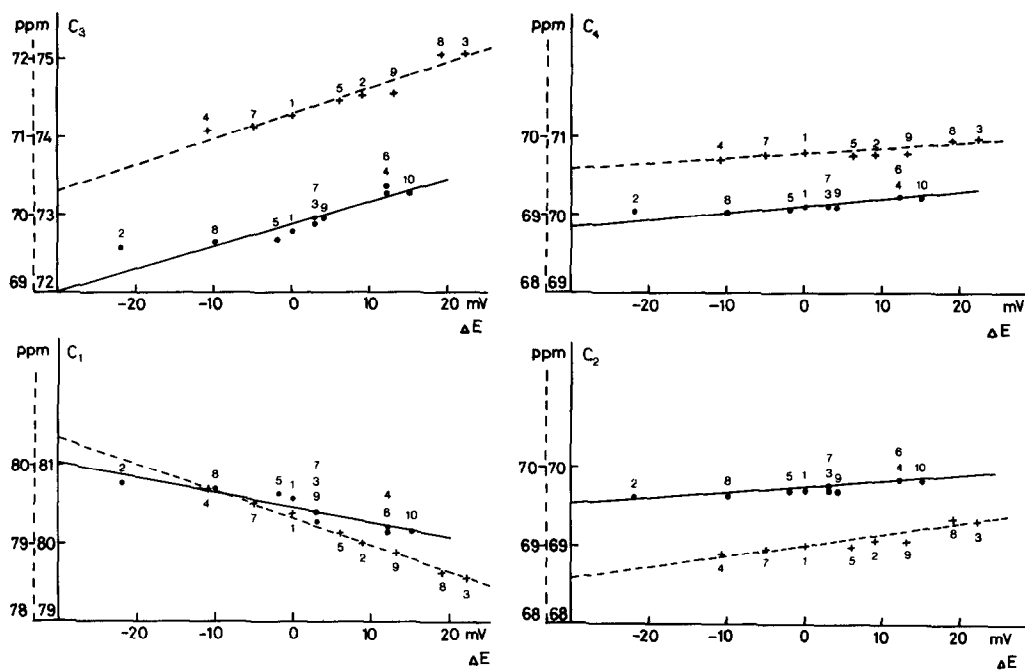


Fig. 4. Chemical shifts of C(1), C(2), C(3) and C(4) of Series II and III as a function of ΔE . (Dashed curve for Series II.) The substituents are indicated by arabic numbers (Tables 2 and 3).

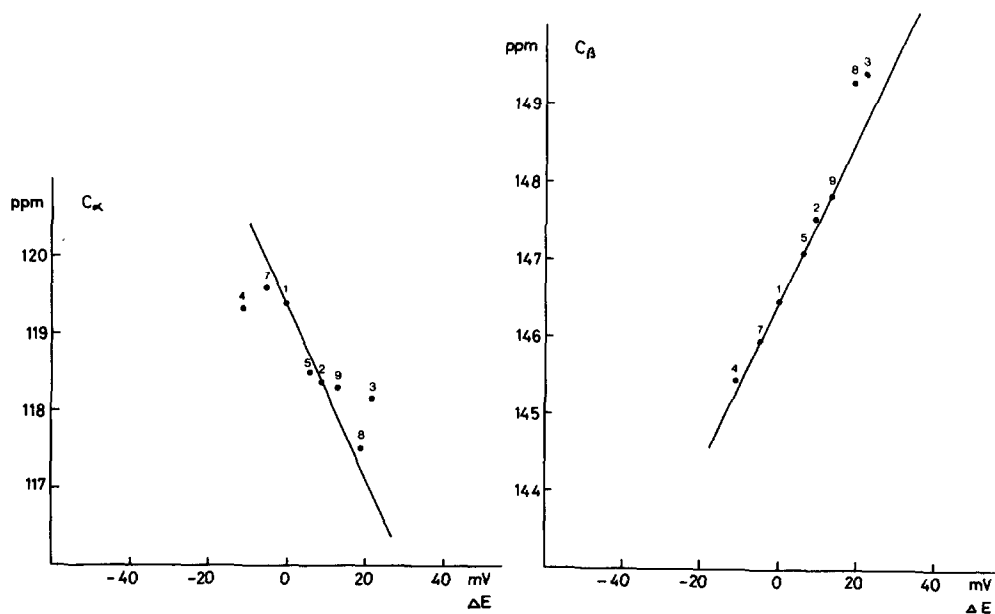


Fig. 5. Chemical shifts of C(α) and C(β) in Series II as a function of ΔE .

the ppm (ΔE) correlations (see Figs. 2–5) show the further changes in the previously perturbed electron density distribution.

The gradients of the curves are shown in Table 4. It can be seen that the slope of curve C(1) in Series I is the most negative. A possible explanation for this would be that the electron density distribution of the cp ring in the basic compound is least perturbed in this Series. As mentioned above, the phenyl group is the weakest electron-withdrawing substituent among the basic compounds (33 mV) and that is why the further influence of the X substituents is more significant. This is also supported by the fact that the slope of curve C(1) in Series II is smaller than that of curve C(1) in Series III. The $-\text{CH}=\text{CH}-\text{CO}-\text{Ph}$ "substituent" of the basic compound of Series II reduces the oxidation potential of the ferrocene by only 125 mV. It is worth mentioning that the X substituent affects the other cp ring too via the iron. The slopes of curves C(4) are, however, the smallest among those having a positive sign (Table 4). Moreover, the slopes of the three Series confirm the assumption that the (2,5) and (3,4) carbon atoms of the cp ring correspond to the *ortho* and *para* position atoms of benzene [11,30,31].

The chemical shifts of C(α) and C(β) in Series II and III are shown in Figs. 4 and 5. It can be seen that the data are scattered and the slope variations of the four curves are larger than those of the previous curves (see Table 4). In spite of the scattered data, however, it is obvious that the slopes of curves C(α),—in direct connection with carbonyl—are negative. This also supports the dominant role of the carbonyl group in the electron density distribution of the whole molecule. The slopes of curves C(β) are, of course, positive. However, it should be taken into account that the oxidation potential measured at the iron is compared to the locally measured chemical shifts of the C(α) and C(β) atoms.

Even though the absolute value of the electron density of the cp ring cannot be given, if this is at all possible, the method presented here offers a numerical relationship between the electron-withdrawing and electron-donating substituent effects of different strengths and the electron shift of carbon atoms of the cyclopentadienyl ring.

As was mentioned in the introduction, phenylferrocenes and directly substituted ferrocenes were studied by the chronopotentiometric method in acetonitrile in an attempt to find a correlation between the Hammett constants (σ) and the oxidation potentials of these compounds; further, to obtain σ constants for substituents for which such data had not been tabulated [16,17].

Concerning these ferrocene analogues of chalcones (Series II and III), the $\Delta E_{1/2}$ values are also plotted vs. the Hammett constants to characterize similar correla-

TABLE 4

CHANGE OF ELECTRON DENSITY DISTRIBUTION IN PHENYLFERROCENE AND CHALCONE-ANALOGOUS FERROCENE DERIVATIVES (all values to be multiplied by 10^{-2})

	C(1) (ppm/mV)	C(2) (ppm/mV)	C(3) (ppm/mV)	C(4) (ppm/mV)	C(α) (ppm/mV)	C(β) (ppm/mV)
Series I	-3.89 ± 0.03^a	0.95 ± 0.01	2.09 ± 0.02	0.64 ± 0.01	—	—
Series II	-3.54 ± 0.01^b	1.38 ± 0.03	3.08 ± 0.04	0.67 ± 0.02	$+5.6 \pm 1$	12 ± 1
Series III	-1.81 ± 0.01^b	0.63 ± 0.01	2.33 ± 0.04	0.64 ± 0.01	-9.6 ± 5	15.1 ± 2

^a $p\text{-OCH}_3$ omitted. ^b $p\text{-CN}$ omitted.

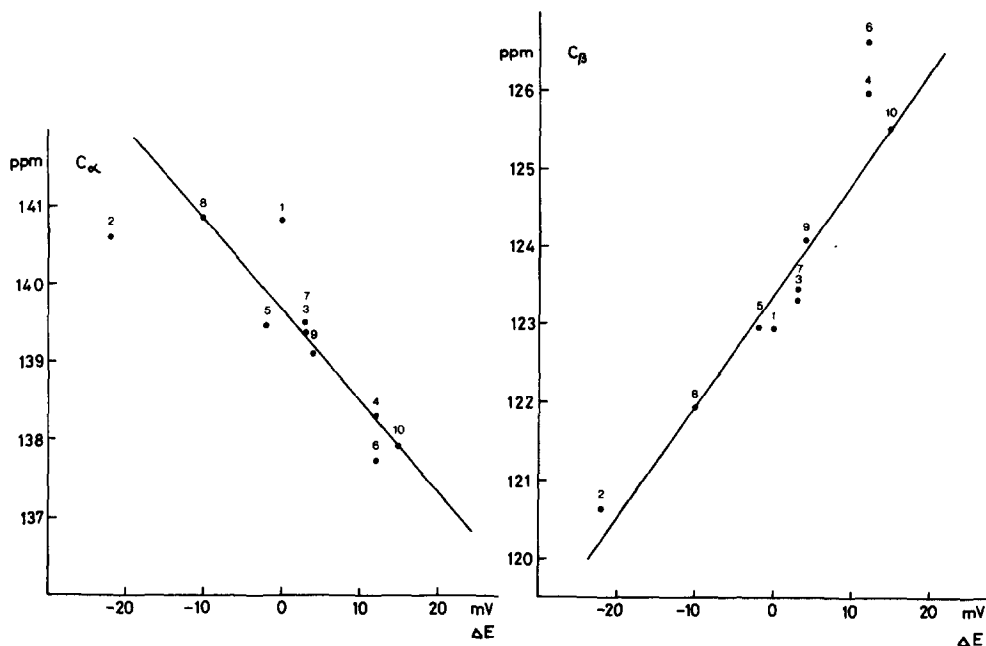


Fig. 6. Chemical shifts of C(α) and C(β) in Series III as a function of ΔE .

tions, if any (Fig. 7, Table 5). As expected, linear correlations exist between the oxidation potentials and σ values. The regression lines, established by a least squares fit are:

$$\Delta E_{1/2 \text{ Ser II}} = 0.030 \sigma + 0.09 \times 10^{-3} \text{ V} \quad (1)$$

$$\Delta E_{1/2 \text{ Ser III}} = 0.025 \sigma - 4.39 \times 10^{-3} \text{ V} \quad (2)$$

The gradients of these equations (ρ) are extremely low; ρ of Series III is lower than that of Series II, i.e. the members of Series II are more sensitive to the effects of substituents than are the compounds of Series III. This can be explained by the position of the X substituent related to the carbonyl group in the molecule, as discussed above.

Concerning the results for substituted phenylferrocenes obtained by cyclic voltammetry in this work (Series I, Table 1, see also the Hammet constants in Table 5) the equation of the regression line is:

$$\Delta E_{1/2} = 0.121 \sigma - 7.42 \times 10^{-3} \text{ V} \quad (3)$$

For a comparison of these $\Delta E_{1/2}$ values with the quarter wave potentials ($E_{1/4}$), that is $\Delta E_{1/4}$ values reported [16,18] the recalculated $\Delta E_{1/4}$ of Little et al. and Hoh et al. are listed in Table 5 and they are also plotted in Fig. 8. (Recalculation is necessary to get such $\Delta E_{1/4}$ values which are related to the $E_{1/4}$ of phenylferrocene instead of that of ferrocene.) As shown in Fig. 8 the $\Delta E_{1/4}$ values measured by chronopotentiometry are in the regression line of the $\Delta E_{1/2}$ values measured by cyclic voltammetry. Consequently, the equation of the regression line for the plot of $\Delta E_{1/4}$ vs. the σ values is identical within experimental error to eq. 3.

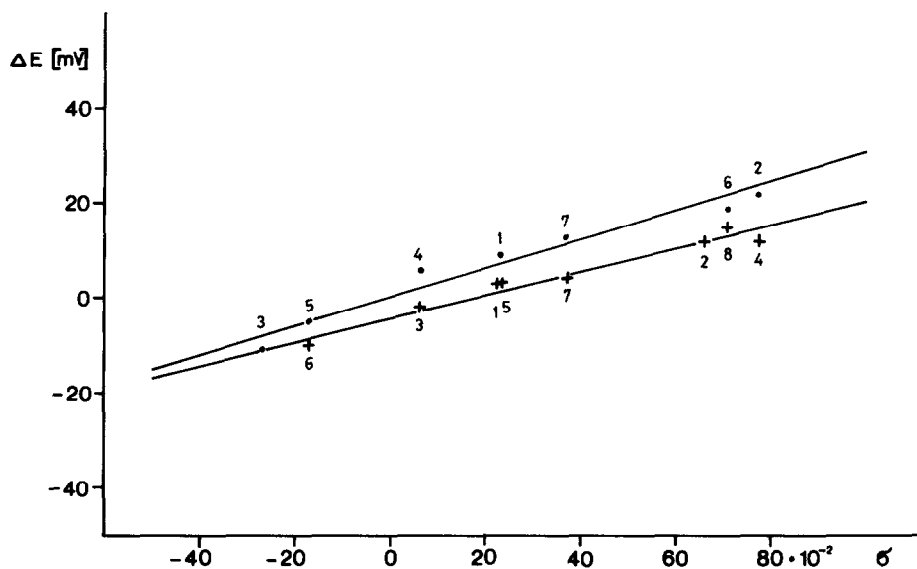


Fig. 7. Relationships between $\Delta E_{1/2}$ and Hammett σ -constants for Series II (solid circles) and Series III (crosses).

TABLE 5

CHRONOPOTENTIOMETRIC QUARTER-WAVE POTENTIALS ($E_{1/4}$) FOR SUBSTITUTED PHENYLFERROCENES IN ACETONITRILE [16,18]

Line number	Substituent	$E_{1/4}$ (mV)	$\Delta E_{1/4}$ (mV)	σ
1	H	346(366) ^a		
2	<i>p</i> -OH	293	-53	-0.37
3	<i>p</i> -OCH ₃	(323)	(-43)	-0.268
4	<i>p</i> -CH ₃	325	-21	-0.17
5	<i>p</i> -Cl	(387)	(21)	0.227
6	<i>p</i> -Br	377(396)	31(30)	0.232
7	<i>p</i> -COCH ₃	(426)	(80)	0.502
8	<i>m</i> -Br	390	44	0.391
9	<i>m</i> -NO ₂	423	67	0.710
10	<i>p</i> -CN	430	84	0.66
11	<i>p</i> -NO ₂	447(461)	101(98)	0.778
12	<i>p</i> -NH ₂	243	-103	-0.66
13	<i>m</i> -NH ₂	328	-18	-0.18
14	<i>m</i> -COOH	381	35	0.37
15	<i>m</i> -CO ₂ C ₂ H ₅	390	44	0.37
16	<i>m</i> -CH ₃	392	46	0.43
17	<i>p</i> -CO ₂ H	397	51	0.45
18	<i>p</i> -CO ₂ C ₂ H ₅	402	56	0.45
19	<i>p</i> -F	-	-	0.062
20	<i>m</i> -Cl	-	-	0.373

^a Taken from data of Hoh et al. [18].

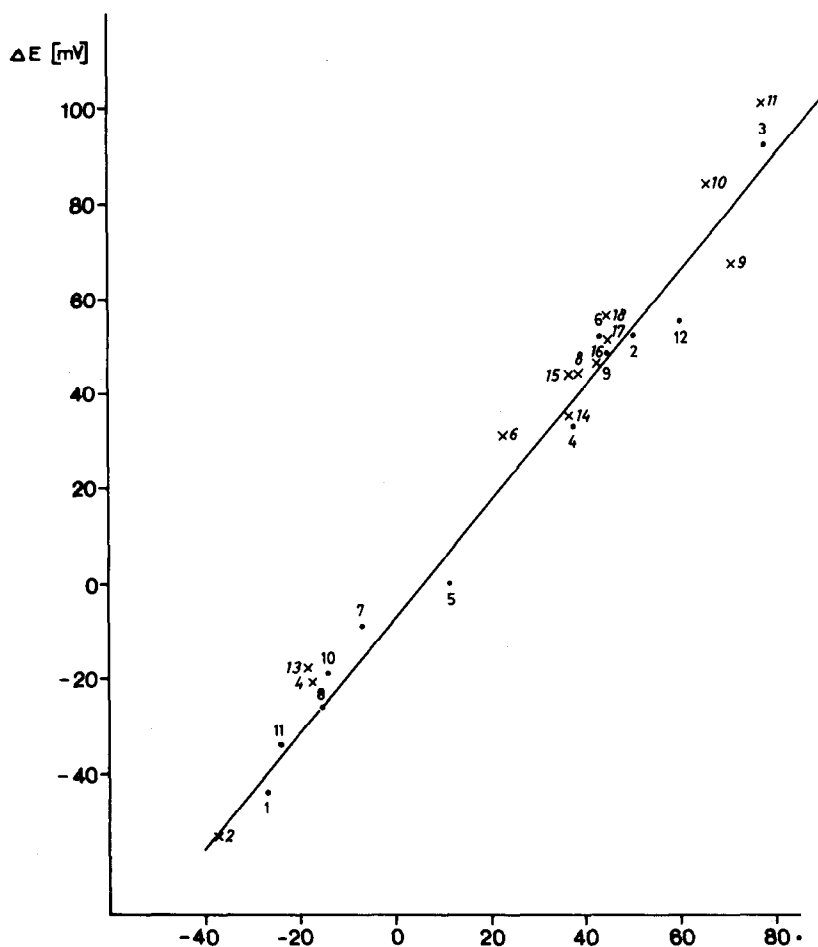


Fig. 8. Relationship between $\Delta E_{1/2}$ and Hammett σ -constants for substituted phenylferrocenes (crosses ($\Delta E_{1/4}$) are taken from ref. 16).

For the calculation of the transmission coefficient let us consider the regression line of directly substituted ferrocenes reported in ref. 17, which is:

$$\Delta E_{1/4} = 0.45 \sigma - 2.2 \times 10^{-3} \text{ V} \quad (4)$$

(Since the $\Delta E_{1/4}$ and $\Delta E_{1/2}$ values of the phenylferrocenes are in the same regression line, we have assumed that the ρ values of eqs. 3 and 4 are comparable, even more so those of eq. 1 and eq. 2 with ρ_4 .) The ρ_4 value, i.e. the effect of substituents in the directly substituted ferrocenes, is 3.7 times greater than that of the phenylferrocenes. From the gradients the transmission coefficient (ρ_3/ρ_4) of the phenyl group is 0.26. This is in agreement with the average value of the transmission coefficients obtained from the single oxidation potentials (see above). The transmission coefficients of the ($-\text{CH}=\text{CH}-\text{CO}-\text{"Ph"}$) and ($-\text{CO}-\text{CH}=\text{CH}-\text{"Ph"}$) groups (Series II and III) are 0.07 and 0.06, respectively. It is considered that the most reliable transmission coefficients for groups or radicals are obtained in this way, although this is possible only in a few cases because such populated series are not always obtainable.

Acknowledgement

The authors are indebted to Miss Anne Szuja for her careful work in the measurements and for technical assistance.

References

- 1 G.C. Levy, G.L. Nelson and J.D. Cargioli, *J. Chem. Soc. Chem. Commun.* (1971) 506; G.C. Levy and G.L. Nelson, *Carbon-13 Nuclear Magnetic Resonance for Organic Chemists*, Wiley-Interscience, New York, 1972.
- 2 G.E. Maciel and R.V. James, *J. Amer. Chem. Soc.*, 86 (1964) 3893.
- 3 H. Spiessacke and W.G. Schneider, *J. Chem. Phys.*, 35 (1961) 731.
- 4 G.E. Maciel and J.J. Natterstad, *J. Chem. Phys.*, 42 (1965) 2427.
- 5 D.W. Slocum, B.W. Rockett and C.R. Hauser, *J. Amer. Chem. Soc.*, 87 (1965) 1242.
- 6 S. Toma, M. Pariciov, E. Solcaniov, *Acta Fac. Rerum Nat. Univ. Comen. (Chimia)*, 26 (1978) 61.
- 7 S.I. Goldberg, L.H. Keith and J. Prokipov, *J. Org. Chem.*, 28 (1963) 850.
- 8 M.D. Rausch and V. Mark, *J. Org. Chem.*, 28 (1963) 3225.
- 9 M.J. Levenberg and J.H. Richards, *J. Amer. Chem. Soc.*, 86 (1964) 2364.
- 10 A.N. Nesmeyanov, P.V. Petrovskii, L.A. Fedorov, V.I. Robas and E.I. Fedin, *Zh. Strukt. Khim.*, 14 (1973) 49.
- 11 A.A. Koridze, P.V. Petrovskii, A.I. Mokhov and A.I. Lutsenko, *J. Organomet. Chem.*, 136 (1977) 57.
- 12 A.A. Koridze, A.I. Mokhov, P.V. Petrovskii and E.I. Fedin, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, (1974) 2156.
- 13 T. Kuwana, D. Bublitz and G. Hoh, *J. Amer. Chem. Soc.*, 82 (1960) 5811.
- 14 J.G. Masson and M. Rosenblum, *J. Amer. Chem. Soc.*, 82 (1960) 4206.
- 15 S.P. Gubin and E.G. Perevalova, *Doklady Akad. Nauk. SSSR*, 143 (1962) 1351.
- 16 W.F. Little, C.N. Reilley, J.D. Johnson, K.N. Lynn and A.P. Sanders, *J. Amer. Chem. Soc.* 86 (1964) 1376.
- 17 W.F. Little, C.N. Reilley, J.D. Johnson and A.P. Sanders, *J. Amer. Chem. Soc.*, 86 (1964) 1382.
- 18 G.L.K. Hoh, W.E. McEwen and J. Kleinberg, *J. Amer. Chem. Soc.*, 83 (1961) 3949.
- 19 T.H. Barr and W.E. Watts, *Tetrahedron*, 27 (1971) 4353.
- 20 A.G. Nagy, I. Dzsi and M. Hillman, *J. Organomet. Chem.*, 117 (1976) 55.
- 21 M. Hillman and A.G. Nagy, *J. Organomet. Chem.*, 184 (1980) 433.
- 22 S. Toma, *Collect Czech. Chem. Commun.*, 34 (1969) 2771.
- 23 S. Toma, A. Maholnyiov and E. Solcnyiov, *Acta Fac. Rerum Nat. Univ. Comen. (Chimia)*, 24 (1976) 53.
- 24 E. Fujita, B. Gordon, M. Hillman and A.G. Nagy, *J. Organomet. Chem.*, 218 (1981) 105.
- 25 A.G. Nagy, *KFKI Kzlemnyek (in English) KFKI-1983-69*.
- 26 A. Maholnyiov, S. Toma and E. Solcnyiov, *Org. Magn. Reson.*, 7 (1975) 372.
- 27 E. Solcnyiov, S. Toma and A. Fiedlerova, *Org. Magn. Reson.*, 14 (1980) 181.
- 28 A.G. Nagy and M. Hillman, *XXIIth Intern. Conf. Coordination Chem. Budapest, Hungary*, 1982.
- 29 N.L. Silver and D.W. Boykin, Jr., *J. Org. Chem.*, 355 (1970) 759.
- 30 G.A. Olah, P.W. Westerman and D.A. Forsyth, *J. Amer. Chem. Soc.*, 97 (1975) 3419.
- 31 A.A. Koridze, P.V. Petrovskii, S.P. Gubin, V.I. Sokolov and A.I. Mokhov, *J. Organomet. Chem.*, 136 (1977) 65.
- 32 D.H. McDaniel and C. Brown, *J. Org. Chem.*, 23 (1958) 420.
- 33 N.B. Chapman and J. Shorter, *Advances in Linear Free Energy Relationships*, Plenum Press, London, 1972.