

The Additivity of the Substituents Effects on the Polarographic Potentials of Ferrocene Derivatives

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Introduction

In connection with our interest in the antianemic properties of ferrocenes [1], we had the opportunity to prepare a number of polysubstituted ferrocenes and to determine the polarographic half-wave potentials for their oxidation to the corresponding ferricenium cations. Although the oxidation of ferrocene derivatives by titrimetric [2–4], polarographic [5–7], and chronopotentiometric techniques [8–11] has been extensively investigated, the sensitivity of the iron redox potential toward the electronic effects of several substituents on the Cp rings has never been studied (there is in the literature only a brief report on the potentials of five tetrasubstituted benzylferrocenes [10]).

Results and Discussion

The polarographic half-wave potentials $E_{1/2}$ vs. the saturated calomel electrode of the ferrocene derivatives in 90% aq. ethanol are collected in Table I. Since the oxidation of ferrocene was found to be +0.34 V vs. SCE, in agreement with the literature data [12], negative $\Delta E_{1/2}$ values indicate that the compound is more readily oxidized than ferrocene, while the reverse is true for a positive value. The results of Table I show that the effect of the poly-substitution of the Cp rings on the polarographic potentials of the iron is substantially additive. Accordingly, 1,1',2-triethyl and 1,1',3-triethylferrocene show the same potential values, independently of the position of the three alkyl groups on the rings. By calculating that the introduction of one alkyl group on ferrocene decreases the iron polarographic potential by ca. 47 mV, it can be easily seen that the potentials of 1,1'-dimethyl-2,2'-diethylferrocene and of 1,1',2,2',3,3',4,4'-octaethylferrocene are those expected on the basis of an additivity of the polar effects of the substituents (Table I). Similar conclusions are reached by considering the phenyl-substituted ferrocenes; the polarographic data indicate that the phenyl groups exert an electron withdrawing effect, which also is additive (see the potentials of 1,2,4-triphenyl

TABLE I. Polarographic Half-Wave Potentials of Polysubstituted Ferrocene Derivatives.^{a,b}

Ferrocene substituents	$E_{1/2}$ (V)	$E_{1/2}$ ^c (V)	Prep. Ref.
H	0.34 ^d	—	—
1,1',2-(C ₂ H ₅) ₃	0.19	—	15
1,1',3 (C ₂ H ₅) ₃	0.20	—	15
1,1'-(CH ₃) ₂ -2,2'-(C ₂ H ₅) ₂	0.16	0.15	16
1,1',2,2',3,3',4,4'-(C ₂ H ₅) ₈	-0.05	-0.04	17
1,1'-(C ₆ H ₅) ₂	0.39	—	18
1,2,4-(C ₆ H ₅) ₃	0.42	0.41	19
1,1',3,3'-(C ₆ H ₅) ₄	0.45	0.43	19
1,2,3,4-(C ₆ H ₅) ₄	0.43	0.43	19
1-C ₂ H ₅ -1,3'-(C ₆ H ₅) ₂	0.33	0.34	20
COOH	0.62	—	21
1-COOH-1',3-(CH ₃) ₂	0.52	0.53	22
1-COOH-1'-COOCH ₃	0.85	0.90	23
1-COOH-2-COOCH ₃	0.79	0.90	24
CH ₂ C ₅ H ₄ RuC ₅ H ₅	0.29	—	25
	0.82	—	
CH ₂ C ₅ H ₄ FeC ₅ H ₅ ^d	0.30	—	
	0.40	—	

^aIn 90% aq. ethanol vs. SCE at 25 °C. ^bThe reproducibility interval was 0.01 Volts.

^cHalf-wave potentials calculated on the basis of the additivity of the substituents polar effects (see text). ^dData from Ref. 12.

and 1,1',3,3'-tetraphenylferrocene), thus allowing one to calculate the effect of a phenyl group on the polarographic potential of ferrocene as nearly +23 mV. This result is consistent with the known polarity of the phenyl substituent and with the non-operativity of the resonance stabilization of the cationic charge by phenyl group. The mixed compound 1-ethyl-1'3-diphenylferrocene shows a potential which is the algebraic sum of the effects of one ethyl and two phenyl groups (Table I).

The above results suggest that the polarographic potentials are negligibly affected by the steric crowding of the rings; however, a substantial influence of the solvent on the $E_{1/2}$ values is observed, since generally the $\Delta E_{1/2}$ values (relative to ferrocene) in 90% aq. ethanol are sharply lower than those in acetonitrile [8–11]. In our opinion this effect must be attributed to the polarity of the hydroxylic solvent which stabilizes more effectively the positive charge of the ferricenium cation, while dipolar aprotic solvents solvate efficiently anions rather than cations [13]. This solvent effect is in agreement with the hypothesis that the anomalous low quarter wave potentials of acetamido and urethano substituted ferrocenes in acetonitrile are the consequence of a direct interaction of the substituents with the positive iron in the oxidized species [11].

The additivity principle is also valid for the substituted ferrocenoic acids (Table I) taking into account that the introduction of the COOH (or COOCH₃) group increases the polarographic potential of ferrocene by nearly 280 mV. The sole exception is represented by the potential of 2-methoxycarbonyl-1-carboxyferrocene which is abnormally lower than that of 1'-methoxycarbonyl-1-carboxyferrocene. As for 2-acetamido-1-acetylferrocene [11], this result may be due to the hydrogen bonding between the two substituents. Possibly this hydrogen bond is sufficiently strong to restrain the substituents from rotating to a favourable position for interacting with the positive iron atom in the oxidized species; otherwise the energy required to break the hydrogen bond is close to that gained for the rotation of the COOH groups and its hydrogen bonding to the iron atom. Furthermore, the "normal" value of $E_{1/2}$ for 1'-methoxycarbonyl-1-carboxyferrocene indicates that there is no hydrogen bonding between the two heteroannular substituents and suggests that in the stable molecular conformation the two substituents are directed toward opposite directions.

In the polarographic oxidation of ferrocenyl-ruthenocenylmethane a two step oxidation process was recorded: the two potentials fall at 0.29 and 0.82 V respectively. The comparison of these values with those of alkylferrocenes (ca. 0.30 V) and of ruthenocene (0.73 V) indicates that while the polarographic potential of the ferrocenyl moiety is essentially unchanged, that of ruthenocene is distinctly affected by the oxidation of iron in the direction that the oxidation of ruthenium(II) becomes more difficult; evaluating the redox potential of methylruthenocene, presumably ca. 0.70 V, the polarographic potential of ruthenium in ferrocenylruthenocenylmethane is increased by 0.12 V. This result is in agreement with a field effect of the iron positive charge and has been suggested to explain the redox potentials of diferrocenylmethane [4, 12].

Experimental

The polarographic measurements were made on a Radiometer model PO₄ instrument and a divided H-shaped cell with a NaCl-saturated calomel reference electrode. The polarograms were obtained in thermostatted cell (25 ± 1 °C) with 90% aq. ethanol solutions containing sodium perchlorate (10⁻² M) and perchloric acid (10⁻² M) as supporting electrolyte, and the substrate (2 × 10⁻⁴ M).

Polarograms were obtained by scanning through a range of increasing potential to the point where the

wave plateau was reached. The potential was then allowed to drop and the scan reversed. Symmetry of the curves was considered an indication of reversibility of the redox reaction. The $E_{1/2}$ values were estimated from the plots of E vs. $\log(I/I - I_d)$ [14]. Ethanol, sodium perchlorate and perchloric acid were reagent grade. The ferrocene derivatives were prepared according to the literature methods (see Table I).

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