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Electron Transfer in Iron Hydroxamates: Substituent Effects on Reduction Potentials

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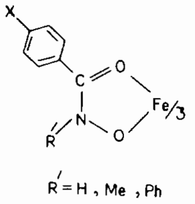
The hydroxamate function is the active site of many siderophores [1, 2]. Since iron(III) is bound much more strongly than iron(II) by this function, it is speculated that reduction may precede release from hydroxamate siderochromes [1]. Hence the current interest [3, 4] in redox properties of such species and model compounds. We report here the first systematic study of substituent effects on redox potentials of a whole group of siderochrome models of type *1*. The red to brown crystalline complexes (Table I) were obtained by reacting hydroxamic acids with iron(III) chloride or tris(acetylacetonato)iron(III). These were characterised by elemental analysis, IR and UV spectra and magnetic moment data (μ_{eff}, 5.85–5.99 BM). The complexes *1f–1h*, *1j*, *1k*, *1m*, are new [3, 5].



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Cyclic voltammetry of *1* was generally performed at hanging mercury drop electrode (HMDE) in acetonitrile (for R' = H complex dimethylformamide was used due to solubility reasons) with tetraethylammonium perchlorate (TEAP) as the supporting electrolyte. Representative voltammograms obtained with Princeton Applied Research 370-4 Electrochemistry System [6] are in Fig. 1. Relevent data are in Table I. Meaning of symbols are: E^0_{298}, formal potential; $E_{pc}(E_{pa})$, cathodic (anodic) peak potential; ΔE_p, peak-to-peak separation; $i_{pc}(i_{pa})$, cathodic (anodic) peak currents; SCE, saturated calomel electrode. The Hammett constant σ (para substituent) has values [7]: OH, –0.37; OMe, –0.27; Me, –0.17; H, 0.00; Cl, +0.23 and NO_2, +0.78.

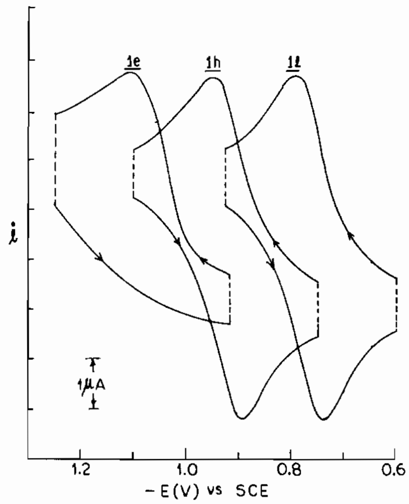

Fig. 1. Cyclic voltammograms of three complexes (concentration ~10^{-3} *M*; scan rate 100 mV s^{-1}) in acetonitrile (0.1 *M* TEAP); for clarity only a part of the scan is shown in each case.

TABLE I. Cyclic voltammetric Data.[a,b]

NO	X	R'	$-E_{pc}$(V)	E_p(mV)	$-E^0_{298}$ (V)
1a	$-NO_2$	H	0.925	–	–
1b	–Cl	H	0.995	–	–
1c	–H	H	1.020	–	–
1d	–Me	H	1.060	–	–
1e	–OMe	H	1.105	–	–
1f	–OH	H	1.105	–	–
1g	$-NO_2$	Me	0.845	65	0.812
1h	–Cl	Me	0.950	65	0.917
1i	–H	Me	1.010	70	0.975
1j	–Me	Me	1.055	75	1.017
1k	–OMe	Me	1.060	65	1.027
1l	$-NO_2$	Ph	0.800	70	0.765
1m	–Cl	Ph	0.905	65	0.872
1n	–H	Ph	0.946	68	0.912
1o	–Me	Ph	0.968	80	0.928
1p	–OMe	Ph	0.985	65	0.952

[a] For complexes *1a–1f* solvent is dimethylformamide (0.1 *M* in TEAP) and for others it is acetonitrile (0.1 *M* in TEAP); reference electrode, SCE; temperature 298 K. [b] Measurements were made in the scan rate rang 50–500 mV s^{-1}; the reported date corresponds to 100 mV s^{-1}.

All complexes except those with R' = H (see below) display a cyclic response having $i_{pc}/i_{pa} \simeq 1$ in the range 0.7 to 1.1 V with ΔE_p of 60–80 mV. The presence of an exactly or nearly reversible one-electron couple (1) is indicated.

$$1 + e^- \rightleftharpoons 2 \qquad (1)$$

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Addition of excess 2,2′-bipyridyl (good affinity for iron(II)) to the electrochemical cell does not effect the voltammogram in any way. Evidently *2*, which is the anionic iron(II) analogue of *1*, does not release the metal ion immediately on formation even in the presence of 2,2′-bipyridyl. In fact colourless solutions of *2* can be produced coulometrically although their isolation in the pure state remains to be achieved.

The E^0_{298} values (Table I) calculated as the average of E_{pa} and E_{pc} are sensitive to both X and R′. For a given R′, greater the electron withdrawing power of the substituent *X*, higher is the E^0_{298}. In fact E^0_{298} correlates linearly with 3σ (the factor 3 appears since *1* is a tris-complex) of X (Fig. 2). The R′ = Me and R′ = Ph lines are nearly parallel but the former is placed above the latter-reflecting the systematically higher electron donating power of Me. The $E^0_{298} - 3\sigma$ linearity can be expressed by eq. (2) where ΔE^0_{298} is the shift of E^0_{298} from the standard complex (X = H) and ρ is the reaction constant [8].

$$E^0_{298} = 3\sigma\rho \qquad (2)$$

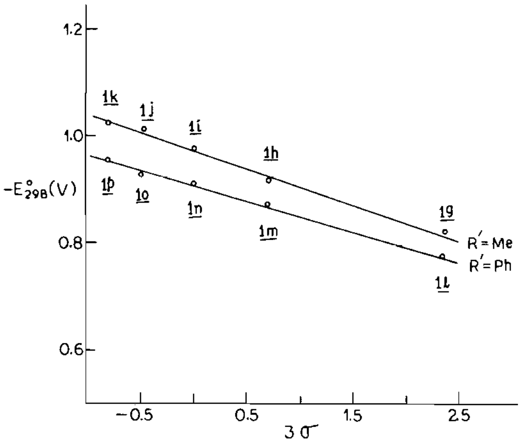

Fig. 2. Linear $E^0_{298} - 3\sigma$ plots; the solid lines are least square fitted.

Experimental ρ values are R′ = Me, 0.07 and R′ = Ph, 0.06 V. The value of ρ depends largely on the number of bonds (t) separating the para substituent X from the metal. In *1* we have t = 7. While example of t = 6 ($\rho > 0.1$ V) are relatively common [9, 10], cases with t = 7 are rare and the present work probably constitutes the most extensive study done to date on t = 7 [10]. In certain triazene-1-oxide iron(III) complexes whose t can be made either 6 or 7, values are: t = 6, 0.14 V and t = 7, 0.08 V [9].

In R′ = H complexes the anodic response is systematically absent. The origin of this behaviour which has been reported earlier [4] for the complex *1c* in acetone is not clear. In the absence of reliable E^0_{298} values, the $E_{pc} - 3\sigma$ correlation was tried here. An excellent linear relationship with ρ = 0.05 V resulted.

Acknowledgements

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