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Two-electron-transfer redox systems. Part 8. Proving the electron stoichiometry for the electrochemical two-electron oxidation of *N*,*N*′-bis(ferrocenoyl)-1,2-diaminoethane☆

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N,*N*′-Bis(ferrocenoyl)-1,2-diaminoethane is electrochemically oxidized at Pt electrodes in non-aqueous solvents with NBu_4PF_6 or $NBu_4[Al(pftb)_4]$ (pftb = $OC(CF_3)_3$) as supporting electrolytes. Cyclic voltammetry (CV) at macro and ultramicro disk electrodes in propylene carbonate (PC) in the presence of the former electrolyte shows a single signal from which the number of transferred electrons n (equal to 2) and the diffusion coefficient D are estimated and confirmed by simulation. In a series of other solvents (DMF, DMSO, CH_3CN, THF, CH_2Cl_2) with the same electrolyte, similar behavior is observed. The latter supporting electrolyte, however, induces signal broadening as compared to NBu_4PF_6 in PC for cyclic and differential pulse voltammetry as well as peak splitting in the case of THF and CH_2Cl_2. This is attributed to interaction between the two ferrocene moieties in the molecule, which is not relayed through a conjugated bridge. Diffusion coefficients in DMF and DMSO were determined by pulse gradient spin echo NMR experiments and compared to electrochemical values. The solvent dependence of D follows the Stokes–Einstein relation. Comproportionation equilibrium constants as calculated from the difference of the formal potentials E^0 range from below 10 (PC, NBu_4PF_6) to approximately 150 (THF and CH_2Cl_2, $NBu_4[Al(pftb)_4]$).

1. Introduction

Redox reactions that are based on the transfer of more than a single electron appear in various natural and technical contexts, for example redox enzymatic processes [2] or catalysis and energy conversion [3–5]. Chemical models for the underlying reactivity are not only found in larger assemblies such as nanoparticles [6–8] or dendrimers [9,10], but also in low molecular weight model systems. Then, simple electroanalytical experiments allow easy access to information related to the thermodynamics, kinetics and mechanisms of multi-electron transfer reactions [11], thus creating an improved understanding of the more complex processes.

Even constraining the discussion to the transfer of just *two* electrons, we are already faced with a "many-faceted" [12] mechanism. If we further restrict ourselves to thermodynamic effects, i.e. assume the electron transfers to proceed fast compared to transport processes and in a stepwise manner (EE mechanism), the reaction can be described by Eq. (1)

$$A^0 \overset{E_1^0,\pm e^-}{\rightleftharpoons} A^{+/-} \overset{E_2^0,\pm e^-}{\rightleftharpoons} A^{2+/2-} \qquad (1)$$

where E_1^0 and E_2^0 are the formal potentials of the two one-electron transfer steps and the superscripts indicate the redox state of the species with respect to that of the starting compound A^0. Eq. (1) is applicable to oxidations *and* reductions. The overall behavior of an oxidation process described by Eq. (1) in cyclic voltammetry (CV) (Fig. 1, see also Ref. [13]) is determined by the difference of the two formal potentials [14], $|\Delta E^0|$ (Eq. (2)).[2]

$$|\Delta E^0| = \begin{cases} E_2^0 - E_1^0 & \text{for oxidation} \\ -(E_2^0 - E_1^0) & \text{for reduction} \end{cases} \qquad (2)$$

☆ Part 7, see [1].

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[2] Note that $|\Delta E^0|$ should be regarded as a *symbol* for the quantity determined according to Eq. (2) rather than an absolute value. Thus, $|\Delta E^0|$ can attain positive or negative values depending on E_1^0, E_2^0, and the type of reaction considered, oxidation or reduction.

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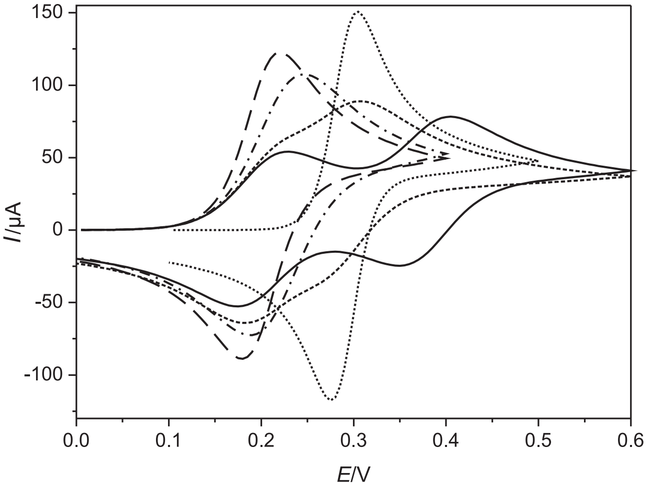


Fig. 1. Simulated cyclic voltammograms of an EE mechanism; current potential curves simulated with scan rate $v = 0.1\,\mathrm{V\,s^{-1}}$, temperature $T = 298.2\,\mathrm{K}$, electroactive area $A = 1\,\mathrm{cm^2}$, transfer coefficients $\alpha_1 = \alpha_2 = 0.5$, heterogeneous electron transfer rate constants $k_{s1} = k_{s2} = 10^4\,\mathrm{cm\,s^{-1}}$ and appropriate E^0 for the two electron transfer steps ($|\Delta E^0| = +180, +90, +35, 0, -180\,\mathrm{mV}$, see text), diffusion coefficient $D = 10^{-5}\,\mathrm{cm^2\,s^{-1}}$ for all species, initial concentration of starting compound $c^0(\mathrm{A}) = 0.2\,\mathrm{mM}$.

Thus, “normal potential ordering” [15] is identified for large values, $|\Delta E^0| > \approx 180\,\mathrm{mV}$, where two separate (“splitted”) voltammetric peak couples are observed (full line in Fig. 1). This case corresponds to the situation where the second electron transfer is thermodynamically more “difficult” than the first one, which is explained by electrostatic considerations [16]. The theoretical peak potential separation, ΔE_p, is 58 mV for both peak couples and the peak currents follow the Randles–Ševčik equation [13].

In such a situation, the comproportionation equilibrium constant K_comp (Eq. (3)) is larger than unity and $\mathrm{A}^{+/-}$ is a stable intermediate not prone to disproportionation (F is the Faraday constant, R the gas constant and T the absolute temperature).

$$K_\mathrm{comp} = \frac{[\mathrm{A}^{+/-}]^2}{[\mathrm{A}][\mathrm{A}^{2+/2-}]} = \exp\left[\frac{F}{RT}|\Delta E^0|\right] \tag{3}$$

With decreasing positive $|\Delta E^0|$ the voltammetric peaks merge and the first one forms a shoulder in the slope ascending to the second one (dotted curve in Fig. 1, for $\Delta E^0 = 90\,\mathrm{mV}$). For $|\Delta E^0| \approx 35\,\mathrm{mV}$ a special situation is encountered [17–19] (short-dashed curve in Fig. 1). The voltammogram corresponds to a simple superimposition of two one-electron current–potential curves, i.e. $\Delta E_\mathrm{p} = 58\,\mathrm{mV}$ and I_p is twice the peak current of a one-electron system with the same diffusion coefficient D. In this case, $|\Delta E^0|$ corresponds to an entropic contribution [20].

For $|\Delta E^0| \leq 0\,\mathrm{mV}$ (dash-dotted line in Fig. 1 for the case of $|\Delta E^0| = 0\,\mathrm{mV}$), the peak intensity increases and ΔE_p decreases, until another extreme case is found for “inverted potentials” [15] (long-dashed line in Fig. 1, for $|\Delta E^0| = -180\,\mathrm{mV}$). Here, a single peak couple is formed with a peak height I_p that is proportional to $n^{3/2}$ (n, number of electrons transferred), i.e. for a two-electron transfer I_p is $2^{3/2} \approx 2.8$ times higher than for a one-electron system with the same D. At the same time, the peak potential difference ΔE_p decreases to $58/n\,\mathrm{mV}$.

For any of the extreme cases, and the $|\Delta E^0| \approx 35\,\mathrm{mV}$ case, with knowledge of D, from these relations, n could be determined from experimental peak currents in CV. Unfortunately, in many cases D is unknown, which results in additional complications.

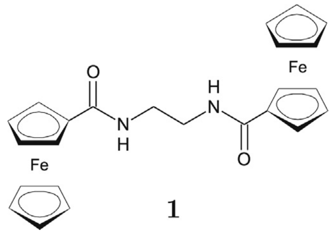
The relative spacing of the E^0 is linked to the structure of the redox centers and their environment as well as on their mutual interaction, and we will further distinguish the following cases: The two electrons may be transferred to or from a *single redox center*, i.e. a part of the molecule that accommodates or releases both electrons. Many of the potential inversion examples studied belong to this class (see e.g. [11,14,15,21–25]), especially if the first electron transfer is accompanied by an appreciable structural change subject to a high activation barrier [14].

Other systems feature *two independent redox active groups* that are linked by a spacer. The groups may be identical or different (resulting in symmetric or non-symmetric systems) and the bridging linker may be conjugated, which is expected to maximize, or non-conjugated, which will minimize direct (through-bond) electronic communication between the redox sites if long enough.

While *non-symmetric* systems will often display two separate redox waves in CV curves owing to the most likely different redox potentials of the two groups, the situation is more complex for *symmetric* systems: if the two identical redox sites do communicate, i.e. the redox state of one of the groups changes the environment of the second to a significant extent, again separate waves are likely to be observed. However, if both through-bond (conjugation) and through-space (possibly, Coulomb interaction based on electric charges) effects are negligible, the redox potential of the second redox site will not be modulated by the redox state of the first.

It is quite obvious that through-space contributions do not only depend on the linking bridge between the redox centers, but also on the molecules' environment, in electrochemistry commonly defined by the solvent and supporting electrolyte. Thus, these will contribute to $|\Delta E^0|$ and possible wave splitting, as discussed in detail previously [26,27].

For non-conjugated centers a wide range of voltammetric behavior is found, from the special superimposition case mentioned above (single peak couple with a reversible shape, see e.g. [19]) through moderate splitting (see e.g. [28]) to two fully separated peak couples with normal potential ordering for strongly interacting redox sites (see e.g. [29–31]).



1

N,*N*′-Bis(ferrocenoyl)-1,2-diaminoethane **1** is a symmetrical system with two identical redox sites. The linker between the two ferrocene (Fc) units is non-conjugated. Despite the simple synthetic approaches to **1** (see [32] and the alternative presented here), only a small number of publications [33–37] deals with this compound, and only two of them [33,37] describe its electron transfer properties. A single redox peak couple in CV is reported. A detailed analysis of the relative formal potential position or the peak currents with respect to the determination of D is, however, missing. In particular, no proof is given for the fact that *two* electrons are transferred. This is in sharp contrast to the multitude of papers discussing the electrochemistry of other bis- (or poly-) ferrocene compounds with conjugated or very short (single atom) bridges, which show clearly separated electrochemical signals by themselves [29,31,38–40] or after appropriate modifications of the electrolyte, preferably using fluorinated supporting electrolyte anions [10,27,28,41–44].

Here, we describe the molecular electrochemistry of **1**, including proof of its two-electron oxidation.