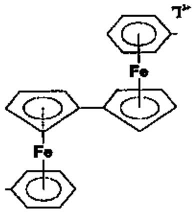
CAPSULES
preliminary notes and applications from Bioanalytical Systems, Inc.

Calculation of the Standard Heterogeneous Charge Transfer Rate Constant (k_S) for Dimeric Iron Fulvalene Complexes Using Cyclic Voltammetry

Purpose

Thermodynamic reversibility for a redox process requires that the concentrations of the reduced and oxidized species at the surface of the working electrode are maintained at the equilibrium values defined by the Nernst equation while the potential is varied. This implies that the rate of electron transfer between the electrode and the interfacial solution is rapid relative to the timescale of the experiment. However, this is not always the case. Slow charge transfer is characterized by increased separation of the peak potentials in the cyclic voltammogram (ΔE_p) as the scan rate (υ) is increased. Such processes are said to be quasi-reversible. Slow charge transfer may be due to intramolecular structural changes and/or changes in the solvent coordination sphere accompanying electron transfer (1). In order to compare the charge transfer kinetics of different processes, it is useful to measure k_s, which is the standard heterogeneous charge transfer rate constant. In this study, three methods were used to calculate k_s for the fourth reduction of a dicationic, electron precise, iron fulvalene dimer (F1) from cyclic voltammetry data.



$[Fe_2(Fv)(tol)_2]^{2+}$

Figure 1. Structure of the toluene iron fulvalene complex $[Fe_2(Fv)(tol)_2]^{2+}$.

Reference

Binuclear Organometallic Electron Reservoirs: Synthesis and Electrochemistry of the Fulvalene Complexes $[Fe_2(\mu_2,\eta_{10}-C_{10}H_8)(arene)_2]^{n+}$, M-H. Dubois and D. Astruc, Organometallics 8 (1989) 1841 - 1847.

Method

Three methods were used, all of which are based on the variation of the peak parameters with υ.

1) In the first method, ΔE_p was related to the kinetic parameter Ψ using published working curves (2). Ψ is related to k_s and υ (this method is discussed in more detail in BAS Capsule 141 - Determination of Heterogeneous Electron Transfer Rate Constant). It is important that the uncompensated resistance between the working and reference electrodes should be minimized when using this method, since iR drop can cause the same effect as slow charge transfer kinetics.

2) The second method used the equation that relates the peak potential (E_{pc}) and peak current (i_{pc}) for a totally irreversible reduction (3) (i.e., the reverse charge transfer is so slow that no oxidation peak is seen). Although this equation is not strictly applicable to quasi-reversible processes, it does provide a good estimate of k_s. The equation is

$$i_{pc} = 0.227nFACk_s\exp[(-\alpha nF/RT)(E_{pc} - E^{o'})]$$

where A is the electrode area (measured using chronocoulometry), α is the charge transfer parameter and $E^{o'}$ is the standard redox potential. Therefore, a plot of ln i_{pc} vs. ($E_{pc} - E^{o'}$) has a slope proportional to αn, and an intercept proportional to ln k_s.

3) The third method uses a modification of an equation used to relate E_p, $E^{o'}$, k_s and α for a totally irreversible process (3). The modification incorporates both E_{pa} and E_{pc}, and is as follows (4):

$$k_s = 2.18(D\alpha nF\upsilon/RT)^{1/2}\exp(-\alpha^2 nF(E_{pa} - E_{pc})/RT)$$

k_s and α can be derived from a plot of ($E_{pa} - E_{pc}$) vs. ln υ. D is the diffusion coefficient, and was measured using chronocoulometry. Again, uncompensated resistance should be minimized for meaningful results.

Results

F2 shows the cyclic voltammogram of the toluene derivative at -35 °C. The first three reductions are reversible, but the fourth is quasi-reversible (shown by the large ΔE_p). The values of k_s from the three methods are 1.7 (±0.2) x 10^{-3} cm/s, 2.2 (±0.4) x 10^{-3} cm/s and 1.9 (±0.3) x 10^{-3} cm/s, i.e., the values are the same (within experimental error).

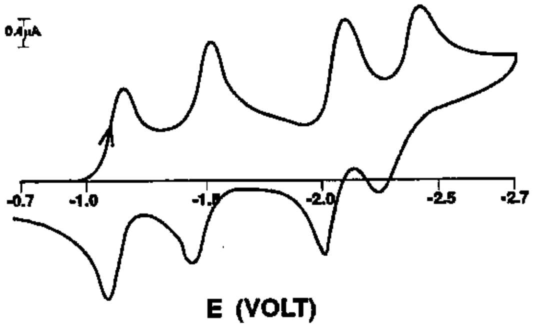


Figure 2. Cyclic voltammogram of $[Fe_2(Fv)(tol)_2]^{2+}$ in DMF (0.033 mM) at -35 °C. Scan rate = 0.4 V/s, supporting electrolyte 0.1M $[^nBu_4N][BF_4]$. All potentials measured with reference to the SCE. Figure adapted from Reference.

As discussed above, the slow charge transfer kinetics may be due to intramolecular structural rearrangements or reorganization of the solvent coordination sphere (1). Structural rearrangement may involve changes in the coordination mode of the ligand in order to decrease the electron density at the metal center (if there is no change in the coordination mode, then the formal electron count for each Fe center in the fully reduced molecule is 20). Various possible structures are shown in F3.

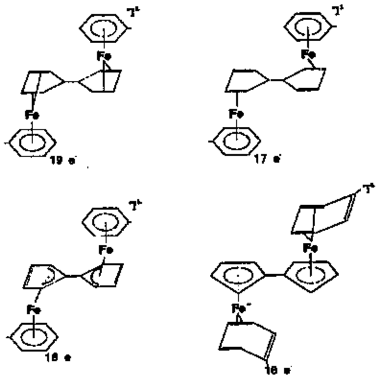


Figure 3. Possible structures for $[Fe_2(Fv)(tol)_2]^{2-}$ (x e^- = formal electron count at each Fe center.)

Additional References

1) T. Gennett, W. E. Geiger, B. Willett and F. C. Anson, J. Electroanalytical Chem. 222 (1987) 151 - 158.

2) J. Heinze, Angew. Chem., Int. Ed. Eng. 23 (1984) 831 - 847.

3) A. J. Bard and L. R. Faulkner, Electrochemical Methods; Wiley: New York, 1980; Chapter 6.

4) R. J. Klinger and J. K. Kochi, J. Phys. Chem. 85 (1981) 1731 - 1739.