Two Electron Reduction of $[CpCo(NO)]_2$

Purpose

One parameter that can be derived from cyclic voltammetry data is the number of electrons (n) that are transferred. In some cases, this number is two. This generally arises from two sequential one electron transfers. For both transfers to occur at the same potential, the second transfer must be more favorable than the first. This implies that there must be a significant change in the molecular structure, otherwise charge repulsion would make the second transfer more difficult. This structural change can occur either concomitant with, or subsequent to, the first electron transfer - an EE or ECE process respectively (E represents an electron transfer, and C represents a chemical reaction). An ECE process can be confirmed by various cyclic voltammetry experiments. These are illustrated in a recent report on the reduction of $[CpCo(NO)]_2$ (I) (F1).

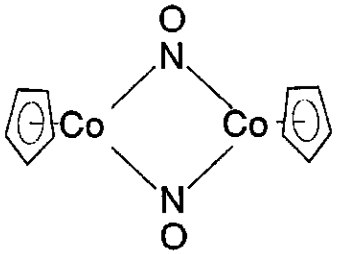

Figure 1. Structure of $[CpCo(NO)]_2$ (I).

Reference

DV-Xα Calculations, UV-PE Spectra, and Redox Properties of Nitrosyl-Bridged Binuclear Cobalt Complexes, G. Pilloni, S. Zecchin, M. Casarin and G. Granozzi, Organometallics 6 (1987) 597 - 606.

Results

The cyclic voltammogram of I at room temperature is shown in F2. The irreversibility of the reduction (peak R_1) is shown by the absence of an associated oxidation peak (i.e., I^{-} undergoes a rapid chemical reaction, so there is no I^{-} remaining to be oxidized on the reverse scan) and by the presence of an oxidation peak at a more positive potential (peak O_2). Peak O_2 is due to oxidation of the product of the ECE reaction. i.e., the product of the chemical reaction is generated at a potential more negative than its reduction potential, so it is reduced upon formation, giving rise to the ECE process.

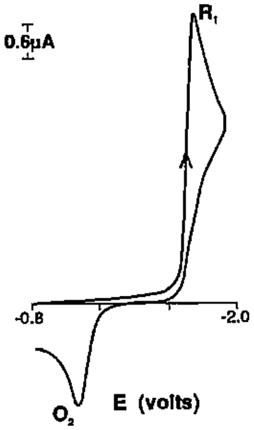

Figure 2. Cyclic voltammogram of I in DME (2.18 mM) at 25 °C, scan rate 200 mV/s, supporting electrolyte 0.2 M $[^{n}Bu_4N][ClO_4]$. Potentials measured with reference to Ag/AgCl. Figure adapted from Reference.

A wide separation of cathodic and anodic peaks can also be an indication of slow electron transfer kinetics. However, slow kinetics cause peak broadening. The width of the cathodic peak R_1 (determined using the difference between the peak potential, E_p, and the half peak current potential, $E_{p/2}$) is 50 mV, which is consistent with rapid electron transfer.

When a chemical reaction follows electron transfer, its effect on the cyclic voltammogram is determined by the rate of the reaction relative to the experimental timescale. Therefore, reversibility can sometimes be restored by decreasing the rate of the chemical reaction (by lowering the temperature) and/or decreasing the experimental timescale (by increasing the scan rate). F3 shows the cyclic voltammogram of I at -20 °C. Although the initial reduction is not fully reversible, the associated oxidation peak is now present (peak O_1).

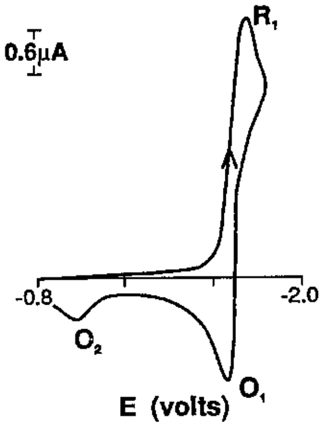

Figure 3. Cyclic voltammogram of I in DME (2.18 mM) at -20 °C, scan rate 4 V/s, supporting electrolyte 0.2 M $[^n\mathrm{Bu_4N}][\mathrm{ClO_4}]$. Potentials measured with reference to Ag/AgCl. Figure adapted from Reference.

There are two other parameters that are affected by the change from an ECE to an E reduction.

1) Cathodic peak current (i_{pc}) - The peak current for a reversible reduction is given by the equation

$$i_{pc} = 2.69\mathrm{x}10^{5} n^{3/2} A D^{1/2} C \upsilon^{1/2}$$

where A is the electrode surface area, D is the diffusion coefficient, C is the concentration of the electroactive species and υ is the scan rate. The cathodic current function $i_{pc}/\upsilon^{1/2}$ is often used to test how closely this relationship is obeyed (i.e., for a reversible reduction, this function is independent of scan rate). Since it is dependent on $n^{3/2}$, the cathodic current function should be affected by the change from an ECE to an E reduction, and it was shown that it did indeed decrease by about a factor of 2 as υ was increased from 100 mV/s to 10 V/s at -20 °C.

2) Cathodic peak potential (E_{pc}) - The reaction of $I^{\cdot-}$ perturbs the equilibrium between the concentrations of I and $I^{\cdot-}$ at the electrode surface. This increases the rate at which I is reduced, which shifts E_{pc} to a more positive value. Therefore, inhibiting the chemical reaction causes a negative shift in E_{pc}.

The proposed mechanism for the ECE reduction is shown in F4. The chemical reaction is the dissociation of the Co dimer to monomers, which is consistent with molecular calculations which show that the LUMO of I is Co-NO anti-bonding.

$$[\mathrm{CoCp(NO)}]_2 + e \leftrightarrow [\mathrm{CoCp(NO)}]_2^{\cdot-}$$
$$[\mathrm{CoCp(NO)}]_2^{\cdot-} \rightarrow \mathrm{CoCp(NO)}^{\bullet} + [\mathrm{CoCp(NO)}]^{-}$$
$$\mathrm{CoCp(NO)}^{\bullet} + e \leftrightarrow [\mathrm{CoCp(NO)}]^{-}$$

Figure 4. Proposed mechanism for the ECE reduction of I.