Chemical reactions coupled to electron transfer

- Electron transfer is often coupled to **homogeneous chemical reactions**
- Electrochemical methods can be used to elucidate the reaction mechanisms, which may be very complex
- Single or multiple chemical steps may precede or follow electron transfer
- Electron transfer processes produce **ionic or radical intermediate species** which may be very reactive, undergoing homogeneous chemical reactions in solution
- **Chemical steps may alter the shape of a voltammogram:** from CV analysis (or using other electrochemical methods) it is possible to extract kinetic and mechanistic information about the chemical reaction(s) coupled to electron transfer
- Chemical reactions may also affect the **apparent reversibility** (**chemical reversibility**) of the redox waves

Basic classification of homogeneous reaction schemes

C = **homogeneous chemical step**
E = **electron transfer step**

Ox, Red = electroactive species
Y, P, S = species not electroactive in the potential range of interest

Subscripts **r** (reversible), **q** (quasi-reversible), **i** (irreversible) are specified for the **E steps**

Examples of schemes involving a single E step

CE mechanism
(preceding reaction)

C $Y \rightleftharpoons Ox$

E $Ox + ne^- \rightleftharpoons Red$

EC mechanism
(follow-up reaction)

E $Ox + ne^- \rightleftharpoons Red$

C $Red \rightleftharpoons P$

(includes dimerization (EC_2) or multiple follow-up chemical steps)

EC' mechanism
(catalytic reaction)

$Ox + ne^- \rightleftharpoons Red$ **E**

$Red + S \rightarrow Ox + P$ **C'**

Examples of schemes involving multiple E steps

ECE mechanism

$Ox_1 + n_1e^- \rightleftharpoons Red_1$ **E** $(E^0{}_1)$

$Red_1 \rightarrow Ox_2$ **C**

$Ox_2 + n_2e^- \rightleftharpoons Red_2$ **E** $(E^0{}_2)$

Large variety of other possible reaction sequence schemes!!!

Effects of homogeneous chemical reactions on CVs

- Perturbation due to a coupled homogeneous chemical reaction may affect the **voltammetric parameters of a redox wave** (e.g. i_p, i_{pa}/i_{pc}, $E_{1/2}$, E_p)
- The extent of this perturbation depends on several factors, including:
  - **Type of chemical reaction scheme** (e.g. CE, EC, ECE…)
  - **Timescale of the electrochemical experiment**
  - **Electrochemical reversibility** of the redox wave (E_r, E_q, E_i)
- Voltammetric techniques are *fast non-destructive methods* and are particularly useful to study fast chemical reactions (e.g. catalysis)
- General approach: systematic analysis of CV response (change of CV parameters) by changing the sweep rate (experimental variable controlling the experiment's timescale)
- The extent and direction of these changes in CV provide **diagnostic criteria** to unravel the **type of mechanism** and to estimate the **rate constants** of the reactions

Chemical reaction following ET (E_rC_i mechanism)

E_rC_i

E $Ox + ne^- \rightleftharpoons Red$ **Reversible ET**

P = non-electroactive species

C $Red \xrightarrow{k_f} P$ **Irreversible follow-up 1st order homogeneous reaction**

Experimental timescale **vs.** **Timescale of the chemical reaction**

Scan rate (v) *Rate constant of the reaction (k)*

The electrochemical response is a function of a **dimensionless kinetic parameter**:

$$\lambda = \frac{RT}{nF}\frac{k_f}{v}$$

Rate constant of the follow-up chemical reaction

Scan rate

Irreversible follow-up chemical reactions

$$\lambda = \frac{RT}{nF}\frac{k_f}{v}$$

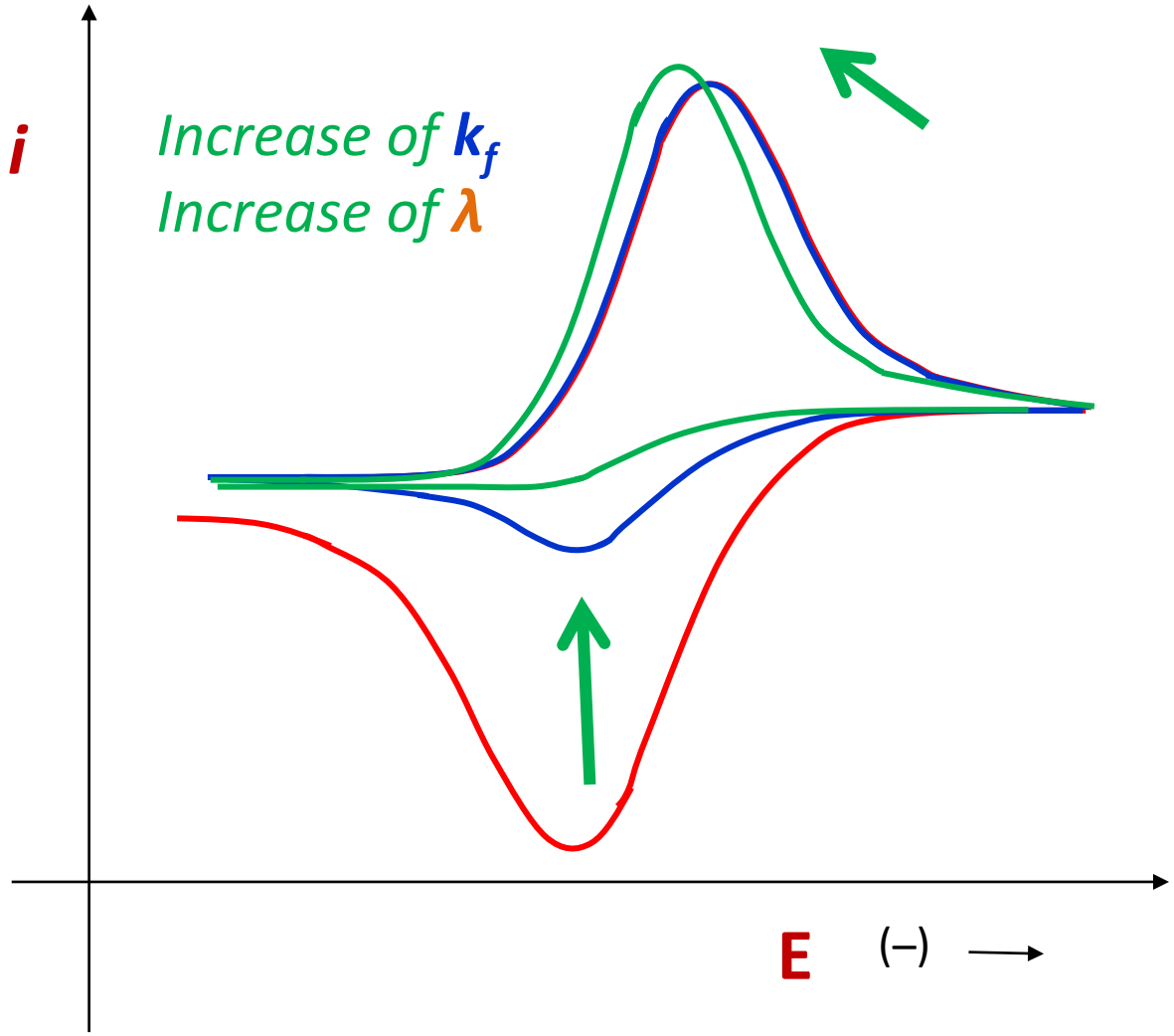
Rate constant of the follow-up chemical reaction

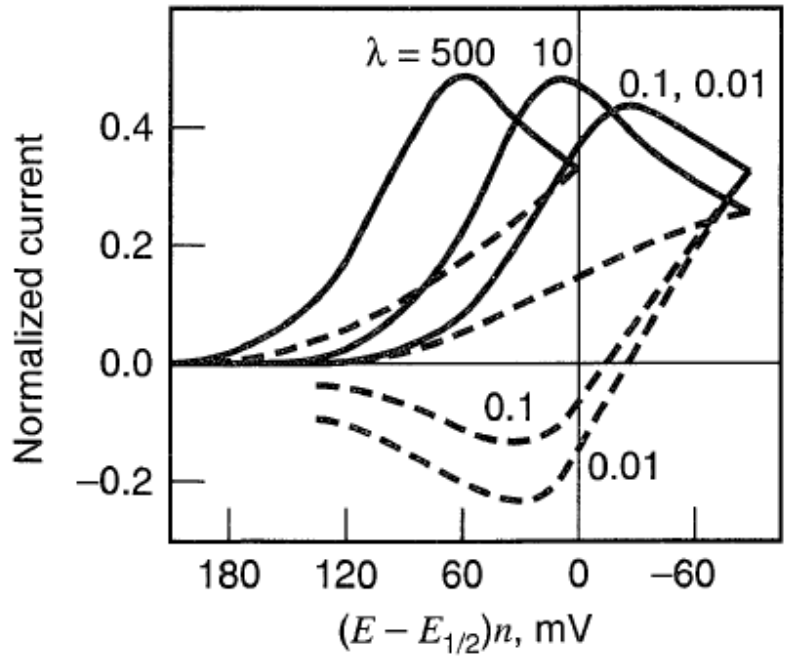
Scan rate

The voltammetric response depends on the **competition between diffusion and the follow-up reaction**

- $\lambda \rightarrow 0$ (*high scan rates and/or slow chemical reaction*): *negligible effect of the chemical process on CV response, which appears as a canonical* ***unperturbed reversible wave (diffusion-controlled conditions)***
- $\lambda \rightarrow \infty$ (*low scan rates and/or fast chemical reaction*): *the rate of the follow-up chemical reaction is significantly higher than the diffusion rate, so that Red species is converted into P as fast as it is formed at the electrode surface* ***(pure kinetic conditions)***

Irreversible follow-up chemical reactions



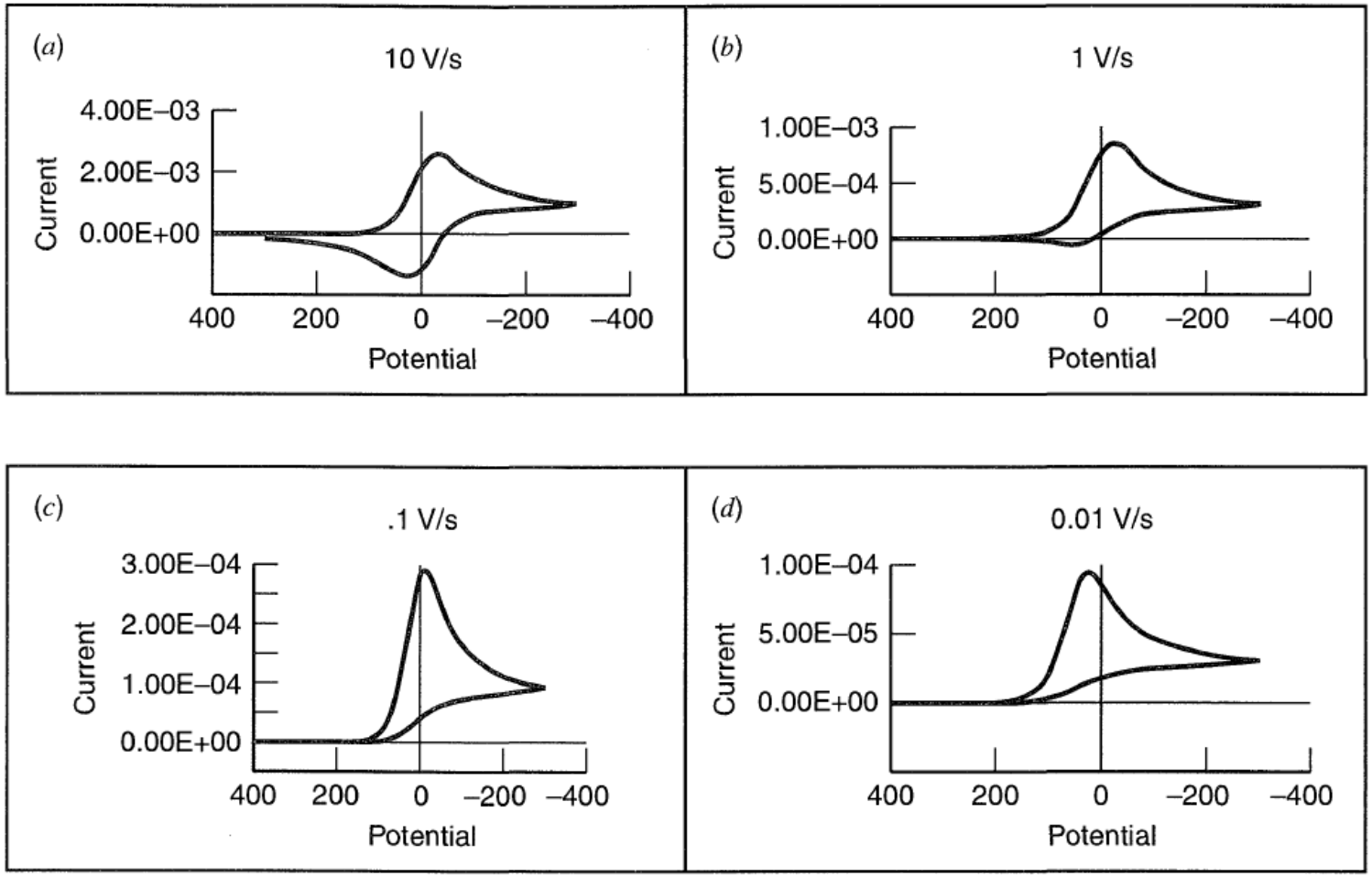


Bard & Faulkner, 2nd Ed., Wiley, 2001

For **large λ values** (pure kinetic region), **no current is observed on reverse scan** (especially at low scan rates) and the **shape** of the curve is **similar to that of a totally irreversible ET (chemically irreversible response)**

Irreversible follow-up chemical reactions

Effect of the scan rate



Bard & Faulkner, 2nd Ed., Wiley, 2001

Irreversible follow-up chemical reactions: pure kinetic conditions

- **Peak current (i_p)** is only **slightly higher (≈10%)** than for a Nernstian wave (same dependence on C*, v and D)

$$i_p = 0.496\left(\frac{F^3}{RT}\right)^{1/2} n^{3/2} A\, D_{Ox}^{1/2} C_{Ox}^{*} v^{1/2}$$

- **Peak width** is only **slightly smaller** than for a Nernstian wave (sharper peak)

$$|E_p - E_{p/2}| = 1.85\frac{RT}{nF}$$

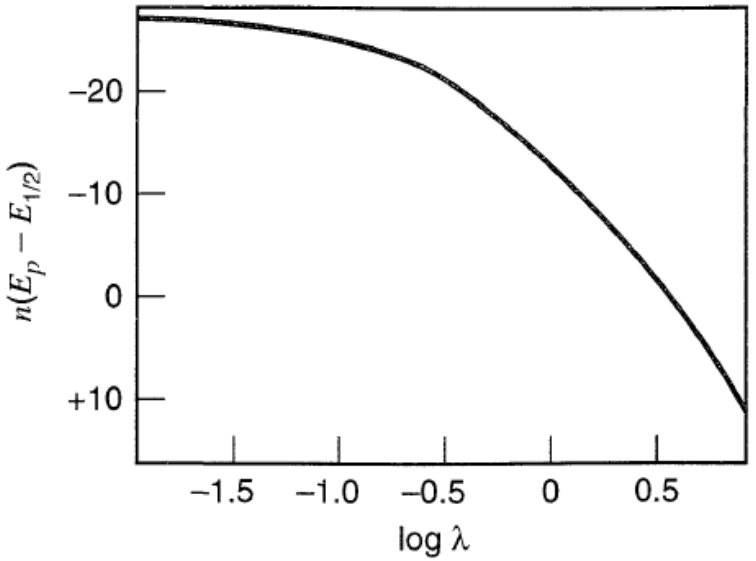
- **Current ratio (i_{pa}/i_{pc})** progressively **increases with the scan rate** up to a value of 1 (equal to a Nernstian wave): in this condition, the chemical reaction is completely prevented and the apparent behavior is purely Nernstian (potential sweep is reversed before the chemical reaction can afford to convert Red into P)

Irreversible follow-up chemical reactions: pure kinetic conditions

- *Kinetic information* is provided by the location of wave (peak potential)
- **Peak potential (E_p) shifts cathodically upon increasing the scan rates** or decreasing the rate constant (linear E_p variation of 29.6 mV/n for every 10-fold increase in the scan rate)

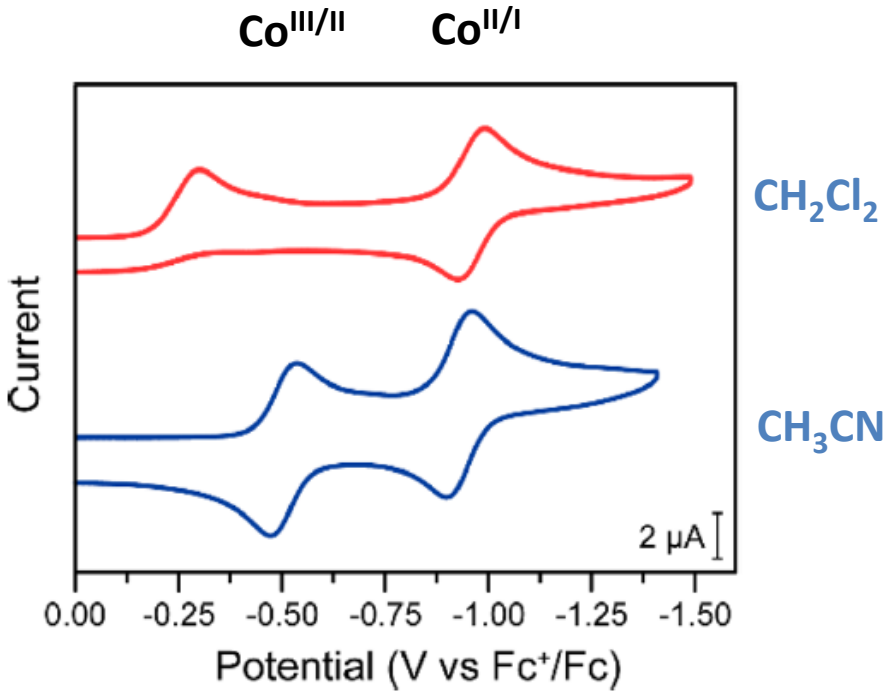
$$E_p = E^{0\prime} - 0.78\frac{RT}{nF} + \frac{RT}{2nF}\ln\lambda \qquad \lambda = \frac{RT}{nF}\frac{k_f}{v}$$

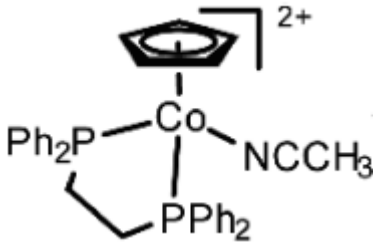
- E_p relationship can be used to estimate the k_f **rate constant** (if $E^{0\prime}$ is known)
- $E^{0\prime}$ can be obtained by recording CVs at increasing scan rates, up to a level for which a reversible Nernstian wave is obtained



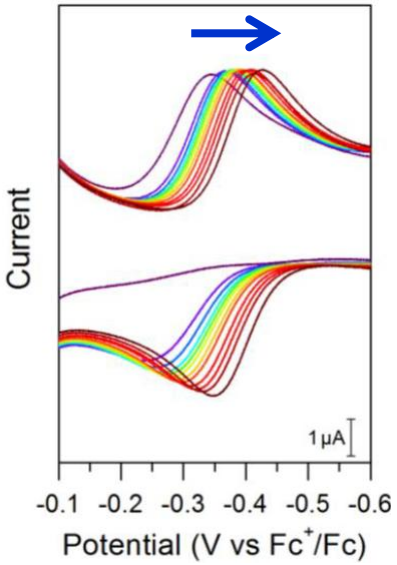
Bard & Faulkner, 2nd Ed., Wiley, 2001

Case study/1

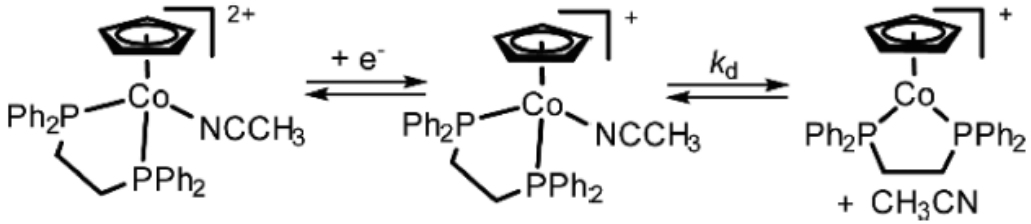




Titration with CH_3CN in DCM

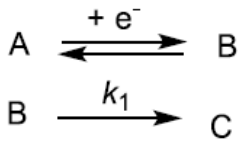


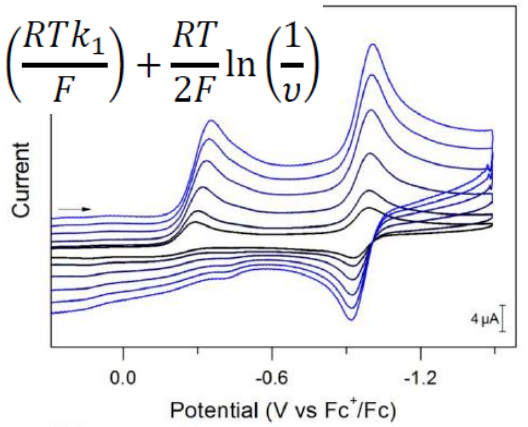
Ligand dissociation



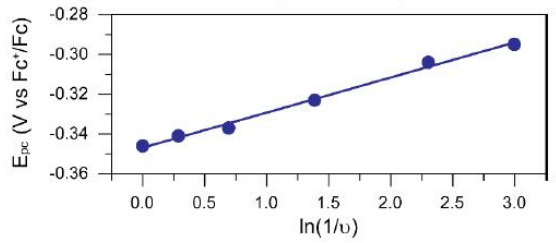
Estimation of rate constant for CH_3CN dissociation in DCM (different scan rates)

$$E_{p,c} = E_{1/2} - \frac{0.78RT}{F} + \frac{RT}{2F}\ln\left(\frac{RTk_1}{F}\right) + \frac{RT}{2F}\ln\left(\frac{1}{\upsilon}\right)$$





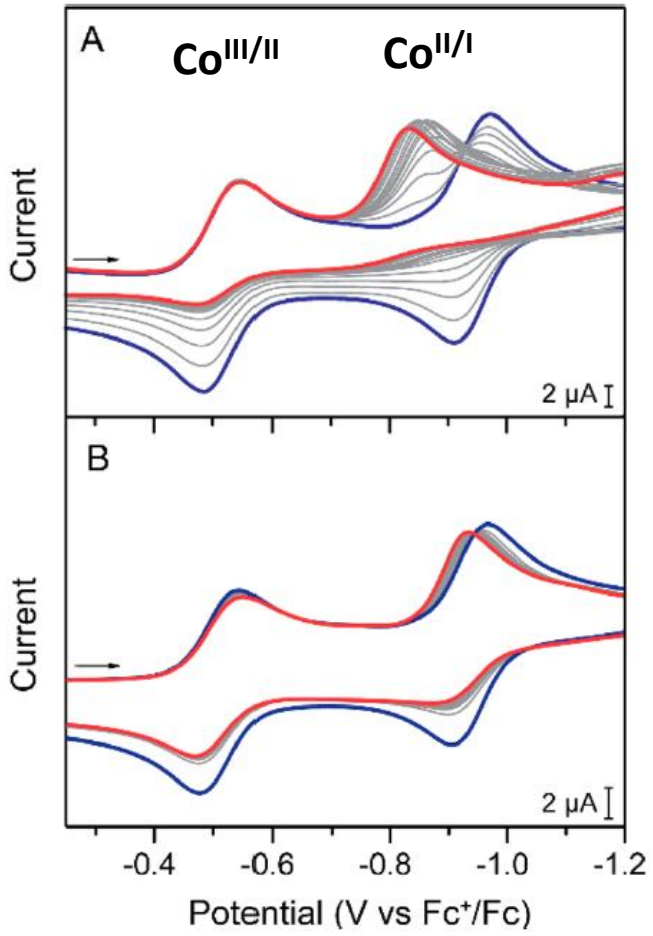
Estimation of k_d (plot intercept)



N. Elgrishi, D. Kurtz, J. Dempsey, *J. Am. Chem. Soc.* **2017**, *139*, 239–244

Case study/2

CH_3CN

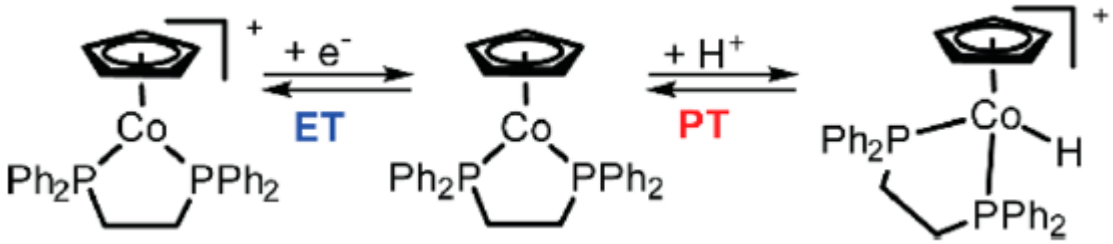


Protonation step

Titration with 4-cyano-anilinium (pK_a = 7)

Titration with Benzoic acid (pK_a = 21.51)

ET-PT mechanism



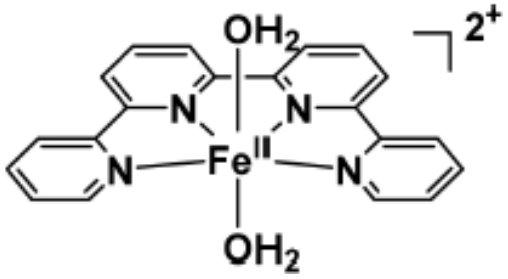
$$E_p = E_{1/2} - \frac{RT}{F}(0.78) + \frac{RT}{2F}\ln\left(\frac{k_{obs}RT}{F\upsilon}\right)$$

$$k_{obs} = k_{PT}C_A$$

N. Elgrishi, D. Kurtz, J. Dempsey, *J. Am. Chem. Soc.* **2017**, *139*, 239−244

Case study/3

Metal binding of small molecules



CO_2 binding

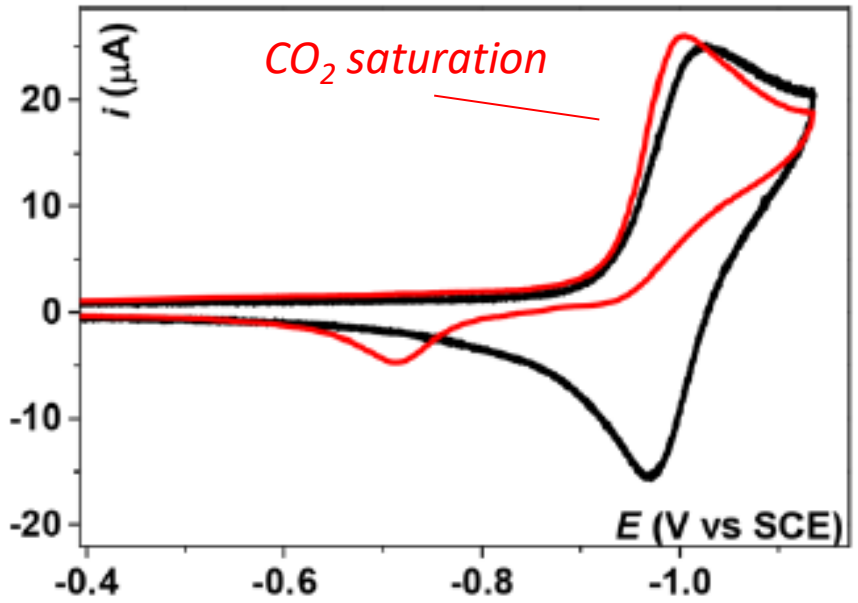
$$[Fe^{II}qpy]^{2+} + 1e^- \rightleftarrows [Fe^{I}qpy]^{+}$$

$$[Fe^{I}qpy]^{+} + CO_2 \rightarrow [Fe^{II}qpyCO_2^{\bullet -}]^{+}, \text{ rate } k$$

$$E_p = E^0(Fe^{II}/Fe^{I}) - 0.78\frac{RT}{F} + \frac{RT}{2F}\ln\frac{RTk[CO_2]}{Fv}$$

$k = 82\ M^{-1}s^{-1}$

$\Delta E_p = 21$ mV (anodic)



C. Cometto, M. Robert et al, *ACS Catalysis* **2018**, *8, 3411−3417*