Supporting Information

Concertedness in Proton-Coupled Electron Transfer Cleavages of Carbon-Metal Bonds Illustrated by the Reduction of an Alkyl Cobalt Porphyrin

Cyrille Costentin, Guillaume Passard, Marc Robert and Jean-Michel Savéant

Experimental Details

Chemicals. Dimethylformamide, from Sigma-Aldrich (>99.8 %) was stored over molecular sieves. The supporting electrolyte NBu₄ClO₄ (Fluka, puriss.) was used in 0.1 M concentration. Chloroacetonitrile (Fluka >99 %) was used as received. CoTPP (Sigma-Aldrich) was provided as a mixture of the metallated and non-metallated porphyrins. It was re-metallated and the purity checked by CCM.

Methods and Instrumentation

Cyclic voltammetry. The working electrode was a 3 mm-diameter glassy carbon (Metrohm) disk carefully polished and ultrasonically rinsed in absolute ethanol before use. The counter-electrode was a platinum wire and the reference electrode an aqueous SCE electrode. All experiments were carried out under argon at 22°C, the double-wall jacketed cell being thermostated by circulation of water. Cyclicvoltammograms were obtained by use of a Metrohm AUTOLAB PG-STAT 12 instrument. Ohmic drop was compensated using the positive feedback compensation implemented in the instrument.

Analysis of the all-concerted mechanism.

\[
\begin{align*}
\text{Co(II)} & \rightleftharpoons \text{Co(I)} \\
\text{Co(I)} + \text{RCI} & \rightarrow k_1 \text{Co(III)R} + \text{Cl}^- \\
\text{Co(III)R} + \text{AH} & \rightleftharpoons \text{Co(II)} + \text{RH} + \text{A}^-
\end{align*}
\]

In the following:

\[
P = \text{Co(II)}, \quad Q = \text{Co(I)}, \quad \text{Co(III)R} = \text{C}, \quad \text{RH} = \text{D}, \quad \text{RCI} = \text{A}, \quad \text{AH} = \text{Z}.
\]

\(v\) is the scan rate, \(i\) the current, \(E\) the electrode potential, \(T\) the temperature, \(S\) the electrode surface, \(t\) the time, \(x\) the space variable, \(C^0\) \(P\) bulk concentration, \(C^0_A\) \(A\) bulk concentration, \(C^0_Z\) \(Z\) bulk concentration, \(D\) the diffusion coefficient, \(k_S\) the standard rate constant, \(E_i\) the initial potential, \(E_f\) the inversion potential.

We introduce the following dimensionless parameters.

\[
\begin{align*}
\tau &= \frac{Fv}{RT} t, \quad \tau_R = \frac{E_i - E_f}{v} = u_i - u_f \\
u_i &= \frac{F}{RT} \left( E_i - E^0_{P/Q} \right), \quad u_f = \frac{F}{RT} \left( E_f - E^0_{P/Q} \right) \\
y &= x \sqrt{\frac{Fv}{RTD}}; \quad \Lambda = k_S C^0_O \sqrt{\frac{RT}{FvD}}, \quad p = \frac{[P]}{C^0_O}, \quad q = \frac{[Q]}{C^0_O}, \quad d = \frac{[D]}{C^0_O}, \quad a = \frac{[A]}{C^0_O}, \quad z = \frac{[Z]}{C^0_O}; \quad \gamma = \frac{C^0_A}{C^0_O} \\
\psi_j &= \frac{i_j}{FSC^0_O \sqrt{RT}} \left( \frac{Fv}{RT} \right) \\
\lambda_j \gamma &= \frac{RT}{F} \left( k_1 C^0_A / v \right) \\
\xi_i &= -\frac{F}{RT} \left( E - E^0_{P/Q} \right)
\end{align*}
\]
\[ \xi_2 = -\frac{F}{RT} \left( E - E_{C+Z/D+P}^0 \right) \]
\[ \Delta E^0 = \frac{F}{RT} \left( E_{C+Z/D+P}^0 - E_{P/Q}^0 \right) \]

In which \( E_{C+Z/D+P}^0 \) is the standard potential for the CPET couple, i.e., it depends on \( pK_{a,Z} \).

The governing partial derivative equations are:
\[
\frac{\partial p}{\partial \tau} = \frac{\partial^2 p}{\partial y^2} \quad (1)
\]
\[
\frac{\partial q}{\partial \tau} = \frac{\partial^2 q}{\partial y^2} - \lambda_1 y q \quad (2)
\]
\[
\frac{\partial c}{\partial \tau} = \frac{\partial^2 c}{\partial y^2} + \lambda_1 y q \quad (3)
\]
\[
\frac{\partial d}{\partial \tau} = \frac{\partial^2 d}{\partial y^2} \quad (4)
\]
\[
\frac{\partial z}{\partial \tau} = \frac{\partial^2 z}{\partial y^2} \quad (5)
\]

Initial and boundary conditions:
\[ 0 \leq \tau \leq \tau_R: \xi_1 = \xi_c = -u_i + \tau \]
\[ \tau_R \leq \tau \leq 2 \tau_R: \xi_1 = \xi_a = -2u_f + u_i - \tau = -u_f - (\tau - \tau_R) \]
\[ \tau = 0, y \geq 0 \text{ and } y = \infty, \tau \geq 0: p = 1, q = 0, c = 0, d = 0, a = \gamma, z = z^0 \]
\[ y = 0, \tau \geq 0: \]
\[ p = q \exp(-\xi_1) \]
\[ \psi_2 = A_0 z_0 \exp(\xi_2/2) \]
\[ \frac{\partial p + q + c}{\partial y} = 0 \]

The subscript 0 indicates the concentration at the electrode surface, i.e. \( y = 0 \).

There are two contributions, \( \psi_1 \) and \( \psi_2 \) to the total dimensionless current, \( \psi \), involving the P/Q and the C/D couples respectively. In normalized terms:
\[ \psi_1 = \left( \frac{\partial q}{\partial y} \right)_0 \quad \text{and} \quad \psi_2 = \left( \frac{\partial c}{\partial y} \right)_0 \quad ; \quad \psi_1 - \psi_2 = \left( \frac{\partial p}{\partial y} \right)_0 \]

Addition of equations (1), (2) and (3) followed by integration leads to:
\[ p_0 + q_0 + c_0 = 1 \]
and after introduction of the two Nernst laws to:
\[ q_0 \left[ 1 + \exp(-\xi_1) \right] + c_0 = 1 \quad (6) \]

Integration of equation (1), taking into account the initial conditions, leads to:
\[ p_0 = 1 - \frac{1}{\sqrt{\pi}} \int_0^\tau \frac{\psi_1(\eta) - \psi_2(\eta)}{\sqrt{\tau - \eta}} d\eta \quad (7) \]

we assume that \( \lambda_1 \) is large (pure kinetic conditions):
\[ q_0 = \frac{\psi_1}{\sqrt{\lambda_1 \gamma}} \]

At the first wave, \( \psi_2 = 0 \), and thus:
\[ \psi = \sqrt{\lambda_1 \gamma} \exp \left( -\xi_1 \right) = 1 - \frac{1}{\sqrt{\lambda_1 \gamma}} \int_0^\tau \frac{\psi(\eta)}{\sqrt{F - \eta}} d\eta \]

i.e., the equation of a voltammogram corresponding to an irreversible EC mechanism.

At the second wave, since \( \rho_0 = 0 \), equation (7) becomes:
\[ \psi_1 - \psi_2 = \frac{1}{\sqrt{\lambda_1 \gamma}} \]

at the level of the second wave, the right-hand side of the second equation is practically nil, thus leading to:
\[ \psi_1 = \psi_2 = \frac{\psi}{2} \]

Equation (6) may be recast as:
\[ \frac{\psi}{2} \frac{1}{\sqrt{\lambda_1 \gamma}} \left[ 1 + \exp \left( -\xi_1 \right) \right] = \frac{\psi}{2} \frac{1}{\sqrt{\lambda_1 \gamma}} \left( 1 + \exp \left( -\xi_1 \right) \right) \exp \left( \xi_2 / 2 \right) = 1 \]

i.e.:
\[ \psi = \frac{2}{\sqrt{\lambda_1 \gamma}} \left[ 1 + \exp \left( -\xi_1 \right) \right] \exp \left( -\xi_2 / 2 \right) \]

\[ \rho_0 = \frac{\xi_2}{A} \]

If we consider that \( Z \) (i.e. the acid \( AH \)) is in a large enough concentration so that it is not consumed then: \( z_0 = z^0 \)

We introduce and apparent standard potential depending on \( Z \) concentration:
\[ \xi_2 = \xi_2 + 2 \ln z^0 = \frac{F}{RT} \left( E - \left( E^{0, C+Z/D+P} + 2 - \frac{RT}{F} \ln \frac{C_0}{C_0} \right) \right) = - \frac{F}{RT} \left( E - E^{0, C+Z/D+P, ap} \right) \]

thus leading to equation:
\[ \psi = \frac{1}{\sqrt{\lambda_1 \gamma}} \left[ 1 + \exp \left( -\xi_1 \right) \right] \exp \left( -\xi_2 / 2 \right) \]

At large overpotential, a plateau is reached:
\[ \psi_\rho = 2 \sqrt{\lambda_1 \gamma} \]

We can assume that at the level of the second wave \( \exp \left( -\xi_1 \right) = 0 \), then an S-shape wave is obtained:
\[ \psi = \frac{1}{\sqrt{\lambda_1 \gamma}} \left[ 1 + \exp \left( -\xi_2 / 2 \right) \right] \]

with:
\[ \xi_2 = 2 \ln \left( \frac{\sqrt{\lambda_1 \gamma}}{A} \right) = \xi_2 + 2 \ln \left( \frac{z^0 A}{\lambda_1 \gamma} \right) \]

The half-wave potential corresponds to: \( \xi_2 = 0 \)
\[ E_{1/2} = E^{0, C+Z/D+P} + \frac{RT}{F} \ln \left( \frac{k_5 C_0}{2} \right) \]

showing how the S-shaped wave shifts toward positive potentials as the concentration of acid is raised.