Supporting Information

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

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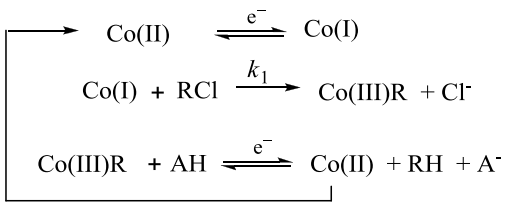
Experimental Details

Chemicals. Dimethylformamide, from Sigma-Aldrich (>99.8 %) was stored over molecular sieves. The supporting electrolyte NBu_4ClO_4 (Fluka, purriss.) 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. Cyclic volt-ammograms 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.



In the following:

P = Co(II), Q = Co(I), Co(III)R = C, RH = D, RCl = A, AH = 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_A^0 A bulk concentration, C_Z^0 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.

$$\tau = \frac{Fv}{RT}t\,,\ \tau_R = \frac{E_i - E_f}{v} = u_i - u_f$$

$$u_i = \frac{F}{RT}\left(E_i - E^0_{P/Q}\right),\ u_f = \frac{F}{RT}\left(E_f - E^0_{P/Q}\right)$$

$$y = x\sqrt{\frac{Fv}{RTD}}\ ;\ \Lambda = k_S C^0\sqrt{\frac{RT}{FvD}}\ ;\ p = \frac{[P]}{C^0},\ q = \frac{[Q]}{C^0}\ d = \frac{[D]}{C^0},\ a = \frac{[A]}{C^0};\ z = \frac{[Z]}{C^0};\ \gamma = \frac{C_A^0}{C^0}$$

$$\psi_j = \frac{i_j}{FSC^0\sqrt{D}\sqrt{\frac{Fv}{\mathcal{R}T}}}$$

$$\lambda_1\gamma = \frac{RT}{F}\left(k_1 C_A^0 / v\right)$$

$$\xi_1 = -\frac{F}{RT}\left(E - E^0_{P/Q}\right)$$

$$\xi_2 = -\frac{F}{RT}\left(E - E^0_{\mathrm{C+Z/D+P}}\right)$$

$$\Delta\xi^0 = \frac{F}{RT}\left(E^0_{\mathrm{C+Z/D+P}} - E^0_{\mathrm{P/Q}}\right)$$

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

The governing partial derivative equations are:

$$\frac{\partial p}{\partial \tau} = \frac{\partial^2 p}{\partial y^2} \qquad (1)$$

$$\frac{\partial q}{\partial \tau} = \frac{\partial^2 q}{\partial y^2} - \lambda_1 \gamma q \qquad (2)$$

$$\frac{\partial c}{\partial \tau} = \frac{\partial^2 c}{\partial y^2} + \lambda_1 \gamma q \qquad (3)$$

$$\frac{\partial d}{\partial \tau} = \frac{\partial^2 d}{\partial y^2} \qquad (4)$$

$$\frac{\partial z}{\partial \tau} = \frac{\partial^2 z}{\partial y^2} \qquad (5)$$

Initial and boundary conditions:

$0 \le \tau \le \tau_R$: $\xi_1 = \xi_c = -u_i + \tau$

$\tau_R \le \tau \le 2\tau_R$: $\xi_1 = \xi_a = -2u_f + u_i - \tau = -u_f - (\tau - \tau_R)$

$\tau = 0, y \ge 0$ and $y = \infty, \tau \ge 0$: $p = 1,\ q = 0,\ c = 0, d = 0, a = \gamma, z = z^0$

$y = 0,\ \tau \ge 0$:

$$p = q\exp(-\xi_1)$$

$$\psi_2 = \Lambda c_0 z_0 \exp(\xi_2/2)$$

$$\frac{\partial p + q + c}{\partial y} = 0$$

The subscript 0 indicates the concentration at the electrode surface, i.e. $y = 0$.

There are two contributions, ψ_1 and ψ_2 to the total dimensionless current, ψ, involving the P/Q and the C/D couples respectively. In normalized terms:

$$\psi_1 = -\left(\frac{\partial q}{\partial y}\right)_0 \quad \text{and} \quad \psi_2 = \left(\frac{\partial c}{\partial y}\right)_0 \ ; \ \psi_1 - \psi_2 = \left(\frac{\partial p}{\partial y}\right)_0$$

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:

$q_0\left[1 + \exp(-\xi_1)\right] + c_0 = 1$ (6)

Integration of equation (1), taking into account the initial conditions, leads to:

$$p_0 = 1 - \frac{1}{\sqrt{\pi}}\int_0^{\tau} \frac{\psi_1(\eta) - \psi_2(\eta)}{\sqrt{\tau - \eta}}\, d\eta \qquad (7)$$

we assume that λ_1 is large (pure kinetic conditions):

$$q_0 = \frac{\psi_1}{\sqrt{\lambda_1 \gamma}}$$

At the first wave,

$\psi_2 = 0$, and thus:

$$\frac{\psi}{\sqrt{\lambda_1\gamma}}\exp\left(-\xi_1\right)=1-\frac{1}{\sqrt{\pi}}\int_0^{\tau}\frac{\psi(\eta)}{\sqrt{\tau-\eta}}d\eta$$

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

At the second wave, since $p_0=0$, equation (7) becomes:

$$\psi_1-\psi_2=\frac{1}{\sqrt{\pi\tau}}$$

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:

$$\frac{\psi}{2\sqrt{\lambda_1\gamma}}\left[1+\exp\left(-\xi_1\right)\right]+\frac{\psi}{2\Lambda z_0\exp\left(\xi_2/2\right)}=1$$

i.e.:

$$\psi=\frac{2}{\frac{1}{\sqrt{\lambda_1\gamma}}\left[1+\exp\left(-\xi_1\right)\right]+\frac{\exp\left(-\xi_2/2\right)}{\Lambda z_0}} \quad (7)$$

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:

$$\xi_2'=\xi_2+2\ln z^0=-\frac{F}{RT}\left(E-\left(E^0_{\mathrm{C+Z/D+P}}+2\frac{RT}{F}\ln\frac{C^0_{\mathrm{Z}}}{C^0_{\mathrm{P}}}\right)\right)=-\frac{F}{RT}\left(E-E^0_{\mathrm{C+Z/D+P,ap}}\right)$$

thus leading to equation:

$$\frac{\psi}{2\sqrt{\lambda_1\gamma}}=\frac{1}{1+\exp\left(-\xi_1\right)+\frac{\sqrt{\lambda_1\gamma}\exp\left(-\xi_2'/2\right)}{\Lambda}}$$

At large overpotential, a plateau is reached:

$$\psi_p=2\sqrt{\lambda_1\gamma}$$

We can assume that at the level of the second wave $\exp\left(-\xi_1\right)\simeq 0$, then an S-shape wave is obtained:

$$\frac{\psi}{2\sqrt{\lambda_1\gamma}}=\frac{1}{1+\frac{\sqrt{\lambda_1\gamma}\exp\left(-\xi_2'/2\right)}{\Lambda}}=\frac{1}{1+\exp\left(-\xi_{2,c}'/2\right)}$$

with

$$\xi_{2,c}'=\xi_2'-2\ln\left(\frac{\sqrt{\lambda_1\gamma}}{\Lambda}\right)=\xi_2+2\ln\left(\frac{z^0\Lambda}{\sqrt{\lambda_1\gamma}}\right)$$

The half-wave potential corresponds to: $\xi_{2,c}'=0$

$$E_{1/2}=E^0_{\mathrm{C+Z/D+P}}+\frac{RT}{F}\ln\left(\frac{\left(k_S C^0_{\mathrm{Z}}\right)^2}{Dk_1C^0_{\mathrm{A}}}\right)$$

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