SUPPORTING INFORMATION

Reorganization Energies and Pre-Exponential Factors in the One-Electron Electrochemical and Homogeneous Oxidation of Phenols Coupled with an Intramolecular Amine-Driven Proton Transfer.

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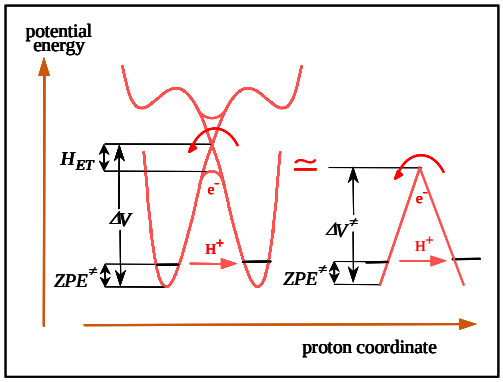
Effect of the proton donor-acceptor distance *Q* vibration on *C*

The modeling of the barrier skeched in scheme S1 has been proposed.[1S] It allows an estimation of $C_0(Q)$ as a function of the barrier height, ΔV , depending on the distance between the donor and acceptor atoms, *Q*.



Modeling of tunneling barrier. The barrier is approximated by an isocele triangle.

Scheme S1.

Within this model, the coupling constant is given by equations S1 and S2:

$$C_0(Q) = h\nu_0^{\neq} \exp\left[-\frac{8\sqrt{2}}{3}\sqrt{\frac{h\nu_0^{\neq}}{\Delta V^{\neq}}}\left(\frac{\Delta V^{\neq}}{h\nu_0^{\neq}} - \frac{1}{2}\right)^{3/2}\right] \qquad \text{(S1)}$$

with:

$$\Delta V^{\neq}(Q) = \frac{f_0^{\neq}}{4}\left(\frac{Q - d_{\mathrm{AH}}^0 - d_{\mathrm{DH}}^0}{2}\right)^2 \qquad \text{(S2)}$$

where $f_0^{\neq} = 4\pi^2 \nu_0^{\neq} m_P$ is the force constant of the proton well and d_{DH}^0 and d_{AH}^0 are the proton equilibrium distances in the reactant and product, respectively.

Theoretical estimation of $\int_0^{\infty} \ln\left(1 + \frac{2\pi^2 C_0^2(Q)}{h\nu_n\sqrt{4\pi\lambda^{het}RT}}\right) P(Q)dQ$ may be done by taking into account the effect of the proton donor-acceptor distance *Q* vibration on the CPET coupling constant with equations S1 and S2. The contribution of each distance *Q* is weighting by the Boltzmann probability $P(Q)$ that the donor and acceptor atoms be at a distance *Q* from one another:

$$P(Q) = \sqrt{\frac{f_Q}{2\pi RT}} \exp\left(-\frac{f_Q(Q - Q_{eq})^2}{2RT}\right) \text{ with } f_Q = 4\pi^2 \nu_Q^2 m_Q \text{ where } \nu_Q \text{ is frequency and } m_Q \text{ is reduced mass.}$$

Calculation was performed with the following parameters: [1S]

$d_{\mathrm{DH}}^0 = 0.96$ Å

$d_{\mathrm{AH}}^0 = 1$ Å

$Q_{eq} = 2.7$ Å

$f_0^{\neq} = 4\pi^2 \nu_0^{\neq} m_P = 21.6$ eV Å^{-2}

$h\nu_Q = 0.08$ eV

$m_Q = 8$ amu

$h\nu_n = \frac{k_B T}{h} = 6\ 10^{12}\ s^{-1}$

$\lambda^{het} = 1.4$ eV

An effective coupling constant C_0^{eff} is defined so that:

$$\ln\left(1+\frac{2\pi^2\left(C_0^{eff}\right)^2}{h\nu_n\sqrt{4\pi\lambda^{het}RT}}\right)=\int_0^{\infty}\ln\left(1+\frac{2\pi^2 C_0^2(Q)}{h\nu_n\sqrt{4\pi\lambda^{het}RT}}\right)P(Q)dQ$$

References:

1S. C. Costentin, M. Robert and J. M. Saveant, *J. Am. Chem. Soc.*, 2007, **129**, 9953.