Communication

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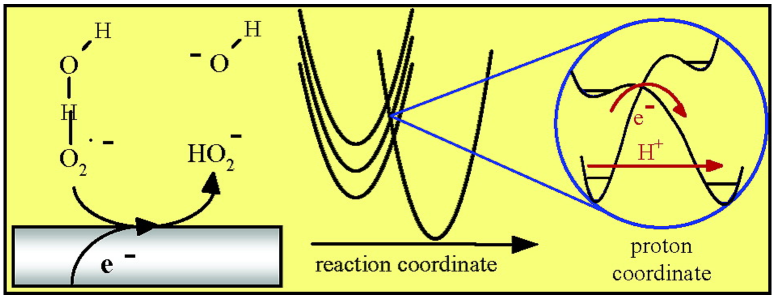

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Electrochemical Approach to Concerted Proton and Electron Transfers. Reduction of the Water−Superoxide Ion Complex

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Concerted proton and electron transfers (CPET)[1] currently attract considerable theoretical and experimental attention both from a fundamental point of view and in connection with their likely involvement in many enzymatic processes.[2] In most available studies, electron transfer is triggered homogeneously by ground-state or excited-state reagents.[2,3] So far, reports of electrochemical reactions involving CPET are scarce, and their CPET character is suggested rather than proved. One of these deals with the Os(III)OH/Os(II)OH$_2$ couple, where the osmium complexes are located at the end of a monolayer self-assembled at an electrode surface.[4] Another interesting example concerns the reduction of the anion radical of an orthoquinone, 3,5-di-*tert*-butyl-1,2-benzoquinone, in the presence of a weak acid.[5]

Electrochemistry, through techniques such as cyclic voltammetry, can provide a quite effective access to CPET in terms of diagnosis and quantitative kinetic characterization. The object of the present communication is to provide the necessary relationships for this purpose. The reduction of the water−superoxide ion complex in acetonitrile and dimethylformamide (Figure 1) will serve as a test example.

We assume that the proton transfer (PT) is adiabatic (strong coupling between the PT diabatic states) and that the electron transfer (ET) is nonadiabatic (weak coupling between ET diabatic states).[6] The system is then described by means of two electronic diabatic states, at the crossing of which both protons and electrons are transferred (Figure 1). All electrode electronic states are taken into account. Once the expressions of the individual rate constants are obtained, they are summed over all electronic states, weighting the contribution of each state according to the Fermi−Dirac distribution.[7] As shown elsewhere, the individual rate constant for the transfer from one electron state in the metal (j) is expressed as[8]

$$k_j = Z_j \exp\left(-\frac{\Delta G_j^{\ddagger}}{RT}\right), \text{ with } \Delta G_j^{\ddagger} = \frac{\lambda}{4}\left(1 + \frac{\mathbf{E}_j - \mathbf{E}^0}{\lambda}\right)^2 \qquad (1)$$

$\mathbf{E}_j$ is the energy of the electron in the metal and $\mathbf{E}°$, its value when the electrode potential is equal to the formal potential of the redox couple, $E°$. λ, the total reorganization energy, is the sum of three contributions, an internal reorganization energy, λ_i, a solvent reorganization energy related to electron transfer, λ_0^{ET}, and a solvent reorganization energy related to proton transfer λ_0^{PT}. Potentials are in volts and energies in electron volts. The following expressions (eqs 2 and 3) of the solvent reorganization energies[9] are obtained from an electrostatic model,[8] different from the ellipsoidal cavity model proposed for homogeneous CPET.[10]

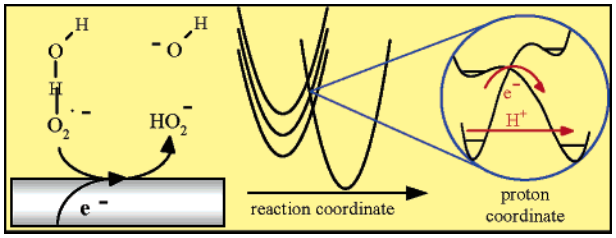

Figure 1. Left: CPET to the water−superoxide ion complex from an electrode. Right: potential energy profiles for electrochemical CPETs.

The individual rate constants are derived from application of the Golden Rule, taking into account the nonadiabaticity due to proton tunneling, thus leading to the expression (eq 4) of the pre-exponential factor:[8]

$$\lambda_0^{ET} = \frac{e_0^2}{4\pi\epsilon_0}\left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_S}\right)\frac{1}{2a} \qquad (2)$$

$$\lambda_0^{PT} = \frac{1}{4\pi\epsilon_0}\left[\left(\frac{\epsilon_S - 1}{2\epsilon_S + 1}\right) - \left(\frac{\epsilon_{op} - 1}{2\epsilon_{op} + 1}\right)\right]\frac{(\mu_R - \mu_P)^2}{a^3} \qquad (3)$$

$$Z_j = \frac{2\pi}{kT\sqrt{2\lambda M}} H_{ET}^2 \sqrt{\frac{\pi^3}{RT\lambda_p}}\, h\nu_0 \exp\left\{-\frac{2\pi}{h\nu_b}\left[\Delta V - \frac{h\nu_0}{2}\right]\right\} \exp\left\{\frac{h^2\beta^2}{8\pi^2 m_Q h\nu_Q}\right\} \qquad (4)$$

H_{ET} is the electronic coupling energy, λ_p the proton reorganization energy, and M the molar mass. The first exponential term represents the proton tunneling probability through a parabolic barrier (ΔV is the barrier height, ν_0, ν_b the frequencies associated with the bottom and top of the barrier, respectively). The last term represents the correlations between the fluctuations of the proton donor−acceptor distance, Q, and the nonadiabatic coupling (ν_Q is the frequency associated with the proton donor−acceptor vibrational mode, m_Q the reduced mass for this mode, and β the attenuation factor with Q for the nonadiabatic coupling).[11] Assuming that Z and the density of states are independent of the energy of the electronic states,[7b] the resulting rate constant is expressed by the following equation:

$$k = Z\sqrt{\frac{RT}{4\pi\lambda}} \int_{-\infty}^{+\infty} \exp\left\{-\frac{RT}{4\lambda}\left[\frac{\lambda}{RT} + \frac{F(E - E^0)}{RT} - \zeta\right]^2\right\} \frac{d\zeta}{1 + \exp(\zeta)} \qquad (5)$$

with $\zeta = (\mathbf{E} - \mathbf{E}_F)/RT$ ($\mathbf{E}_F$ is the Fermi level energy).

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At zero-driving force, i.e., for $E = E^\circ$

$$k = k_\mathrm{S} = Z\sqrt{\frac{RT}{4\pi\lambda}}\int_{-\infty}^{+\infty}\exp\left[-\frac{RT}{4\lambda}\left(\frac{\lambda}{RT} - \zeta\right)^2\right]\frac{\mathrm{d}\zeta}{1 + \exp(\zeta)} \qquad (6)$$

The structure of the activation/driving force relationship (5) is formally the same as for outersphere[7,12a] and dissociative[12b] electron-transfer electrochemical reactions. Typical values of Z and λ are, however, different in each case.

The cyclic voltammetry of dioxygen in acetonitrile and dimethylformamide (DMF) is similar. In both cases, the second wave corresponds to the reduction of the water−superoxide ion complex. Figure 2 shows an example of cyclic voltammetric response obtained in DMF. Application of eq 5 led, after estimation of the standard potential, $E^\circ = -0.59$ V vs SCE,[13] to the parameter values listed in Table 1.[14]

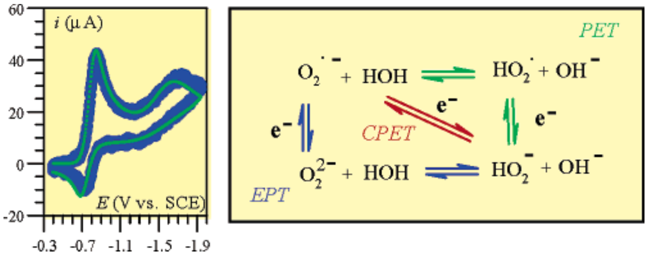

Figure 2. Left: Cyclic voltammetry of the reduction of dioxygen in DMF (+0.1 M NBu_4BF_4) at a glassy carbon electrode in the presence of 0.55 M H_2O. Scan rate: 0.2 V/s. Green line: simulated curve.[13] Right: competing mechanisms.

The peak-width of the second wave indicates a remarkably small value of the transfer coefficient (symmetry factor), α. It is much smaller than 0.5, the value typical of outersphere electron transfer, and is more reminiscent of dissociative electron transfers.[12] However, the reasons behind these small α values are different in the two cases. With dissociative electron transfers, reorganization energies are large because they include the dissociation energy of a bond linking two heavy atoms.[12] The reaction, therefore, takes place at a potential that is far more negative than the standard potential, thus causing α to be small. With CPET, the driving force is also large, but this is now because Z is small (much smaller than the heterogeneous collision factor, 9000 cm/s), while λ is not particularly large. One of the reasons for the nonadiabaticity, i.e., the smallness of Z, is that the reactant and product vibrational wave functions are localized in different wells and have very small overlap, as illustrated in the insert of Figure 1.[10] The proton has to tunnel through a substantial barrier as opposed to simple proton transfer involving Eigen acids, where the proton vibrational wave function is above the activation barrier along the electronic adiabatic state.[15]

Table 1. Experimental and Theoretical Characteristics for the Reaction ($O_2^{\bullet -}$, HOH) → (O_2H^-, OH^-)[16]

	λ (eV)	k_S (cm/s)	Z (cm/s)	$k_\mathrm{H}/k_\mathrm{D}$
Exp	1.23 ± 0.08	$(9 \pm 5) \times 10^{-7}$	1.45 ± 0.09	2.5 ± 0.5
Theor	1.27 ($\lambda_i = 0.35$ $\lambda_0^{\mathrm{ET}} = 0.79$ $\lambda_0^{\mathrm{PT}} = 0.13$)	6×10^{-7}	1.44	2.9

The parameter values that can be derived from theory are compared to the experimental values in Table 1. λ_i was obtained from gas-phase ab initio calculations, while λ_0^{ET} and λ_0^{PT} were obtained from eqs 2 and 3.[13] Z was derived from eq 4 with the help of ab initio quantum chemical calculations for the estimation of the required parameters.[13] The predicted kinetic isotope effect was likewise obtained from eq 7.[9] The good agreement between the experimental values and the theoretically predicted values (Table 1) shows that the observed kinetic characteristics are compatible with a CPET reaction.

$$\frac{k_\mathrm{H}}{k_\mathrm{D}} = \left[\exp\left\{\frac{2\pi}{h\nu_\mathrm{b}}(\sqrt{2} - 1)\Delta V\right\}\right]\left[\exp\left(-\frac{h^2\beta^2}{8\pi^2 m_Q h\nu_Q}\right)\right] \qquad (7)$$

What about the two concurrent stepwise mechanisms in which protonation either precedes or follows electron transfer (PET and EPT mechanisms, respectively), as sketched in Figure 2; this is the question that should be addressed next.

Prior protonation of the superoxide radical ion produces the neutral radical, which is easier to reduce than dioxygen. The first reduction response should then pass from a one-electron reversible wave to a two-electron irreversible wave, as observed with a proton donor stronger than water (e.g., benzimidazole). The fact that this does not happen with water rules out the stepwise PET mechanism. In the case of a stepwise EPT mechanism, the follow-up protonation makes electron transfer occur at a potential more positive than its standard potential, resulting in an α value larger than 0.5. The small value found for α, therefore, ruled out this mechanism.

Beyond the reduction of the water−superoxide ion complex, eqs 1−7 provide the theoretical framework that can be used to analyze electrochemical concerted proton-electron transfers, in general. We hope that it will help the discovery and further analysis of new or already existing experimental examples.

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Supporting Information Available: Details on experimental and simulation procedures. Estimation of the various theoretical parameters for the reduction of the water−superoxide ion complex. This material is available free of charge via the Internet at http://pubs.acs.org.

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