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Electrochemical concerted proton and electron transfers. Potential-dependent rate constant, reorganization factors, proton tunneling and isotope effects

Cyrille Costentin, Marc Robert, Jean-Michel Savéant *

Laboratoire d'Electrochimie Moléculaire, Université de Paris 7, Denis Diderot, Case Courrier 7107, 2 place Jussieu, 75251 Paris Cedex 05, France

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Abstract

Electrochemistry, through techniques like cyclic voltammetry, can provide a quite effective access to CPET in terms of diagnosis and quantitative kinetic characterization. The relationships expressing the electrochemical rate constant as a function of the electrode potential are derived. Besides the CPET standard potential, it depends on two main factors. One is the reorganization energy, which is the sum of an intramolecular contribution and a solvent reorganization energy. This last term appears to be the sum of proton and electron transfer contributions. Procedures are proposed to model and estimate these factors. The pre-exponential factor is a distinctive feature of CPET reactions. It indeed mainly depends upon proton tunneling through the activation barrier. Procedures for estimating this factor, and accordingly, the H/D kinetic isotope effect are described.

Keywords: Concerted proton–electron transfers; Activation–driving force realtionships; Isotope effects

1. Introduction

The coupling between electron and proton transfers has a long experimental and theoretical history in chemistry and biochemistry. Just to take one example, the understanding of organic electrochemistry is towered over by the fact that accepting an electron triggers the addition of an acid or the removal of a base and vice versa for oxidations. Coupling of a follow-up protonation with an electron transfer reaction offers an additional driving force, whether the two steps are successive or concerted. More generally, for the same thermodynamics of the global proton coupled electron transfer reaction (PCET), leading from $A + BH + e^-$ to $B^- + AH$, three mechanisms may be envisaged: two stepwise mechanisms, in which proton transfer precedes (PET) or follows (EPT) electron transfer and a one-step mechanism in which proton and electron transfer are concerted (Scheme 1) [1]. We term the latter mechanism CPET (concerted proton and electron transfer). The proton exchange reactions are fast when they involve oxygen or nitrogen acids, as often the case in practice. For the stepwise mechanisms, kinetic limitations to the gain in driving force are imposed by the electron transfer steps. In the concerted case, the kinetics responds directly to changes in the thermodynamics of the global reaction. What is the price to pay for this direct responsiveness is the question we discuss below for electrochemical CPET reactions. The problem bears some similarity with reactions in which electron transfer is concerted with the breaking of a bond linking two heavy atoms [2]. The breaking of the bond also brings about a gain of driving force to which the kinetics of the reaction responds directly. This is however partly compensated by the inclusion of the bond dissociation energy in the reorganization factors that control the intrinsic barrier. In CPET reactions, the trade off is different: it rather involves a

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* Corresponding author. Tel.: +33 44275582.
E-mail address: saveant@paris7.jussieu.fr (J.-M. Savéant).

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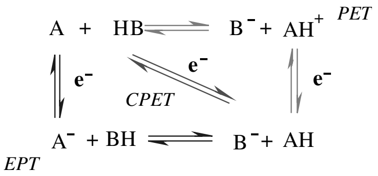

Scheme 1.

decreased pre-exponential factor that originates from proton tunneling through a substantial barrier resulting from proton–electron coupling.

Concerted proton and electron transfers currently attract active theoretical and experimental attention both from a fundamental point of view and in connection with their likely involvement in many enzymatic processes [3]. In the experimental investigation of these processes, electron transfer has been so far triggered homogeneously by ground state or excited state reagents in most cases [3,4]. Although electrochemistry appears as a promising approach to CPET in terms of diagnosis and quantitative kinetic characterization [5], reports of electrochemical reactions involving CPET are scarce and their CPET character often suggested rather than demonstrated [6,7]. The reason is presumably that the well detailed theoretical framework available for CPET requiring calculation of multiple mixed electronic/vibrational states [8] is not in a suitable form for an easy analysis of electrochemical data although it has been applied to numerous homogeneous systems [9]. Another approach has been proposed where both electron and proton are considered as tunneling objects. It is refereed to as the two-dimensional approach [10]. The purpose of the following discussion is to provide activation/driving force relationships applicable to electrochemical CPET reactions based on a simplified semi-classical treatment in the framework of the two-dimensional approach as well as procedures for estimating the key-parameters involved in these relationships. In particular, we take advantage of the specificity of electrochemical CPET reactions to introduce an electrostatic model leading to a simple expression for solvent reorganization energy (Section 2.2). Moreover, a quasi-classical approach is used to evaluate the pre-exponential factor (Section 2.3). Restriction of the rate constant calculation to the proton vibrational ground state allows providing a rate constant with the same expression as for outersphere ET and dissociative electron transfer. It can therefore be used to analyze experimental data from cyclic voltammetry as already shown elsewhere [5].

2. Results and discussion

2.1. Expression of the rate constant

A basic theoretical description of concerted electron proton transfer requires four diabatic states, shown at the corners of Scheme 1, namely, $\mathrm{A} + \mathrm{BH} + \mathrm{e}^-$, $\mathrm{AH}^+ + \mathrm{B}^- + \mathrm{e}^-$, $\mathrm{A}^- + \mathrm{BH}$ and $\mathrm{AH} + \mathrm{B}^-$. This simplified model is a particular case of a general multi-state model for multiple charge transfer reactions in solution [9d]. Based on the Born–Oppenheimer approximation, electron and proton being light particles, their transfer requires a reorganization of the solvent and of heavy atoms to reach a transition state where both reactants and products have the same configuration. The free energy surfaces of the four diabatic states are thus functions of solvent coordinates and internal coordinates involving heavy atoms. Consequently, the reaction coordinate for a CPET pathway is made up of three ingredients, an internal coordinate, Y_i, representing all interatomic distance and angle changes involving heavy atoms, a fictitious charge number, X_{ET}, representing solvent reorganization upon electron transfer and a dipole variation index, X_{PT}, representing solvent reorganization upon proton transfer. Separation of the solvent coordinates into two independent coordinates X_{ET} and X_{PT} is established in Section 2.2. Three reorganization energies noted, λ_i, λ_0^{ET}, λ_0^{PT} respectively are introduced accordingly. There are three distinct regimes of CPET depending on the coupling between the four diabatic states, namely, electronically adiabatic PT and ET, electronically non-adiabatic PT and ET, and electronically adiabatic PT–non-adiabatic ET [11]. When proton donor and acceptor are connected by a hydrogen-bond between Eigen acid and base, proton transfer is adiabatic, meaning that there is a strong coupling between the pairs of PT diabatic states, $\mathrm{A} + \mathrm{BH} + \mathrm{e}^-$, $\mathrm{AH}^+ + \mathrm{B}^- + \mathrm{e}^-$ on one hand and $\mathrm{A}^- + \mathrm{BH}$ and $\mathrm{AH} + \mathrm{B}^-$ on the other hand [12]. Since this situation is most relevant for biological CPET, we focus on this case. The system is then described by two states, each of them being obtained from a pair of proton diabatic states. Note also that the donor–acceptor distance, Q, is not considered as a classical reaction coordinate. However vibrational donor–acceptor motion plays a major role in the reaction dynamics, as we will see in Section 2.3 [13]. Electrochemical approach to CPET implies an electron transfer through the electrode–solution interface. The usual theoretical descriptions of interfacial electron transfer involve a coupling between two diabatic states [14]. The corresponding resonance energy is usually assumed to be large enough for not considering non-adiabatic effects but small compared to the activation barrier. Is this situation still relevant for CPET reaction? As discussed above, the CPET system may be described by means of two electronic diabatic states, at the crossing of which both proton and electron are transferred (Fig. 1) as detailed in the two-dimensional method [10]. At the transition state, which corresponds to a defined solvent and heavy atom configuration, the Born–Oppenheimer approximation allows separating electron transfer from proton transfer. Consequently, both electronic states are functions of a proton coordinate q, with electron transfer occurring at their crossing (see inset in Fig. 1). The coupling of these electronic states is similar to the usual interfacial electron transfer coupling. In most practical cases where CPET takes place within an intermolecular hydrogen-bonded complex, the proton activation barrier