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Kinetic isotope effects in proton coupled electron transfer

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ABSTRACT

Simple mathematical expressions describing the thermodynamic and kinetic dependencies of proton coupled electron transfer (PCET) processes have been used to examine the effects of electrolyte composition. Two charge transfer mechanisms have been considered, (i) a stepwise (*sw*) process and (ii) a concerted (*cc*) process involving the initial formation of a complex between the redox center and a proton donating/accepting species from the electrolyte. The hydrogen/deuterium kinetic isotope effect (KIE) for both the stepwise and concerted PCET mechanisms has been discussed by considering the variation in pK_a for solutes dissolved in light water and heavy water. Simulations demonstrate that different types of kinetic isotope effects can be observed for both stepwise and concerted pathways and, under certain conditions, the KIE of the former can be expected to be of equal magnitude to the latter. The KIE in a monolayer system of aminobenzoquinone has been studied in buffered water and heavy water electrolytes. The results are strongly in accordance with the fact that acid dissociation constants shift in D_2O compared to H_2O, and this leads to an appreciable KIE even when the stepwise PCET mechanism is operative.

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1. Introduction

Proton coupled electron transfer (PCET), which can be viewed as a redox reaction paired with a proton transfer reaction, has been extensively investigated both experimentally and theoretically because of its extensive application in important fields of research extending from biology to catalysis [1–8]. For electrochemical PCET processes where electrons are provided/removed by an electrode, two different mechanisms have been proposed and investigated in the past decade, namely the stepwise (*sw*) mechanism and the concerted mechanism (*cc*) [2]. In the *sw* PCET mechanism, it is generally assumed that any proton transfer steps are sufficiently fast enough that they can be treated as equilibrium processes and hence render the electron transfer processes as the rate determining steps. A prototypical example of PCET under control of the *sw* mechanism is the overall 2e/$2H^+$ reduction of benzoquinone in aqueous electrolytes [9]. As a function of pH, potential pathways for this PCET process include exclusively sequential electron then proton transfers (*ept*), exclusively sequential proton then electron transfer (*pet*), and mixtures of both. In contrast to the *sw* PCET mechanism, both the proton transfer and the electron transfer occur in one kinetic step in the concerted PCET mechanism [2,10–12]. An example of a concerted PCET transfer is the 1e/$1H^+$ oxidation of phenol and its derivatives in organic solvent systems [13,14]. As the *cc* process inherently requires a multi-bodied transition involving tunnelling of an electron between redox center and electrode as well as a simultaneous proton tunnelling event between redox center and proton acceptor/donor, it is intrinsically disfavored relative to the *sw* process from a kinetic point of view. However, as the *cc* process by-passes potentially high energy intermediates that must be formed in the *sw* transfer, it can be an energetically favored route for charge transfer.

Experimental evidence has shown that the kinetics of the *sw* PCET process is inversely proportional to the difference in the acid dissociation constants of the oxidized and reduced forms of the redox probe [8,15]. In cases where this pK_a difference is large, the *cc* pathway can become kinetically competitive with the *sw* pathway. Theoretical analyses using Butler–Volmer type equations to describe charge transfer kinetics verify such observations [11,15]. Experimental studies that attempt to discern between concerted and stepwise mechanisms are hampered by the observation of *apparent* rate constants rather than direct measures of individual charge transfer events. In principle, the hydrogen/deuterium kinetic isotope effect (KIE) should be a convenient experimental tool to probe the existence of concerted PCET mechanisms. Since simple electron transfer is always the rate determining step for *sw* processes, one would not expect to observe a KIE effect for *sw* PCET redox reactions under purely kinetic control [16]. On the other hand, because the concerted PCET mechanism involves an atom tunnelling event, a pronounced H/D kinetic isotope effect is theoretically predicted [2,17]. Such KIEs have been observed experimentally, for example, in an osmium aquo complex monolayer system, Madhiri and Finklea observed that the apparent rate constant in D_2O is approximately a factor of two slower than in H_2O in high pH/pD electrolytes [18]. Subsequently, Costentin et al. attributed this pH dependent KIE as evidence of charge transfer under concerted control [19].

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In this contribution we use previously developed expressions describing the thermodynamic and kinetic properties of PCET mechanisms to discuss the influence of solvent isotope exchange on observed charge transfer rates. Emphasis is placed on the fact that an observed KIE can be caused by an *intrinsic* contribution owing to isotope dependent differences in standard charge transfer rate constants as well as a *thermodynamic* contribution arising from differing pK_a values of acid donating/accepting species in D_2O and H_2O solvents [20,21]. We have modelled the influence of the thermodynamic contribution and demonstrated that it can lead to pronounced kinetic isotope effects on the apparent rate constant. Experimental evidence using a system that we have previously shown to be under *sw* control [22,23], namely a self-assembled monolayer of aminobenzoquinone, verifies this and serves to illustrate that the observation of a KIE should not be used exclusively as definitive evidence of concerted PCET.

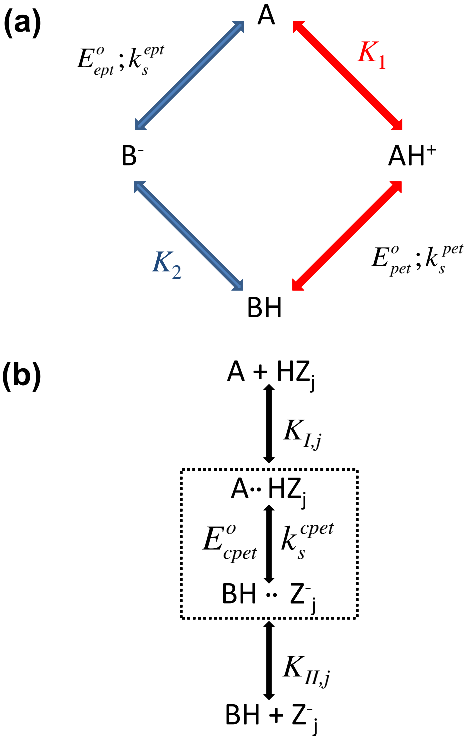
2. Experimental

Details of the method used to prepare aminobenzoquinone monolayers have been described elsewhere [22,23]. Briefly, the redox active films were made by first modifying a clean, gold electrode with a mixed monolayer of 11-aminoundecylthiol (AUT) and octanethiol (OT). Benzoquinone was then coupled to the AUT through a Michael-like addition. Experimental rate constants were determined using relatively slow (~5 mV/s) scan rates following the procedure previously outlined by Finklea and Haddox [24]. 99.9% deuterium oxide was purchased from Sigma–Aldrich and used as received. The electrolyte in the aminobenzoquinone monolayer studies consisted of 0.1 M sodium perchlorate and 0.04 M Britton–Robinson buffer, which is composed of acetic acid, phosphoric acid and boric acid. The pH of the electrolyte was adjusted using sodium hydroxide.

3. Model

Costentin and co-workers have extensively developed a suitable model for investigating the role of electrolyte composition on PCET mechanisms [25,26] which we summarize as succinctly as possible below. We utilize this model with the intention of providing insight into kinetic isotope effects as they apply to electrochemical PCET systems (i.e. those where the source/sink for electrons is an electrode), specifically those that involve redox active monolayers. Scheme 1a shows the mechanistic paths for the two possible stepwise pathways (*ept* and *pet*) which differ simply in the order of electron and proton transfer. In the stepwise mechanism it is assumed that the discrete proton transfer processes are sufficiently fast as to allow the protonation/deprotonation reactions to be considered at equilibrium [9,16]. The *sw* transfer scheme is further characterized by acid dissociation constants K_1, K_2, formal potentials E^o_{pet}, E^o_{ept} and standard heterogeneous rate constants k_s^{ept}, k_s^{pet}. It is assumed that the concerted mechanism in Scheme 1b involves an initial association of a transitory adduct $A\cdot\cdot HZ_j$, which participates in a rate limiting concerted charge transfer process (outlined by the dotted line in Scheme 1b and characterized by $E^o_{cpet,j}$ and k_s^{cpet}) followed by adduct dissociation [19,25–28]. HZ_j and Z_j^- are the acidic forms and conjugate bases of either the solvent or the *j*th component of the buffer system and are linked through the acid dissociation constant $K_{a,j}$. The equilibrium concentration of adducts before and after charge transfer are described by the formation constants $K_{I,j}$ and $K_{II,j}$ respectively.

3.1. Stepwise PCET thermodynamics



Scheme 1. Stepwise pathways (a) and associated concerted pathway (b) for a 1e1H proton coupled electron transfer process.

Whereas a simple electron-transfer event such as the redox reaction in the *ept* pathway of Scheme 1b requires the straight-forward application of the Nernst equation, e.g.,

$$E = E^o_{ept} + \frac{RT}{F}\ln\frac{[A]}{[B^-]} \qquad (1)$$

the global *sw* and *cc* processes are described by a Nernst expression that relates an apparent formal potential, E^o_{app} (which is experimentally observable), to the summations of the concentrations of all the oxidized and reduced forms participating in the overall redox reaction.

$$E = E^o_{app} + \frac{RT}{F}\ln\left(\frac{\sum(\mathrm{Ox})}{\sum(\mathrm{Red})}\right) \qquad (2)$$

The full treatment of the *sw* case has been described with rigor elsewhere [16,23] and results in two further expressions pertinent to the development of the model.

$$E^o_{pet} = E^o_{ept} + \frac{RT}{F}\ln\left(\frac{K_1}{K_2}\right) \qquad (3)$$

and

$$E^{o,sw}_{app} = E^o_{ept} + \frac{RT}{F}\ln\left(\frac{1+[H^+]/K_2}{1+[H^+]/K_1}\right) \qquad (4)$$

3.2. Concerted PCET thermodynamics

When considering the *cc* mechanism, the Nernst equation for the electron transfer step $(A\cdot\cdot HZ_j) + e^- \Longleftrightarrow (BH\cdot\cdot Z_j^-)$ is

$$E = E^o_{cpet,j} + \frac{RT}{F}\ln\left(\frac{[A\cdot\cdot HZ_j]}{[BH\cdot\cdot Z_j^-]}\right) \qquad (5)$$

which can be combined with Eq. (1) to provide

$$E^o_{cpet,j} = E^o_{ept} + \frac{RT}{F}\ln\left(\frac{K_{II,j}K_{a,j}}{K_{I,j}K_2}\right) \qquad (6)$$

where $K_{a,j}$ is the acid dissociation constant for the *j*th proton donating species present in the electrolyte. In by-passing the potentially

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