



New Processes and Materials Based on Electrochemical Concepts at the Microscopic Level  
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## Influence of the electron transfer rate on electrochemically controlled hydrogen bonding

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### Abstract

Hydrogen bonding is an essential interaction in natural and artificial systems. Its strength can be modulated by employing process known as Electrochemically Controlled Hydrogen bonding (ECHB). Although these processes are assumed to operate under thermodynamic control no experimental evidence for kinetic control exists. In this work, ECHB processes were studied using electrogenerated radical anions from 5-nitroimidazole derivatives as receptor molecules and 1,3-diethylurea as hydrogen bond donor species. Results revealed that kinetic control occurs due to an increase in the internal reorganization energy of the receptor molecule, which cause a decrease in electron transfer rate. Electronic structure calculations and experimental  $K_b$  values suggested that kinetic limitations were the product of a competition between intra and intermolecular hydrogen bonding formation during the global process.

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*Keywords:* Electrochemically controlled hydrogen bonding; cyclic voltammetry; 5-nitroimidazole derivatives, kinetic control.

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### 1. Introduction

Hydrogen bonding is a fundamental interaction that occurs in a wide variety of natural systems. For example, it defines the protein structures and it is also a key element in formation of DNA.<sup>1, 2</sup> Because of its directional character, hydrogen bonding is one of the most important and useful intermolecular interaction available for the

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construction of molecular devices<sup>3,4</sup>, with specific applications<sup>5-7</sup>, such as molecular machines<sup>7, 8</sup>, and sensors<sup>9, 10</sup>. Hydrogen bonding is a mainly electrostatic interaction; therefore the degree of affinity of the reactive species to form hydrogen bonds can be enhance (or diminish) by using electron transfer (ET) reactions to change the redox state of the species.<sup>4, 11</sup> Regarding this, several authors have demonstrated the effectiveness of the cyclic voltammetry to produce such redox disturbances,<sup>4, 12-14</sup> by using processes known as Electrochemically Controlled Hydrogen Bonding (ECHB),<sup>4, 12</sup> in which a switching molecule experiment changes in its reduction (or oxidation) potential towards less negative (or more positive) values, respectively, insofar as hydrogen bonding donor species (DH) are added. Below are represented the reactions occurring during ECHB.<sup>15</sup>

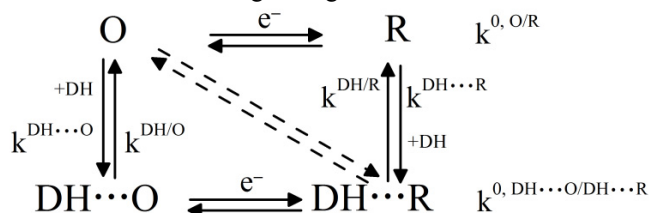


Fig. 1. Representation of the reactions occurring during ECHB. The three dots denote the bond

As is shown above, hydrogen bond (•••) may be form after reduction of the receptor molecule (R), or when it is in its neutral state (O). In the first possibility the strength of the bond is measure by the binding constant,  $Kb_{anion} = k^{DH...R}/k^{DH/R}$ , and in the second one employing  $Kb_{neutral} = k^{DH...O}/k^{DH/O}$ . Another possibility is the evolution of the concerted pathway, following the diagonal arrow in the Scheme. Regardless of the mechanistic route, the overall rate of the reactions is determined by that of the slowest step, which could be the ET (determined by the values of the standard rate constants  $k_s^{O/R}$  or  $k_s^{DH...O/DH...R}$ , or the association reactions ( $Kb_{neutral}$  or  $Kb_{anion}$ ). ECHB can be used for different applications, for example, to design building blocks for supramolecular ensembles<sup>3,4</sup> and also helps as an experimental system to analyze these specific interactions in compounds with biological significance.<sup>16</sup> That is why these processes have been extensively studied: many authors by using nitrocompounds<sup>4, 12, 14</sup> and quinones<sup>13</sup> as receptor and ureas<sup>4, 12, 14</sup> and alcohols<sup>13</sup> as DH have assumed ET reactions very fast and concluded which ECHB occurs under thermodynamic control. However, kinetic control cannot be ruled out, because slow ET processes are known to be dependent on the modifications occurring in the structures of the states O and R (Scheme 1), as referred by Marcus and Hush model.<sup>17-19</sup> This would be particularly important for compounds with high biological activity, such as derivatives of 5-nitroimidazole,<sup>20, 21</sup> where ECHB could act as regulator of their activity due to modification of redox potential of the electro-active nitro function. In this work, evidence for kinetic limitations in ECHB employing 5-nitroimidazole derivatives is presented. Results are discussed in terms of the chemical structure of the receptor molecules.

### Nomenclature

$R_u$	Uncompensated Resistance, $\Omega$
$E^0$	Standard potential, V
$E_{p_{a/c}}$	Anodic/cathodic peak potential, V
ECHB	Electrochemically Controlled Hydrogen Bonding
ET	Electron transfer
O, R	Receptor molecule in its neutral state and in its reduce form
DH	Hydrogen bond donor species
•••	Hydrogen Bond
$K_b$	Binding constant
$k_s$	Electron transfer constant

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