

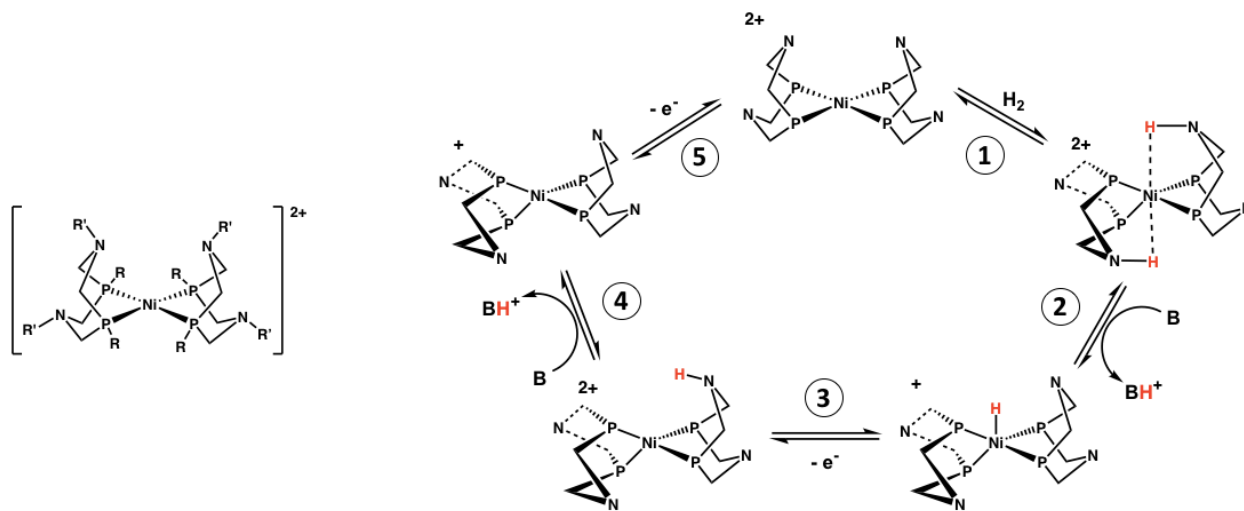
## Secondary Sphere Effects on Metal Hydride Oxidations

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Literature Seminar

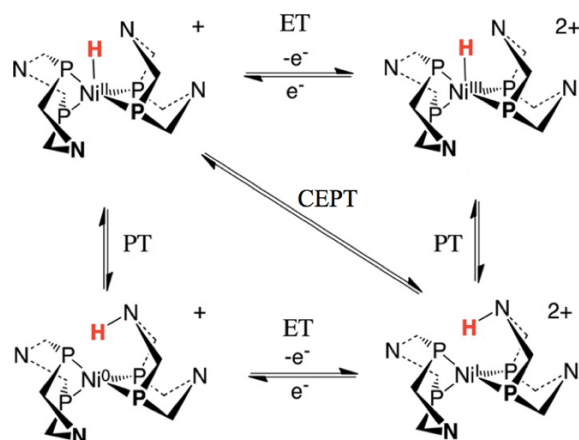
October 29, 2019

Realization of a “hydrogen economy,” in which molecular hydrogen is used as a means of energy storage, requires the development of hydrogen oxidation catalysts for use in fuel cells.<sup>1</sup> An ideal catalyst would be fast (high turnover frequency), robust (high turnover number), and energetically efficient (low overpotential).<sup>2</sup> Current platinum-based catalysts meet all of these criteria, but are not cost-effective for widespread application.<sup>1</sup> Consequently, research has been directed toward the development of hydrogen oxidation catalysts that avoid the need for noble metals. Biological examples of such systems exist within hydrogenase enzymes, which often contain bimetallic iron/iron or iron/nickel active sites.<sup>3</sup> By mimicking the structural features of these active sites, synthetic electrocatalysts for hydrogen oxidation have been developed. One of the most successful and well-studied systems for hydrogen oxidation is based on a four coordinate nickel(II) complex<sup>4</sup>, abbreviated “[Ni(P<sub>2</sub>R<sup>N</sup><sub>2</sub>R<sup>R'</sup>)<sub>2</sub>]<sup>2+</sup>,” a general structure and hydrogen oxidation mechanism for which are depicted in **Figure 1**.



**Figure 1.** The general structure (left) and proposed mechanism<sup>5</sup> (right) of the [Ni(P<sub>2</sub>R<sup>N</sup><sub>2</sub>R<sup>R'</sup>)<sub>2</sub>]<sup>2+</sup> hydrogen oxidation catalysts where R and R' are alkyl groups; these substituents are omitted from the catalytic cycle for clarity. The oxidation/deprotonation of the nickel(II) hydride in step 3 usually determines the overpotential for the overall cycle.<sup>5-7</sup>

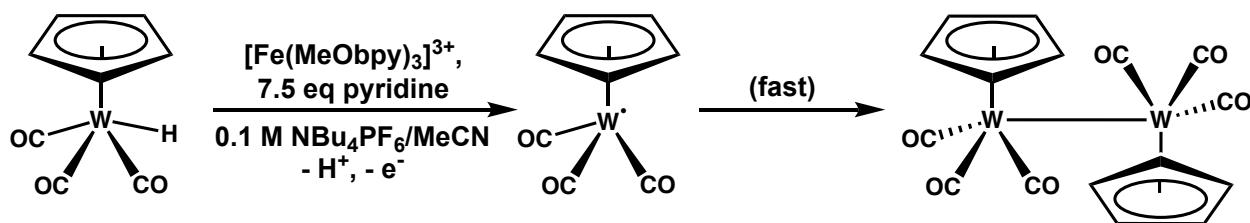
The rate-determining step of this mechanism is usually the binding and splitting of dihydrogen (step 1),<sup>8,9</sup> and the effects of primary-, secondary-, and outer-sphere structural modifications on this process are well-understood.<sup>10</sup> Much less is known about step 3, in which the nickel(II) hydride is oxidized and deprotonated. This step is an example of a proton-coupled electron-transfer (PCET) reaction in which the proton and electron are transferred to different sites (“bidirectional”). This step can occur by one of three different pathways (Figure 2).<sup>10</sup> Two of these pathways are stepwise: either the proton is transferred first (PT-ET), or the electron is transferred first (ET-PT). Alternatively, the proton and electron can transfer at the same time in a concerted mechanism.



**Figure 2.** The three possible reaction pathways for the nickel(II) hydride oxidation/deprotonation: proton transfer then electron transfer (PT-ET), electron transfer then proton transfer (ET-PT), or concerted transfer of the proton and electron (center path). Image adapted from reference 10.

While PCET reactions can proceed by more than one of these mechanisms, operating in parallel, often one path is dominant.<sup>11</sup> The ability to control which mechanism is dominant could be useful for catalyst design; the concerted pathway in particular has attracted interest because it has been proposed that this pathway should require a lower overpotential than the stepwise mechanisms.<sup>7, 12</sup> Theoretical studies of  $[\text{Ni}(\text{P}_2^{\text{R}}\text{N}_2^{\text{R}'})_2]^{2+}$  systems have suggested that reducing the equilibrium distance between the proton donor and acceptor, and decreasing the frequency of their vibrational motion relative to each other, would make the rate of the concerted mechanism more competitive.<sup>7</sup> However, until recently there was little experimental evidence to suggest that bidirectional metal hydride oxidation/deprotonation could proceed through a concerted pathway, or that structural modifications, particularly the positioning of the proton acceptor, had an effect on the operative PCET mechanism.

This seminar describes studies of tungsten hydride model systems which provide support for both of the above hypotheses.<sup>11-13</sup> When exposed to a molecular oxidant and a base, these complexes undergo irreversible oxidation/deprotonation to a tungsten radical species, which rapidly forms an inert dimeric species (Figure 3). The driving force for stepwise PCET mechanisms can be decreased by using an oxidant and base that are weak relative to the  $\text{pK}_a$  and  $E^0$  of the metal hydride. Bourrez et al. monitored the rate of the reaction via stopped-flow UV-visible spectrophotometry and found that under these conditions, it proceeds by a concerted pathway.<sup>13</sup> This result suggests that, under the right conditions, the concerted mechanism could be accessible for catalytic metal hydride intermediates as well.<sup>14</sup>



**Figure 3.** Oxidation/deprotonation of a tungsten hydride model system used in these studies.

A follow-up study investigated whether the strength and positioning of the proton acceptor contributed to the PCET rate or influenced its mechanism. The results suggested that, without any change in oxidant strength, the PCET mechanism of the reaction could be shifted to ET-PT, PT-ET, or the concerted pathway simply by changing the basicity of the proton acceptor, and whether the acceptor was located in the bulk solvent or in the second coordination sphere.<sup>12</sup> Shortly thereafter, it was demonstrated that the contributions of each mechanism differ under high pressure, providing further evidence to support the role of base positioning on the PCET mechanism.<sup>11</sup> Finally, both studies noted that altering the reaction mechanism resulted in very different rate sensitivities to base and oxidant strength. These results are significant because they experimentally validate theoretical work and improve our understanding of structural effects on metal hydride reactivity. It is expected that these principles will be applied when designing new catalysts for reactions involving metal hydrides, which include hydrogen oxidation and the reduction of protons or carbon dioxide.

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