Literature Discussion of

“Pre-Equilibria Reaction Mechanism as a Strategy to Enhance Rate and Lower Overpotential in Electrocatalysis”

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This literature Discussion LO was created for the 2024 ACS Inorganic Chemistry Award Winners Collection.  Professor Louise A. Berben was awarded the ACS Award in Organometallic Chemistry.  This literature discussion covers the study of a pre-equilibrium mechanism which increases rates of hydride transfer catalysis by 6 orders of magnitude.  The study is focused on the metal carbonyl cluster, [Co11C2(CO)23]2− as an electrocatalyst.

**Answer these questions after reading the Abstract and Introduction.**

1. This paper describes electrocatalysis of CO2 into formate using a cobalt cluster, [Co11C2(CO)23]3−, as a homogeneous electrocatalyst.

a) Use Wade’s Rules to calculate the number of electrons in this cluster. What shape is predicted? For example, *closo*, *nido*, *arachno, or other*.

b) How does the structure/charge of the cluster contribute to the fast proton transfer step?

2. In this paper, a pre-equilibrium mechanism is observed for formate production.

a) What does it mean for a reaction to undergo a pre-equilibrium mechanism? How does this mechanism differ from the more common steady state mechanism?

b) What is the relationship between *K* and *k*obs? Explain this relationship qualitatively.

c) The catalytic cycle is shown in Scheme 2 of the paper. In the catalytic cycle, which steps are fast steps and which are slow steps?

d) Write a the balanced chemical equation for the conversion of CO2 to formate, by electron and proton transfer, as described in this paper?

**Answer the following questions about the Results section of the paper.**

3. Consider figure 1 in the paper.

a) What does a peak in cyclic voltammetry (CV) represent? What does it mean when a peak is irreversible? Why are the red and blue CVs on the left irreversible?

b) What change to the CV is expected when a catalytic reaction takes place? Which set of conditions (figure 1 right or figure 1 left) has a larger catalytic current?

c) What does it mean for the peak to shift anodically?

4. Answer the following questions to understand more about the mechanism of formate formation in this paper.

a) Depending on the reaction conditions, there are several proton sources possible for catalysis. What is that acid source and pka in the following conditions?

* + 5.1 mM AnsdH+ under CO2
  + MeCN/H2O (95:5) under CO2

b) What do we learn by running experiments with both water and ansdH+?

c) What does it mean to be under kinetic control? How is this useful in determining the rate of reaction?

6. Answer the following questions to understand more about overpotential.

a) What is overpotential? How is it calculated?

b) Why is overpotential an important catalyst property?

c) Consider figures 5 and 6. How does the performance of this catalyst compare to the other data points in the figure?

Read the Conclusion to the paper and answer the following question.

7. What was the major accomplishment or contribution of this study?

8. Why is the pre-equilibria mechanism beneficial for the catalysis of CO2?