Literature Discussion Learning Object:

Kinetic and Mechanistic Aspects of Atom Transfer Radical Addition (ATRA) Catalyzed by Copper Complexes with Tris(2-pyridylmethyl)amine

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1. Define the acronym ATRA. Describe what the overall ATRA reaction is and what side reactions can be observed. Why is it necessary to have a reducing agent in the copper catalyzed system described by Pintauer and are there any advantages to having this reducing agent present? How does the use of a reducing agent in ATRA lead to a greener synthesis than traditional ATRA? Explain your reasoning.

2. Define ISET and OSET. Describe the mechanism for both ISET and OSET. Include both concerted and stepwise pathways for OSET.

3. Under the section titled “Triphenylphosphine Inhibition Reactions” define AIBN and address why it was added to the reaction mixture? What purpose does this reagent serve (oxidizing agent, reducing agent, etc.)? What is the purpose of the copper complex?

4. In the section titled “Determination of Activation Rate Constants” explain what the activation rate constant is a measurement of in this section and draw out the overall chemical reaction being evaluated here (Scheme 3 will help). What is the role of TEMPO in this reaction? Write out the equation that can be used to determine thermodynamic principles, ΔH⧧ and ΔS⧧. (Cite any references used.)

5. Write out the ATRA reaction between CCl4 and 1-hexene. Summarize all of the results listed in Table 1.

6. Which type of counterion (coordinating or noncoordinating) causes the rate constant, *kobs*, to greatly increase? According to the article, why does this occur? Address if this makes sense based upon your knowledge of reactive metal species.

7. What standard techniques did the researchers use to measure the rate constant of activation for the reaction of the copper complexes with benzyl thiocyanate? Why could they not use carbon tetrachloride to determine the activation rate constant?

8. What are the two proposed pathways for catalyst activation? Is an ISET or OSET proposed to occur in these reactions?

9. Define cyclic voltammetry. What information can you gather from a cyclic voltammogram? (You may want to use outside sources to answer this question.) How was cyclic voltammetry used to prove that halide dissociation was most likely not occurring to a significant degree in this system?

10. List three methods for which the level of halide dissociation is measured in this paper. What two conclusions about the ATRA process can be made after completing these studies?

11. Address how the authors determined that TPMA is a labile ligand by explaining Figure 6. Why did the authors add 1 equivalent of TPMA to the NMR sample containing the Copper complex?

12. Address how the authors determined that the TPMA ligand is crucial to the catalytic ability of the copper complex for ATRA reactions.

13. When looking at the results for ATRA experiments with a styrene and methyl acrylate (Table 4), why is there a relatively low yield of product observed in the absence of PPh3?

14. Why was it important to conduct these kinetic experiments using PPh3? Address how the product formation varies from 0-40 equivalents of PPh3. How do these experiments support the proposed catalyst activation pathway described in Scheme 4?

15. What is the purpose of synthesizing the tris(2-(dimethylamino)phenyl)-amine (TDAPA) ligand, and why is it a good ligand to use for this experiment?

16. How do the results of the experiment using the [CuII[TDAPA]Cl][A] complex as a catalyst support the claim that the mechanism for the activation step involves a ligand arm dissociation?