Questions for Literature Discussion – 12/7/07


1. What is a Heck reaction?

2. Is a Heck reaction different from a Keck-Mizoroki reaction? If so, how?

3. What is the definition of the turnover number in catalysis?

4. What is a palladacycle?

5. What is the structure of $N(nBu)_4Br$?

6. What is meant by colloidal palladium?

7. What form would the Pd be in if it were a heterogeneous catalyst? A homogeneous catalyst? What types of experiments can be used to distinguish between the two types of catalyst?

8. What is a Schlenk tube or Schlenk line?

9. What does ATR stand for in IR spectroscopy? How does this technique work and what are its advantages?

10. What is the actual reaction that is being studied in each of the experiments described on p. 12056?

11. In the Hammett competition reaction, how was the reaction rate determined? What data was actually collected?

12. In what way can a Hg poisoning test be ambiguous? What can and can’t it confirm?

13. What is the likely conclusion of the Hg poisoning test performed in this study?

14. What evidence indicates that homogeneous catalytically active species are responsible for the catalytic activity observed in the study? What is the Collman test?

15. What is Crabtree’s test? How does it work and what does it prove or disprove?

16. What is the explanation of the difference in shape between curves A and B in Fig. 2?
17. What is being investigated in Fig. 3? What does the decrease in the 360 nm band over time imply? What about the growth of the baseline?

18. In Fig. 4, what is a likely cause of the very intense band at around 300 nm (based on what chemical species are in the solution)?

19. How does Fig. 4 help support the conclusion that the catalytically active species are in a homogeneous form?

20. What role do palladium colloids play in the formation of the catalytically active species (according to TEM analysis)?

21. What does TEM stand for? What does EDS stand for?

22. What is the structure of \( n \)-butyl acrylate?

23. What technique is used to monitor the reactant and product concentrations during the kinetic analysis (starting on p. 12059)? How are the reactant and product concentrations determined from the experimental data?

24. Review what is meant by the initial rate method.

25. What is meant by saturation kinetics?

26. Where did the rate law reported on p. 12059 come from (experiment or prediction)? What is the rate determining step in the proposed mechanism?

27. What was the software Dynafit used for?

28. Examine Fig. 9. Which part of the figure shows actual experimental data? How well does the proposed rate law seem to fit the data (based on a visual inspection)?

29. Based on the numbers in Table 3, what range of percent uncertainties is observed in the fitted rate constants?

30. Why is it not possible to reduce eq. 1 (p. 12059) to a much simpler rate equation?

31. Based on Fig. 10, is the steady state approximation justified in the case of this mechanism? Why or why not?

32. What is the difference between what is shown in the curve in Fig. 12 and the curves in Fig. 9?

33. What is demonstrated by Fig. 13? What role does NBu₄Br play in the reaction mechanism? What happens (and doesn’t happen) if NBu₄Br is not added to the reaction mixture?
34. What is the difference between the $\sigma$ and $\sigma^\prime$ parameters? (You may need to check another source or two to find this out.)

35. Why is it preferable to compare Hammett parameters for different catalyst precursors instead of looking at actual values of the parameters for this reaction?

36. How can it be shown that the change in reactivity for different aryl halides in a competitive Heck reaction only depends on the oxidative addition step of the mechanism ($k_1$ in Fig. 8)?

37. What conclusions can be drawn from Figs. 16 and 17?

38. What can be concluded from the fact that all four palladacycles used led to the same $\rho$ value?

39. In determining the activation energy of the reaction, how were first order kinetics ensured experimentally?

40. What is the Eyring equation? What parameters were determined by using it?