

423/523 Organometallic Chemistry
Problem set 7

1. In 1968, the Shell Oil Company reported that adding tertiary phosphine such as PBu_3 to the oxo reaction resulted in hydroformylation taking place at less than 100 atm. Though it the new catalyst is a less active hydroformylation catalyst than $\text{HCo}(\text{CO})_3$, it is a better hydrogenation catalyst. Separation of catalyst from products is improved. The ratio of linear to branched product is as high as 9 to 1. Studies of the reaction failed to observe alkyl or acyl-containing intermediates.
 - (a) Explain the greater selectivity of the new catalyst by drawing an appropriate transition state.
 - (b) What are the advantages and disadvantages of the new catalyst being a good hydrogenation catalyst?
 - (c) What does the failure to observe intermediates tell you about the likely rate-determining step?
 - (d) Why is it easier to remove the products from the catalyst?
2. Draw a catalytic cycle for phosphine-rhodium-catalysed hydroformylation. The catalyst precursor is $\text{H}(\text{CO})\text{Rh}(\text{PPh}_3)_3$.
3. Explain why increasing the concentration of phosphine in the phosphine-rhodium cycle slows the reaction rate, but also raises the linear/branched product ratio.
4. Rate of Rh/HI -catalysed carbonylation of 2-propanol to give a mixture of butanoic and 2-methylpropanoic acids is actually a little faster than that for carbonylation of ethanol and up to seven times more rapid than that for 1-propanol. If OA is still the rate-determining step in the pathway, what can be said about the mechanism of that step when 2-propanol is the starting material?